



Exciton Photoemission Orbital Tomography

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Doctoral thesis

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*Stets findet Überraschung statt
Da, wo man's nicht erwartet hat;
Doch daß dieselbe überall
Grad angenehm, ist nicht der Fall.
Gar oft erschreckt uns eine sehr
Und eine andre noch viel mehr.*

— Wilhelm Busch, *Überraschung*
[*Wilhelm Busch: Werke.*
Historisch-kritische Gesamtausgabe, Bde.
I-IV, Band 4. Hamburg:
Standard-Verlag, 1959, S. 356-358.]

Abstract

The formation, dynamics and decay of excitons – bound electron-hole pairs – play a central role in the optical and electronic response of semiconducting and insulating materials, thus making a deep understanding of these processes crucial for the design and optimization of optoelectronic devices like solar cells, LEDs or lasers. Experimentally, time- and angle-resolved photoemission spectroscopy (trARPES) has been shown to be particularly suited for studying the properties of excitons on a microscopic level. In order to interpret the experimental photoemission data, the development of a first-principles quantum-mechanical description of photoemission from excitons is indispensable.

The recently developed formalism of “exciton photoemission orbital tomography” (exPOT) is particularly suited for the analysis of such data and is computationally efficient, hence allowing for its application to real-world systems. Until now, however, it has been restricted to photoemission simulations based on isolated model systems like single molecules or molecular clusters. In order to apply exPOT to systems with non-negligible substrate-adsorbate or inter-molecular interactions and to novel 2D semiconductors, an extension to periodic systems is imperative. This is the primary objective of this thesis, in which the theoretical framework is extended in a detailed derivation. The focus lies on the involved approximations as well as a comparison between exPOT and the related formalism of ground-state photoemission orbital tomography, both on the level of isolated and periodic systems.

Having successfully extended exPOT to periodic systems, we then give details on an efficient implementation, which enables us to apply it to monolayer hexagonal boron nitride (hBN) to show how quasiparticle (GW) energy bands, Kohn-Sham wave functions and the exciton’s transition weights (obtained from the eigenvectors of the Bethe-Salpeter Hamiltonian) are related to calculated photoemission intensity distributions.

In a second application, photoemission data obtained in trARPES experiments involving four molecular layers of sexithiophene (6T) molecules adsorbed on a crystalline substrate is analyzed. Using the extended exPOT approach, we show that photoemission simulations involving a free-standing monolayer of 6T molecules are able to explain the distinct photoemission distribution observed experimentally. We find that inclusion of the correlated nature of the excited state is crucial for reproducing the experimental data. Additionally, we show that cluster-based simulations can be used as a first estimate for photoemission from the system, while inter-molecular interactions ultimately require a periodic treatment.

As a third application and motivated by the success of the previous findings, we simulate exciton photoemission from an isolated dimer consisting of a single PTCDA and a single H2TPP molecule and show that the system is a promising

candidate for future studies of charge-transfer excitons in type-II organic hetero-interfaces. This motivates more sophisticated studies which take the realistic interface structure into account using our extended exPOT formalism, but is beyond the scope of this thesis.

To conclude, comparison with experimental data has shown the practical applicability of exPOT for periodic systems. In addition, our theoretical studies have shown its predictive strength for the planning of future experimental studies. Our formalism thus provides not only a sophisticated framework for the analysis of experimental data but also a powerful tool for streamlining material selection and determining key experimental parameters.

Kurzzusammenfassung

Die Entstehung, zeitliche Entwicklung und der Zerfall von Exzitonen – gebundenen Elektron-Loch-Paaren – spielen eine zentrale Rolle in der optischen und elektronischen Reaktion halbleitender und isolatorischer Materialien. Ein grundlegendes Verständnis dieser Prozesse ist daher entscheidend für Design und Optimierung optoelektronischer Geräte wie Solarzellen, LEDs oder Laser. Auf experimenteller Ebene hat sich zeit- und winkelaufgelöste Photoemissions-Spektroskopie (trARPES) als besonders geeignete Methode zur Untersuchung von Exzitoneigenschaften auf mikroskopischer Ebene erwiesen. Um die experimentell erhaltenen Daten zu analysieren, ist die Entwicklung einer quantenmechanischen Ab-initio-Beschreibung der Exzitonen-Photoemission unerlässlich.

Der vor Kurzem entwickelte Formalismus „exciton photoemission orbital tomography“ (exPOT) ist für die Analyse solcher Daten besonders geeignet und ist dabei recheneffizient genug, um eine Anwendung auf reale Systeme zu ermöglichen. In seiner bisherigen Form konnte exPOT allerdings nur auf isolierte Systeme wie einzelne Moleküle oder molekulare Cluster angewandt werden. Um ihn auch auf Systeme mit nichtvernachlässigbaren Substrat-Adsorbat- oder intermolekularen Wechselwirkungen und auf neuartige 2D-Halbleitersysteme anwenden zu können, muss er auf periodische Systeme erweitert werden. Diese Erweiterung ist das zentrale Ziel der vorliegenden Dissertation und wird detailliert hergeleitet. Der Fokus liegt dabei auf den involvierten Näherungen sowie einem Vergleich des exPOT-Formalismus zur verwandten Methode für Grundzustands-Photoemission, wobei sowohl isolierte als auch periodische Systeme betrachtet werden.

Nach erfolgreicher Erweiterung des exPOT-Formalismus auf periodische Systeme erklären wir, wie dieser effizient implementiert werden kann und wenden ihn schließlich auf eine Monolage hexagonales Bor-Nitrid (hBN) an, um den Zusammenhang zwischen (GW) Quasiteilchenenergiebändern, Kohn-Sham-Wellenfunktionen sowie exzitonischen Übergangsgewichten (welche wir aus Eigenvektoren des Bethe-Salpeter-Hamiltonians erhalten) und den berechneten Photoemissions-Intensitätsverteilungen zu erklären.

Als zweites Beispiel analysieren wir trARPES-Photoemissionsdaten eines vierlagigen Films von Sexithiophen-Molekülen (6T) auf einem kristallinen Substrat. Wir zeigen, dass exPOT-Photoemissions-Simulationen basierend auf einer freistehenden 6T-Monolage die experimentelle Photoemissions-Verteilung erklären können, wobei die Berücksichtigung der korrelierten Natur des angeregten Zustands von entscheidender Bedeutung ist. Zusätzlich zeigen wir, dass Cluster-basierte Simulationen zwar für eine erste Analyse der Photoemission von diesem System geeignet sind, intermolekulare Wechselwirkungen im System aber letztlich eine Verwendung unserer periodischen Erweiterung erfordern.

Motiviert durch die bisherigen Erkenntnisse simulieren wir als dritte Anwen-

dung Exzitonen-Photoemission aus einem isolierten Dimer, bestehend aus einem PTCDA- und einem H2TPP-Molekül und zeigen, dass dieses System ein vielversprechender Kandidat für zukünftige Untersuchungen von Ladungsübertrags-Exzitonen in Typ-II-organischen Hetero-Grenzflächen darstellt. Dies motiviert weiterführende Untersuchungen, welche die realistische Grenzflächenstruktur unter Verwendung unseres erweiterten exPOT-Formalismus berücksichtigen, jedoch über den Rahmen dieser Dissertation hinausgehen.

Zusammenfassend konnten wir also durch den Vergleich mit experimentellen trARPES-Daten die praktische Anwendbarkeit des auf periodische Systeme erweiterten exPOT-Formalismus zeigen. Zusätzlich unterstreichen unsere theoretischen Untersuchungen dessen prädiktive Stärke für die Planung zukünftiger Experimente. Unser Formalismus bietet daher nicht nur einen fortgeschrittenen Ansatz zur Analyse experimenteller Daten, sondern auch ein leistungsfähiges Werkzeug zur gezielten Materialauswahl und zur Festlegung entscheidender experimenteller Parameter.

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Artificial intelligence (AI) tools – mostly ChatGPT and UniGPT – have been used by the author of this thesis to various degrees and at various stages of the research and writing process. Examples of such use cases are generating code, bug fixing, literature search, improving language and assistance in learning new concepts. While small parts of the text may therefore be traceable to an AI source, the vast majority of the text was personally written by the author of this thesis. Note that Chapters 4 and 5 contain text partially written by co-authors of the respective publications and that the usage of AI tools by co-authors cannot be ruled out.

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The author of this thesis takes full responsibility for the content printed.

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1 Introduction

The formation, dynamics and decay of *excitons* – bound electron-hole pairs – plays a central role in the optical and electronic response of semiconducting and insulating materials. A deep understanding of these processes is therefore essential for the design and optimization of optoelectronic devices, for example in light-harvesting [1–3] or in LEDs and lasers [4–6].

As an experimental tool, *time- and angle-resolved photoemission spectroscopy* (trARPES) has been shown to be particularly suited for the time-dependent microscopic study of excitons [7–15], where the usage of ultrafast probe pulses has been shown to allow for the time-dependent measurement of exciton dynamics on *femtosecond* timescale [12–16].

To analyze the experimentally obtained photoemission data from trARPES experiments at a quantum-mechanical level, a first-principles theoretical description of photoemission from electronically excited systems is required. A noteworthy and in principle very powerful approach is given by real-time *time-dependent density functional theory* (TDDFT) [17, 18], which allows for the direct simulation of trARPES experiments. In practical calculations however, computational limitations typically restrict us to the usage of local or semi-local *exchange-correlation* functionals, which are not well-suited for describing the correlated nature of *charge-transfer* (CT) or *Wannier* excitons – essential types of excitons for many applications. A particularly suited theoretical framework for the description of not only localized Frenkel-type excitons, but also CT and Wannier excitons is given by *many-body perturbation theory* (MBPT) [19]. Within the field of MBPT, the *nonequilibrium Green’s function* (NEGF) approach [20] poses a highly accurate formalism for the simulation of trARPES experiments based on the *nonequilibrium lesser Green’s function*. Again, however, computational costs make practical applications intractable for most systems of interest such that simulations based on the NEGF approach have so far been restricted to model systems or Wannier-Hamiltonians [21, 22], often neglecting the influence of the probe pulse on the transition probability to the photoelectron state [23, 24]. In one-step models for photoemission, effects related to the probe pulse are encoded in the photoemission matrix element, which is therefore crucial for accurately describing the photoemission process and is further found to encode rich information about quantum geometrical effects [25, 26], such as the Berry curvature [27, 28] or orbital angular momentum [29, 30]. Moreover, matrix element effects often become the dominant contribution to the observed angular dependence in the photoemission signal of organic or hybrid organic/inorganic systems, forming the basis of the successful framework of photoemission orbital tomography (POT) [31–33]. While originally developed for photoemission from the electronic ground state, POT has recently been extended to *exciton photoemission orbital tomography* (exPOT) [34]

which forms a cost-effective approach for the simulation of trARPES experiments while still incorporating matrix element effects. The exPOT formalism is based on *Fermi's golden rule* and uses an excitonic initial state which is in practice obtained via MBPT calculations. As a consequence of this construction, it is restricted to low exciton densities, while the approaches mentioned above can in principle be used in the linear and nonlinear pump-regime. It is thus particularly suited for investigations of isolated exciton dynamics in trARPES experiments involving low pump-pulse intensities. Due to its low computational cost, exPOT's practical applicability is in that regard only limited by the underlying *ab initio* MBPT calculations, hence allowing for its successful application to real materials [12, 16]. Until now, however, exPOT has been limited to photoemission simulations based on isolated model systems like single molecules or molecular clusters. While such model systems are often warranted, an extension to photoemission simulations from periodic surfaces is needed to incorporate substrate-adsorbate interactions or inter-molecular interactions [35] as well as for the simulation of photoemission from 2D semiconductors which form an important class of materials for the practical applications mentioned in the beginning [4, 5].

An extension of exPOT to photoemission simulations of periodic systems therefore poses a promising path for simulating trARPES experiments and is the primary objective of this thesis. We begin in Chapter 2 with an overview of the theoretical framework underlying the exPOT formalism. After applying the *Born-Oppenheimer approximation* to the nuclear-electronic Hamiltonian and clamping nuclei, we focus on the electronic part of the Hamiltonian. Ground-state density functional theory (DFT) is introduced first generally and then in the Kohn-Sham flavor. Based on the DFT calculation, MBPT is introduced with a focus on the GW approximation for the calculation of *quasiparticle ionization energies and electron affinities*. Based on these results, the *Bethe-Salpeter equation* (BSE) is introduced, allowing us to calculate the excitonic states of the materials of interest.

Equipped with this theoretical framework, Chapter 3 gives a brief introduction into the experimental conditions under which exPOT is applicable, followed by a detailed derivation of not only exPOT but also ground-state photoemission orbital tomography [33, 35] (ground-state POT). The two frameworks are closely related and their derivations largely coincide, thus motivating a combined derivation which allows us to compare them and point out similarities and differences. For similar reasons, both exPOT and ground-state POT are derived on the level of isolated systems as well as on the level of periodic systems, which allows us to directly connect our extended formalism to the original formulation of Ref. [34]. During the derivation, we focus on the approximations underlying ground-state POT and exPOT and discuss their viability. Finally, Chapter 3 also contains details for an efficient implementation of ground-state POT and exPOT for periodic systems.

With this implementation at hand, Chapter 4 presents monolayer hexagonal boron nitride (hBN) as a first example system for the exPOT formalism for periodic systems. The calculated photoemission angular distributions (k-maps) are discussed by decomposing k-maps in terms of the formalism's building blocks. The direct influence of the *BSE eigenvector* which describes the correlated nature of an exciton, on the k-maps is explained, with a particular focus on the influence of the pump pulse's polarization direction.

Next, Chapter 5 discusses photoemission from sexithiophene (6T) molecules

adsorbed on an oxygen-passivated copper substrate. Being the only chapter that features experimental results [16], exPOT is used to reproduce and explain the distinct photoemission distribution observed in trARPES experiments involving four layers of adsorbed 6T molecules. In contrast, it is shown that a simplified approach that neglects the correlated nature of the excited state fails to do so. Photoemission simulations using molecular clusters are compared with those performed for a calculation involving a free-standing monolayer of 6T molecules. In addition to this analysis on the influence of the system size on the simulated photoemission pattern, the importance of including excitonic effects for reproducing the experimental k-map is discussed in detail.

Finally, Chapter 6 gives an outlook for future applications of exPOT for CT excitons in systems involving a type-II organic heteromolecular interface, with the particular example of an interface between PTCDA and H2TPP molecular layers. We perform calculations on the level of an isolated molecular dimer, analyze how exciton dynamics may be observed in corresponding trARPES experiments and argue why an extension to simulations based on the realistic interface structure is promising and advisable, thus again reinforcing the importance of exPOT for periodic systems.

2 Theoretical Background

2.1 Introduction

In this chapter, we introduce the theory framework underlying the photoemission simulations of Chapter 3. We will start from the electronic-nuclear Hamiltonian of a generic atomic system and use the *Born-Oppenheimer approximation* to arrive at the electronic Hamiltonian. From thereon, we focus on the electronic problem: starting with the description of the electronic ground state, we will first introduce the general framework of *density functional theory* and then focus on the *Kohn-Sham* formalism for the calculation of ground-state properties, notably, electronic orbitals and -energies. Equipped with these orbitals, we then use *many-body perturbation theory* to calculate (electronically-) excited-state properties: we first introduce the *one-particle Green's function* and demonstrate its close relation to photoemission simulations. Then, we show how it can in principle be calculated using *Hedin's equations*, and how it is calculated in practice based on the *quasiparticle approximation* and the *GW approximation*. Finally, we introduce the *two-particle Green's function* and the *two-particle correlation function*. We will start from the latter's equation of motion, the *Bethe-Salpeter equation*, in its exact form and derive the commonly-used version based on additional, commonly-used approximations. We explicitly derive the final equations for systems using periodic boundary conditions (termed *periodic* systems throughout the text) and locally constrained systems (termed *gas-phase* systems), allowing us to effectively describe charge-neutral excited states in terms of *excitons*, which will then serve as a basis for our excited-state photoemission formalism.

Throughout the text and unless stated otherwise, we will include electronic spin in our equations, however, neglect spin-orbit coupling. Note that many parts of the theory are however compatible with and easily adapted to an inclusion thereof (see e.g. Footnote 17 in Ref. [36]). Similarly, all other relativistic effects will be neglected and we will start from the commonly used nonrelativistic Hamiltonian describing an atomic system of nuclei and electrons.

For this Hamiltonian and throughout the text, we will use *atomic units*, unless stated otherwise. That is, we set the reduced Planck constant to $\hbar = 1$, the electronic mass to $m = 1$, the elementary charge to $e = 1$ and the vacuum permittivity to $\epsilon_0 = \frac{1}{4\pi}$.

Lastly, we will occasionally use the following shorthand notations: Denoting position, spin and time-arguments as $\mathbf{r}_i$, s_i and t_i , respectively, we first define

($i, j = 1, 2, 3, \dots$ here and below¹):

$$\begin{aligned} x_i &\equiv (\mathbf{r}_i, s_i) \\ i &\equiv (x_i, t_i) \equiv (\mathbf{r}_i, s_i, t_i) \end{aligned} \quad (2.1)$$

Defining $t^\pm \equiv t \pm \eta$ ($\eta > 0$, infinitesimal), we write:

$$i^\pm \equiv (x_i, t_i^\pm) \quad (2.2)$$

We write delta-functions as

$$\begin{aligned} \delta(x_i, x_j) &\equiv \delta(\mathbf{r}_i - \mathbf{r}_j) \delta_{s_i, s_j} \\ \delta(i, j) &\equiv \delta(x_i, x_j) \delta(t_i - t_j) \end{aligned} \quad (2.3)$$

and integrals as

$$\begin{aligned} \int dx_i &\equiv \sum_{s_i=\uparrow, \downarrow} \int_{\mathbb{R}^3} d^3r_i \\ \int d(x_i, x_j) &\equiv \int dx_i \int dx_j \\ &\dots \end{aligned} \quad (2.4)$$

and:

$$\begin{aligned} \int d(i) &\equiv \int dx_i \int_{\mathbb{R}} dt_i \\ \int d(i, j) &\equiv \int d(i) \int d(j) \\ &\dots \end{aligned} \quad (2.5)$$

Note that we above assumed the particle to be of spin- $\frac{1}{2}$, since we typically use this notation for electrons. The notation can trivially be adapted to other particle-types by summing accordingly over the spin coordinate. Occasionally it will also be useful to use a shorthand for a set of coordinates, for example:

$$\begin{aligned} \{x\} &\equiv x_1, x_2, \dots, x_N \\ \{\mathbf{r}\} &\equiv \mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N \end{aligned} \quad (2.6)$$

Finally, the Coulomb interaction kernel will occasionally be written as:

$$\begin{aligned} v(x_1, x_2) &\equiv \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \\ v(1, 2) &\equiv \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \delta(t_1 - t_2) \end{aligned} \quad (2.7)$$

2.1.1 System Types

Throughout this text, and especially when applying our photoemission formalism to real systems, we will meet two types of atomic structures which we label *gas-phase systems* and *periodic systems*.

¹We will occasionally also use primed arguments as well as contextually obvious variations like y instead of x_i .

Gas-Phase Systems

We will routinely perform *ab initio* calculations and photoemission simulations from isolated molecules or isolated molecular clusters. Since such calculations involve a single molecule or cluster which is not adsorbed on a surface, we call them gas-phase calculations.

Details on the spectrum of corresponding effective one-electron Hamiltonians (e.g. from Kohn-Sham DFT) can be found in Appendix A.1.1, where the Hamiltonian's potential V is roughly localized around the molecule's/cluster's nuclear positions. When solving such one-electron problems, electronic orbitals are usually expanded in *Gaussian basis sets*, such that the Schrödinger equation is transferred from a differential equation to an algebraic equation in terms of the basis expansion coefficients and the resulting solutions are expressed as linear combinations of Gaussians. See also Secs. 5.6.1 and 6.6 on the basis sets we used in our practical calculations.

Lastly, note that gas-phase calculations mostly serve as a first step to simulate the photoemission from molecules adsorbed on some substrate (by rotating the molecule to the same orientation it would have on the substrate, see also Sec. 3.3.11), but for comparison to experiments, we usually want to go a step further and perform periodic calculations.

Periodic Systems

As hinted above, single molecules and molecular clusters often only serve as a first step in the simulation of photoemission experiments. This is the case because we want to focus on experiments investigating photoemission from a sample that consists of an adsorbate on a (planar) crystalline substrate (together forming a periodic – hence the naming of such systems and of calculations involving them – structure, see Sec. 3.2) such that inter-molecular interactions and often also substrate-adsorbate interactions become important.

Usually, we are in particular interested in photoemission from the adsorbate (and maybe the substrate's surface below it), while the sample's bulk properties are of minor relevance. This justifies the approach commonly taken in theoretical surface science of approximating the substrate by an atomically thin structure, usually consisting of around five layers of atoms. Note that, due to this approximation, the calculated photoemission signal for photoemission from the substrate has to be taken with caution. Luckily, we are usually more interested in the photoemission signal from the adsorbate, which is often (partly) energetically separated from the substrate signal. Additionally, given the limited mean-free-path length of photoemitted electrons, the substrate photoemission signal is additionally weakened relative to the adsorbate photoemission signal [35], which additionally justifies our approach of focusing on the latter. While the theoretical calculations for substrate photoemission could in principle be converged by gradually increasing the number of used layers, we can also go the opposite way and remove the substrate completely from the simulation! That is, we first optimize the geometry of the adsorbate on the substrate, but then remove it and calculate the photoemission signal from the *free-standing* adsorbate. This is for example done in Chapter 5 where this approach is justified by the electronic decoupling of the adsorbate from the substrate.

Additionally, we are usually not interested in surface/edge effects stemming from the lateral sides of the sample. As long as we make sure not to focus the experiment's light sources *solely* on the edge of the sample, photoemission from the “inner part” of the surface will be dominant and the outer edges of the sample are practically irrelevant. Given that focus areas are generally much larger than inter-atomic distances, this is in practice automatically the case. The interaction of the photoelectron with the surface is then independent of the size of the surface, as long as it is macroscopically large (that is, a surface area of 1 cm^2 or of 1 m^2 will lead to the same results). This justifies our second simplification, where we model the sample by an infinitely extended surface (which we usually align such that the surface-normal of the side with the adsorbate points in the positive z direction).

In summary, we model the real sample by an infinitely extended, periodic and atomically thin surface. In practice, this is done by defining a surface unit cell containing the system's atomic structure (thin substrate + adsorbate), whose infinite repetition in the in-plane directions gives us the infinite, thin surface. The potential V of a corresponding effective one-electron Hamiltonian (see Appendix A.1.1) is then – in z direction – roughly localized around the infinitely extended, thin atomic region. In contrast to gas-phase systems, the Schrödinger equation is then usually solved using *plane-wave basis sets*, see for example Secs. 4.6 and 5.6.2.

On a technical point, note that modelling our system as an infinite plane can lead to mathematical difficulties. For example, the *bound states* of an effective one-electron Hamiltonian (e.g. Kohn-Sham DFT) become non-normalizable (see Appendix A.1.1 for details) and extensive quantities, like the number of electrons in the system, diverge. In the following, the theoretical frameworks of density functional theory (DFT) and many-body perturbation theory (MBPT) is therefore first developed for finite systems – which can in principle be single molecules, but also macroscopically large, but still finite, crystals. In the end, we then show how the key quantities and equations needed for our photoemission formalism behave (and stay well-defined) when performing the *thermodynamic limit*, that is, approaching the infinite (thin) plane described above. Occasionally we will explicitly perform this limit by starting with a macroscopically sized but finite surface and arguing that key quantities like Kohn-Sham wave functions or the electron density (compare Ref. [37]) in the *interior region* of the finite surface should be – to very good approximation – identical to those of the infinite system with differences only occurring around the lateral sides of the finite surface (and of course beyond the lateral ends of the finite surface, where for example its ground-state density quickly vanishes while that of the infinite system does not).

Finally, note that while we usually keep the theory general, our practical calculations consider gapped systems, in particular semiconductors. In preparation for this we will occasionally focus on such systems, which is then either stated explicitly or should be obvious from the given equations.

2.1.2 Many-Body Hamiltonian

We use the many-body Hamiltonian operator as our starting point for the quantum-mechanical description of atomic systems. We separate the atoms into nuclei and electrons and denote the position and momentum operator (vector) of electron i by $\hat{\mathbf{r}}_i$ and $\hat{\mathbf{p}}_i$, respectively. Similarly, we denote the position and momentum operator

of nucleus k by $\hat{\mathbf{R}}_k$ and $\hat{\mathbf{P}}_k$, while the Z_k denotes its charge and M_k its mass. The Hamiltonian operator for a system of K nuclei and N electron then reads:

$$\hat{H} = \hat{T}_e + \hat{T}_n + \hat{U}_{ee} + \hat{U}_{nn} + \hat{U}_{en}, \quad (2.8)$$

with the electronic kinetic energy (with $\hat{p}^2 = \hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2$)

$$\hat{T}_e = \frac{1}{2} \sum_i^N \hat{p}_i^2, \quad (2.9)$$

the nuclear kinetic energy

$$\hat{T}_n = \frac{1}{2} \sum_{k=1}^K \frac{\hat{P}_k^2}{M_k}, \quad (2.10)$$

the electron-electron Coulomb interaction

$$\hat{U}_{ee} = \frac{1}{2} \sum_{i=1}^N \sum_{j=1, j \neq i}^N \frac{1}{|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|}, \quad (2.11)$$

the nucleus-nucleus Coulomb interaction

$$\hat{U}_{nn} = \frac{1}{2} \sum_{k=1}^K \sum_{l=1, l \neq k}^K \frac{Z_k Z_l}{|\hat{\mathbf{R}}_k - \hat{\mathbf{R}}_l|} \quad (2.12)$$

and the electron-nucleus Coulomb interaction

$$\hat{U}_{en} = - \sum_{i=1}^N \sum_{k=1}^K \frac{Z_k}{|\hat{\mathbf{r}}_i - \hat{\mathbf{R}}_k|}. \quad (2.13)$$

Using the Hamiltonian Eq. 2.8 we can then solve the time-independent Schrödinger equation

$$\hat{H} |\Upsilon_m\rangle = U_m |\Upsilon_m\rangle \quad (2.14)$$

to obtain the eigenstates $\{|\Upsilon_m\rangle\}$ representing stationary states of the system with energies $\{U_m\}$. These states serve as a basis of the system's Hilbert space, i.e., any physically allowed state can be written as a linear combination (compare also Appendix A.1)

$$|\Upsilon\rangle = \sum_m c_m |\Upsilon_m\rangle. \quad (2.15)$$

Exact solution of this many-body Hamiltonian would yield correlated (anti-/symmetric with respect to indistinguishable particles; compare Appendix A.1.2) nuclear-electronic states with wave functions

$$\Upsilon_m(\{x\}, \{X\}), \quad (2.16)$$

where we used the notation of Eqs. 2.1 and 2.6 to express electronic spin- and position coordinates. Similarly, $X_k \equiv (\mathbf{R}_k, S_k)$ denotes the k -th nuclear position and spin coordinate and we introduced:

$$\{X\} \equiv X_1, X_2, \dots, X_K \quad (2.17)$$

The only system of nuclei and electrons for which exact analytical solutions exist is the Hydrogen atom (and hydrogen-like atoms, that is a nucleus surrounded by a single electron), which poses a two-body problem involving a nucleus and a single electron. Already the Helium atom, comprised of a nucleus and two electrons, poses a three-body problem and is not solvable analytically (details on these two systems can be found in standard quantum mechanics textbooks, e.g. [38, 39]). In addition, the cost of solving the many-body Schrödinger equation Eq. 2.16 numerically generally grows dramatically with the system size – compare for example Ref. [40], which shows the *exponential wall* we hit when using simple variational methods (there, in terms of electrons only, see below) – necessitating the introduction of cost-reducing approximations and alternative computational and theoretical approaches (compare for example Sec. 2.2 where we calculate the *electron density* instead of a wave function). In the upcoming sections we will introduce and build upon such approximations and methods, eventually allowing us to calculate properties of systems involving hundreds of electrons in the practical calculations at the end of this text.

2.1.3 Born-Oppenheimer Approximation

As a first step towards solving the Schrödinger equation of larger systems, we use the Born-Oppenheimer approximation (BOA) to separate the problem into two individual tasks, one for the nuclei and one for the electrons. While this approximation is often presented in a form that omits spin, we explicitly include it in the derivation (compare also Ref. [41]).

Electronic Problem

To arrive at the BOA, we start by introducing the electronic subproblem. In analogy to Eq. 2.17, we create a shorthand for the set of nuclear positions:

$$\{\mathbf{R}\} \equiv \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_K \quad (2.18)$$

We then clamp the nuclei to a given set of positions $\{\mathbf{R}\}$, and define the *electronic Hamiltonian* as:

$$\hat{H}_e^{\{\mathbf{R}\}} = \frac{1}{2} \sum_i^N \hat{p}_i^2 + \frac{1}{2} \sum_{i=1}^N \sum_{j=1, j \neq i}^N \frac{1}{|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|} - \sum_{i=1}^N \sum_{k=1}^K \frac{Z_k}{|\hat{\mathbf{r}}_i - \mathbf{R}_k|} \quad (2.19)$$

Importantly, in contrast to the full Hamiltonian Eq. 2.8, the nuclear positions only enter as parameters, instead of being operators. For a given $\{\mathbf{R}\}$, solution of the electronic Schrödinger equation

$$\hat{H}_e^{\{\mathbf{R}\}} |\Psi_g^{\{\mathbf{R}\}}\rangle = E_g^{\{\mathbf{R}\}} |\Psi_g^{\{\mathbf{R}\}}\rangle \quad (2.20)$$

gives us the electronic eigenstates $\left\{ \left| \Psi_g^{\{\mathbf{R}\}} \right\rangle \right\}$ with energies $\left\{ E_g^{\{\mathbf{R}\}} \right\}$. Note that we indicate the dependence on the nuclear positions by the superscript $\{\mathbf{R}\}$. Assuming a smooth dependence of the electronic energies $\left\{ E_g^{\{\mathbf{R}\}} \right\}$ on the nuclear coordinates $\{\mathbf{R}\}$, their index g can then be thought of as indexing different potential energy surfaces (PES²) as a function of the nuclear positions, thus influencing the nuclear equation of motion (see Eq. 2.35 below).

Born-Oppenheimer Expansion

We continue by noting that for each nuclear configurations $\{\mathbf{R}\}$, solving the electronic Schrödinger equation Eq. 2.20 will give us a distinct set of solutions $\left\{ \left| \Psi_g^{\{\mathbf{R}\}} \right\rangle \right\}$. More importantly for the derivation of the BOA, however, each of these sets of solutions forms a basis for the electronic subspace of the full Hilbert space (see Appendix A.1). Using in addition the spin-position states $|\{X\}\rangle$ (compare Eq. 2.17) as a basis for the nuclear subspace, we can construct a basis for the full Hilbert space using (tensor-product) basis vectors:

$$|g, \{X\}\rangle \equiv \left| \Psi_g^{\{\mathbf{R}\}} \right\rangle \otimes |\{X\}\rangle, \quad (2.21)$$

where $\{\mathbf{R}\}$ is implicitly contained in $\{X\}$. Note that, in this construction, we use for each nuclear basis vector $|\{X\}\rangle$ the specific electronic solutions corresponding to the corresponding nuclear positions $\{\mathbf{R}\}$. This thus deviates from the definition of the tensor-product basis given in Def. 6. Since the electronic eigenfunctions at each $\{\mathbf{R}\}$ form a basis of the electronic subspace, it is however immediately obvious that the vector of Eq. 2.21 also form a basis of the tensor-product space (for each $|\{X\}\rangle$, simply rotate the electronic basis vectors). We now use this product basis to expand the solutions $\{|\Upsilon_m\rangle\}$ of the full Schrödinger equation Eq. 2.14. Using orthonormality of the basis vectors (compare Appendix A.1), we can write:

$$|\Upsilon_m\rangle = \sum_g \int d\{X\} |g, \{X\}\rangle \langle g, \{X\} | \Upsilon_m \rangle, \quad (2.22)$$

where $\int d\{X\}$ is to be understood in analogy to the electronic notation of Eq. 2.4³. This expansion is commonly known as the Born-Oppenheimer expansion [43]. In position-spin-representation, Eq. 2.22 becomes (using Eqs. 2.1 and 2.6, the spin-position basis vectors $\{|\{x\}, \{X\}\rangle\}$ and the tensor-product space's inner product)

$$\begin{aligned} \Upsilon_m(\{x\}, \{X\}) &= \langle \{x\}, \{X\} | \Upsilon_m \rangle \\ &= \sum_g \Psi_g^{\{\mathbf{R}\}}(\{x\}) \Xi_m^{(g)}(\{X\}), \end{aligned} \quad (2.23)$$

with the electronic wave function

$$\Psi_g^{\{\mathbf{R}\}}(\{x\}) \equiv \langle \{x\} | \Psi_g^{\{\mathbf{R}\}} \rangle \quad (2.24)$$

²Not to be confused with *photoemission electron spectroscopy*, for which we also use the abbreviation *PES*.

³ Deviating from the notation of Eq. 2.4, we assume that the position integral and spin summation does not contain identical states multiple times, compare Eq. 2.47 and Ref. [42] on anti-/symmetrized position states. Otherwise, prefactors taking into account the “multi-counting” have to be included in Eq. 2.22

and

$$\Xi_m^{(g)}(\{X\}) \equiv \langle g, \{X\} | \Upsilon_m \rangle. \quad (2.25)$$

Nuclear Problem

The remaining derivation is simpler when switching to position-spin-representation, where we can use the well-known position-representation of the momentum operator to get:

$$\langle \{x\}, \{X\} | \hat{T}_n | \Upsilon \rangle = -\frac{1}{2} \sum_{k=1}^K \frac{\nabla_{\mathbf{R}_k}^2}{M_k} \langle \{x\}, \{X\} | \Upsilon \rangle \quad (2.26)$$

Inserting the Born-Oppenheimer expansion Eq. 2.22 into the full Schrödinger equation Eq. 2.14 and projecting onto the position-spin basis state $|\{x\}, \{X\}\rangle$, we write:

$$\langle \{x\}, \{X\} | \hat{H} | \Upsilon_m \rangle = U_m \langle \{x\}, \{X\} | \Upsilon_m \rangle \quad (2.27)$$

Using

$$\langle \{x\}, \{X\} | \hat{U}_{nn} | \Upsilon \rangle = \frac{1}{2} \sum_{k=1}^K \sum_{l=1, l \neq k}^K \frac{Z_k Z_l}{|\mathbf{R}_k - \mathbf{R}_l|} \langle \{x\}, \{X\} | \Upsilon \rangle \quad (2.28)$$

and

$$\begin{aligned} \langle \{x\}, \{X\} | \hat{T}_e + \hat{U}_{ee} + \hat{U}_{en} | \Upsilon_m \rangle &= \\ &= \langle \{x\}, \{X\} | \hat{T}_e + \hat{U}_{ee} + \hat{U}_{en} \sum_g \int d\{X'\} |g, \{X'\}\rangle \langle g, \{X'\} | \Upsilon_m \rangle \\ &= \langle \{x\}, \{X\} | \sum_g \int d\{X'\} \left(\hat{H}_e^{\{\mathbf{R}\}} | \Psi_g^{\{\mathbf{R}\}} \rangle \right) \otimes | \{X'\} \rangle \langle g, \{X'\} | \Upsilon_m \rangle \\ &= \langle \{x\}, \{X\} | \sum_g \int d\{X'\} \left(E_g^{\{\mathbf{R}\}} | \Psi_g^{\{\mathbf{R}\}} \rangle \right) \otimes | \{X'\} \rangle \langle g, \{X'\} | \Upsilon_m \rangle \\ &= \sum_g E_g^{\{\mathbf{R}\}} \langle \{x\} | \Psi_g^{\{\mathbf{R}\}} \rangle \langle g, \{X\} | \Upsilon_m \rangle, \end{aligned} \quad (2.29)$$

the full Schrödinger equation in position-spin-representation becomes:

$$\begin{aligned} \frac{1}{2} \sum_{k=1}^K \left[-\frac{\nabla_{\mathbf{R}_k}^2}{M_k} + \sum_{l=1, l \neq k}^K \frac{Z_k Z_l}{|\mathbf{R}_k - \mathbf{R}_l|} \right] \sum_g \Psi_g^{\{\mathbf{R}\}}(\{x\}) \Xi_m^{(g)}(\{X\}) + \\ + \sum_g E_g^{\{\mathbf{R}\}} \Psi_g^{\{\mathbf{R}\}}(\{x\}) \Xi_m^{(g)}(\{X\}) = U_m \sum_g \Psi_g^{\{\mathbf{R}\}}(\{x\}) \Xi_m^{(g)}(\{X\}), \end{aligned} \quad (2.30)$$

where we have used the definitions Eqs. 2.24 and 2.25. The equation of motion for the electronic wave functions $\{\Psi_g^{\{\mathbf{R}\}}\}$ is given by the electronic Schrödinger equation Eq. 2.20. To find an equation for the $\{\Xi_m^{(g)}\}$, we project the Schrödinger

equation onto a specific electronic wave function $\Psi_h^{\{\mathbf{R}\}}$ (at the same $\{\mathbf{R}\}$) and use their orthonormality⁴ to get:

$$\begin{aligned} \frac{1}{2} \sum_{k=1}^K \sum_g \int d\{x\} \Psi_h^{\{\mathbf{R}\}} * (\{x\}) \left[-\frac{\nabla_{\mathbf{R}_k}^2}{M_k} + \sum_{l=1, l \neq k}^K \frac{Z_k Z_l}{|\mathbf{R}_k - \mathbf{R}_l|} \right] \Psi_g^{\{\mathbf{R}\}}(\{x\}) \Xi_m^{(g)}(\{X\}) + \\ + E_h^{\{\mathbf{R}\}} \Xi_m^{(h)}(\{X\}) = U_m \Xi_m^{(h)}(\{X\}) \end{aligned} \quad (2.31)$$

Using the Leibniz rule for the second derivative

$$\nabla_{\mathbf{r}}^2 f(\mathbf{r}) g(\mathbf{r}) = (\nabla_{\mathbf{r}}^2 f(\mathbf{r})) g(\mathbf{r}) + 2 (\nabla_{\mathbf{r}} f(\mathbf{r})) (\nabla_{\mathbf{r}} g(\mathbf{r})) + f(\mathbf{r}) (\nabla_{\mathbf{r}}^2 g(\mathbf{r})) \quad (2.32)$$

and, again, orthonormality of the electronic basis functions, we then get:

$$\begin{aligned} \frac{1}{2} \sum_{k=1}^K \left[-\frac{\nabla_{\mathbf{R}_k}^2}{M_k} + \sum_{l=1, l \neq k}^K \frac{Z_k Z_l}{|\mathbf{R}_k - \mathbf{R}_l|} \right] \Xi_m^{(h)}(\{X\}) + E_h^{\{\mathbf{R}\}} \Xi_m^{(h)}(\{X\}) \\ - \sum_{k=1}^K \frac{1}{M_k} \sum_g (\nabla_{\mathbf{R}_k} \Xi_m^{(g)}(\{X\})) \int d\{x\} \Psi_h^{\{\mathbf{R}\}} * (\{x\}) (\nabla_{\mathbf{R}_k} \Psi_g^{\{\mathbf{R}\}}(\{x\})) \\ - \frac{1}{2} \sum_{k=1}^K \frac{1}{M_k} \sum_g \Xi_m^{(g)}(\{X\}) \int d\{x\} \Psi_h^{\{\mathbf{R}\}} * (\{x\}) (\nabla_{\mathbf{R}_k}^2 \Psi_g^{\{\mathbf{R}\}}(\{x\})) = U_m \Xi_m^{(h)}(\{X\}) \end{aligned} \quad (2.33)$$

Introducing the nonadiabatic⁵ coupling coefficients $\Lambda_{h,g}$ (which are actually operators in the nuclear Hilbert space, here represented in the position basis) as

$$\begin{aligned} \Lambda_{h,g} = -\frac{1}{2} \sum_{k=1}^K \frac{1}{M_k} \int d\{x\} \Psi_h^{\{\mathbf{R}\}} * (\{x\}) (\nabla_{\mathbf{R}_k}^2 \Psi_g^{\{\mathbf{R}\}}(\{x\})) \\ + 2 \int d\{x\} \Psi_h^{\{\mathbf{R}\}} * (\{x\}) (\nabla_{\mathbf{R}_k} \Psi_g^{\{\mathbf{R}\}}(\{x\})) \nabla_{\mathbf{R}_k}, \end{aligned} \quad (2.34)$$

we can more compactly write:

$$\begin{aligned} \frac{1}{2} \sum_{k=1}^K \left[-\frac{\nabla_{\mathbf{R}_k}^2}{M_k} + \sum_{l=1, l \neq k}^K \frac{Z_k Z_l}{|\mathbf{R}_k - \mathbf{R}_l|} \right] \Xi_m^{(h)}(\{X\}) + \\ + E_h^{\{\mathbf{R}\}} \Xi_m^{(h)}(\{X\}) + \sum_g \Lambda_{h,g} \Xi_m^{(g)}(\{X\}) = U_m \Xi_m^{(h)}(\{X\}) \end{aligned} \quad (2.35)$$

Born-Oppenheimer Approximation

Note that, until this point, no approximations have been made. In the Born-Oppenheimer approximation, we now neglect the nonadiabatic coupling terms,

⁴Compare Footnote 3.

⁵As is shown below, neglecting these coefficients decouples the different potential energy surfaces. That is, changes in the nuclear positions cannot lead to transitions of the electronic state from one PES to another one (*adiábatos* is ancient Greek for “impassable”). On the contrary, inclusion of these coefficients allows for the electronic state to transition between PESs, giving rise to the chosen naming.

that is, we set⁶

$$\Lambda_{h,g} \approx 0. \quad (2.36)$$

Eq. 2.35 then becomes

$$\begin{aligned} \frac{1}{2} \sum_{k=1}^K \left[-\frac{\nabla_{\mathbf{R}_k}^2}{M_k} + \sum_{l=1, l \neq k}^K \frac{Z_k Z_l}{|\mathbf{R}_k - \mathbf{R}_l|} \right] \Xi_m^{(g)}(\{X\}) + \\ + E_g^{\{\mathbf{R}\}} \Xi_m^{(g)}(\{X\}) = U_{m,g} \Xi_m^{(g)}(\{X\}), \end{aligned} \quad (2.37)$$

or in operator-form

$$\left(\hat{T}_n + \hat{U}_{nn} + E_g(\{\hat{\mathbf{R}}\}) \right) |\Xi_m^{(g)}\rangle = U_{m,g} |\Xi_m^{(g)}\rangle, \quad (2.38)$$

where:

$$\begin{aligned} E_g(\{\hat{\mathbf{R}}\}) |\{X\}\rangle &\equiv E_g^{\{\mathbf{R}\}} |\{X\}\rangle \\ \langle \{X\} | \Xi_m^{(g)} \rangle &\equiv \Xi_m^{(g)}(\{X\}) \end{aligned} \quad (2.39)$$

That is, for each electronic PES $E_g^{\{\mathbf{R}\}}$, we get a decoupled/ individual equation of motion for a nuclear-position dependent function. It is at this point adequate to think of $\Xi_m^{(g)}$ as the nuclear wave function for nuclei in an “external” potential given by the electronic PES. For each electronic PES $E_g^{\{\mathbf{R}\}}$, we thus get a set of nuclear solutions⁷ $\{\Xi_m^{(g)}\}_m$, and the solutions of the full Schrödinger equation become⁸⁹:

$$\begin{aligned} \Upsilon_{m,g}(\{x\}, \{X\}) &= \Psi_g^{\{\mathbf{R}\}}(\{x\}) \Xi_m^{(g)}(\{X\}) \\ |\Upsilon_{m,g}\rangle &= \int d\{x\} d\{X\} |\{x\}, \{X\}\rangle \Upsilon_{m,g}(\{x\}, \{X\}) \\ &= |\Psi_g^{\{\cdot\}}\rangle \otimes |\Xi_m^{(g)}\rangle, \end{aligned} \quad (2.40)$$

where the last line is to be understood in a symbolic way, since $|\Psi_g^{\{\cdot\}}\rangle$ is not a specific electronic state but signifies that the electronic state depends on the nuclear positions ($\langle \{x\}, \{X\} | \Psi_g^{\{\cdot\}} \rangle \otimes |\Xi_m^{(g)}\rangle = \langle \{x\} | \Psi_g^{\{\mathbf{R}\}} \rangle \langle \{X\} | \Xi_m^{(g)} \rangle$ with $\{\mathbf{R}\}$ from $\{X\}$). Note that, since both, the electronic (Eq. 2.19) and nuclear (Eq. 2.38)

⁶Note that, following the nomenclature of Ref. [43], this approximation would be called the Born-Oppenheimer *adiabatic* approximation, to distinguish it from the Born-Oppenheimer approximation where the diagonal elements $\Lambda_{g,g}$ are not neglected. Note also, that more precisely, we may write the (adiabatic) BOA as $\sum_g \Lambda_{h,g} \Xi_m^{(g)}(\{X\}) \approx 0$

⁷Note, that in “ $\{\Xi_m^{(g)}\}_m$ ”, the subscript m implies that the set contains elements for all the different values of m . Conversely, g is fixed. Similar notation is occasionally used throughout the text.

⁸Upon insertion of the solutions Eq. 2.40 into Eq. 2.27, we get terms of the form $-\sum_{k=1}^K \frac{1}{2M_k} \left[2 \left(\nabla_{\mathbf{R}_k} \Psi_g^{\{\mathbf{R}\}}(\{x\}) \right) \left(\nabla_{\mathbf{R}_k} \Xi_m^{(g)}(\{X\}) \right) + \left(\nabla_{\mathbf{R}_k}^2 \Psi_g^{\{\mathbf{R}\}}(\{x\}) \right) \Xi_m^{(g)}(\{X\}) \right]$. It is not immediately obvious that those terms vanish within the BOA, such that the used product functions are really solutions of the full Schrödinger equation. However, given the BOA Eq. 2.36 and using the fact that the electronic states form a (complete) basis of the electronic Hilbert space, it can be immediately shown that these terms must be zero, since all their linear coefficients in the BOA product-basis (BOA solutions form basis, see below) are zero.

⁹Compare Footnote 3 regarding the position-spin integrals.

Hamiltonians are Hermitian, such products of their eigenstates form a (complete) basis for the full Hilbert space (compare comments below Eq. 2.21 but now rotate the full electronic-nuclear basis according to the nuclear solutions). Solutions beyond the BOA may therefore be built from linear combinations thereof. Secondly, it is important to note that the product wave function shown in Eq. 2.40 must not be confused with the product wave function of independent particles. The electronic factor still depends parametrically on the nuclear positions (and the nuclear factor depends on the electronic state/PES), thereby accounting for the interaction between electrons and nuclei.

To summarize, we have found that within the Born-Oppenheimer approximation Eq. 2.36, solutions of the full Hamiltonian reduce from a sum over electronic states Eq. 2.23, to simple products Eq. 2.40 of an electronic and a nuclear wave function. These two factors can be calculated separately, with the electronic problem having to be solved first. The electronic PES is then used to obtain the nuclear wave functions. In other words, through the BOA, we neglect coupling of the different electronic PESs via the nuclei. The eigenstates of the full Schrödinger equation are restricted to a single PES, with nuclei living inside this PES without any nuclear state leading to mixtures of/ transitions between different electronic PESs. Note that, starting from Eq. 2.37, we have therefore labeled the eigenenergy of the full system as $U_{m,g}$ (instead of U_m), with g indexing electronic PESs and m indexing different nuclear states within that PES.

The validity of the BOA is discussed in detail in Refs. [43, 44]: to summarize, the nonadiabatic coupling terms Eq. 2.34 can be neglected as long as electronic potential energy-surfaces are well-separated energetically (which is violated in case of conical intersections between potential-energy surfaces) and improves with growing nuclear masses. While we omit a detailed discussion here, these results were to be expected from the observation that the BOA decouples different electronic potential-energy surfaces and by the fact that the nonadiabatic coupling terms scale inversely with the nuclear masses.

Lastly it shall be mentioned, that the commonly given justification of the BOA in terms of large electronic *velocities* and small nuclear *velocities* should be taken with caution. To briefly state the argument, the idea is that nuclear positions are quasi-static from the point of view of the electrons, such that the electronic motion depends only parametrically on the nuclear position, giving rise to the electronic Schrödinger equation Eq. 2.20. Conversely, from the nuclear point of view, electrons move very fast, such that their instantaneous positions do not influence the nuclei. Still, the nuclei are affected by the potential energy due to their interaction with an electron-cloud (averaged over the electronic movement), resulting in the nuclear equation of motion Eq. 2.38. This argument is problematic, since for both electrons and nuclei, solution of the time-independent Schrödinger equation gives the quantum-mechanical wave function, and with it a static probability distribution of electronic and nuclear positions in space. Within this time-independent wave function, the concept of a particle's *velocity* is unclear, as the particles do not move on classical trajectories, but rather follow the aforementioned probability distribution. The velocity argument should therefore be treated as a classical intuition for, but not a complete justification of the BOA.

2.1.4 Electronic Problem

For the rest of this text we now invoke the BOA. In addition, we assume that in the energetic ground state of the full system, nuclear delocalization is negligible, that is, nuclei can be approximated to be fixed in space at the positions denoted by $\{\mathbf{R}\}$ (essentially treating them like classical particles with fixed position¹⁰). Moreover, we will assume that nuclei stay in these positions when the system is excited electronically (compare also comments in Sec. 3.1). Assuming lastly that (energetic) effects due to the nuclear spins can be neglected, these approximations together then allow us to identify the full system's stationary states with the stationary electronic states obtained by solving the electronic problem at the nuclear configuration $\{\mathbf{R}\}$. In other words, we describe the system's behavior purely based on its electronic states (for a given $\{\mathbf{R}\}$), which can in principle be obtained by solving the electronic Schrödinger equation Eq. 2.20:

$$\hat{H}_e^{\{\mathbf{R}\}} |\Psi_g^{\{\mathbf{R}\}}\rangle = E_g^{\{\mathbf{R}\}} |\Psi_g^{\{\mathbf{R}\}}\rangle, \quad (2.41)$$

with

$$\hat{H}_e^{\{\mathbf{R}\}} = \sum_i^N \hat{h}_i^{\{\mathbf{R}\}} + \frac{1}{2} \sum_{i=1}^N \sum_{j=1, j \neq i}^N \frac{1}{|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|}, \quad (2.42)$$

where we introduced shorthand notation for the one-electron part $\hat{h}$ of the electronic Hamiltonian:

$$\hat{h}_i^{\{\mathbf{R}\}} = \frac{1}{2} \hat{p}_i^2 - \sum_{k=1}^K \frac{Z_k}{|\hat{\mathbf{r}}_i - \mathbf{R}_k|}, \quad (2.43)$$

which in position-spin-representation becomes (for a one-electron state ψ):

$$\begin{aligned} \langle x | \hat{h}^{\{\mathbf{R}\}} | \psi \rangle &= \langle x | \frac{\hat{p}^2}{2} - \sum_{k=1}^K \frac{Z_k}{|\hat{\mathbf{r}} - \mathbf{R}_k|} | \psi \rangle \\ &= \left[-\frac{\nabla^2}{2} - \sum_{k=1}^K \frac{Z_k}{|\mathbf{r} - \mathbf{R}_k|} \right] \psi(\mathbf{r}, s) \\ &\equiv h^{\{\mathbf{R}\}}(\mathbf{r}) \psi(\mathbf{r}, s), \end{aligned} \quad (2.44)$$

with commonly used notation introduced in the last line. Note that we will drop the superscript $\{\mathbf{R}\}$ in the rest of the text.

Now, even after the Born-Oppenheimer approximation and after clamping the nuclei, we are left with a problem of N interacting particles (electrons) where we still run into the exponential wall of Ref. [40] when using rather direct variational approaches to solve it. To still be able and (approximately) solve the electronic Schrödinger equation, we will introduce new computational methods and cost-reducing approximations in the upcoming sections. There is, of course, a wide field of available methods [45]. Without giving an exhaustive list, among the available

¹⁰These ground-state positions are obtained by minimizing the function $f(\{\mathbf{R}\}) = U_{nn}(\{\mathbf{R}\}) + E_{g=0}(\{\mathbf{R}\})$ ($g = 0$ denotes the lowest potential-energy surface) – a procedure we call *geometry optimization*. In this context, f is often called the *total energy*.

methods for ground-state calculations we find wave-function-based methods like the Hartree-Fock method (HF) or (truncated) Configuration-Interaction methods (CI), density-based methods like Kohn-Sham density functional theory (KS-DFT) and quantum Monte Carlo methods like variational Monte Carlo (VMC). From this list of available methods, we choose KS-DFT for our ground-state calculations, due to its favorable scaling with the number of electrons ($O(N^3)$, see Ref. [46]) and its easy applicability to both molecular systems (via Gaussian basis sets) and periodic systems (via plane-wave basis sets). Both of these properties will later be needed when performing calculations involving molecular clusters and periodic surfaces involving hundreds of electrons.¹¹

¹¹Also, on a more practical note, we will use the GW/BSE method for excited-state calculations. This is a further reason for choosing KS-DFT as our method for calculating the ground state, since many available GW/BSE codes rely on the availability of a ground state calculated with a KS-DFT code.

2.2 Density Functional Theory

As mentioned before, we will use density functional theory (DFT) to calculate properties of the electronic ground state of our system. As is detailed below, we will, however, not try to obtain the ground-state wave function, but instead try to find the *ground-state electron density*, which is the central object in DFT.

Given the success of density functional theory (DFT), there is a wide range of available literature. We will therefore keep this section rather short and focus on the general formalism. The interested reader can find left-out derivations in classical DFT textbooks, see e.g. Refs. [46–49].

As noted in Sec. 2.1.1, we first focus on finitely sized atomic systems and finally explain in Sec. 2.2.6 how the thermodynamic limit can be performed to approach the infinite surfaces we are interested in modelling.

2.2.1 Electron Density

Let us now introduce the *electron density*, the central quantity of DFT. To get there, we first recall the precise meaning of the N -electron wave function.

N -Electron Wave Function

First, the *symmetrization postulate* tells us that only antisymmetric N -electron states are physically allowed (since electrons are fermions), see Appendix A.1.2 for details. Thus, also the N -electron spin-position state $|\{x\}\rangle$ must be an antisymmetric state [42, 50]! We symbolically write it as (note that we understand product states here as antisymmetrized and omit the subscript A from the notation of Appendix A.1.2)

$$\begin{aligned} |\{x\}\rangle &= |x_1, x_2, \dots, x_N\rangle \\ x_i &= (\mathbf{r}_i, s_i) \end{aligned} \quad (2.45)$$

and interpret it as a state where one electron is at position $\mathbf{r}_1$ with spin s_1 , one electron is at position $\mathbf{r}_2$ with spin s_2 and so on. Importantly, the states $|x_1, x_2, x_3, \dots, x_N\rangle$ and $|x_2, x_1, x_3, \dots, x_N\rangle$, as well as all other permutations, are therefore equivalent configurations, i.e., they describe the same physical state of an N -electron system. As detailed in Eq. A.22, they are in fact the same mathematical object except for a possible, unphysical overall phase of -1 . These antisymmetric spin-position states form a basis of the N -electron (antisymmetric) Hilbert space, such that the unity operator can be written as [42]

$$\frac{1}{N!} \sum_{s_1=\uparrow,\downarrow} \sum_{s_2=\uparrow,\downarrow} \cdots \sum_{s_N=\uparrow,\downarrow} \int_{\mathbb{R}^3} d^3r_1 \int_{\mathbb{R}^3} d^3r_2 \cdots \int_{\mathbb{R}^3} d^3r_N |(\mathbf{r}_1, s_1), \dots\rangle \langle(\mathbf{r}_1, s_1), \dots| = \hat{1}, \quad (2.46)$$

or, more compactly:

$$\frac{1}{N!} \int d\{x\} |\{x\}\rangle \langle\{x\}| = \hat{1} \quad (2.47)$$

Note that the $\frac{1}{N!}$ prefactor must be included, since every physically distinct state is included $N!$ in the expression.

Let us now suppose our N -electron system is in the (antisymmetric) state $|\Psi\rangle$. Then, the overlap of $|\Psi\rangle$ with the spin-position state $|\{x\}\rangle$ is written as

$$\langle\{x\}|\Psi\rangle \quad (2.48)$$

and $|\langle\{x\}|\Psi\rangle|^2$ is therefore the probability (-density function for positions and -mass function for spins) of finding the system in the antisymmetric spin-position state $|\{x\}\rangle$. Note that this interpretation assumes that the N -electron state is properly normalized (importantly, bound states of finitely-sized atomic systems can be normalized in such a way, see Appendix A.1)

$$\langle\Psi|\Psi\rangle = 1, \quad (2.49)$$

such that insertion of Eq. 2.47 gives us:

$$\frac{1}{N!} \int d\{x\} |\langle\{x\}|\Psi\rangle|^2 = 1 \quad (2.50)$$

Instead of only summing and integrating over physically distinct states (the result of which should also be 1), we use unrestricted integrals and summations. As a result, every physically distinct configuration/state is included $N!$ times, via physically equivalent permutations of the coordinates. These redundancies are then accounted for by the prefactor.

Note that, due to the antisymmetrization, the physically allowed spin-position states can not include two identical spin-positions $x_i = x_j$, since using two identical coordinates and the antisymmetrized construction $|x_1, x_2, \dots, x_N\rangle$ would result in a 0 (compare Eq. A.21). Thus, $|\langle\{x\}|\Psi\rangle|^2$ vanishes whenever at least two spin-positions are equal – a result known as the Pauli principle (here for the special case of spin-position one-electron states). We will get back to this later

Before continuing, let us look at the simplified situation of a simple 2-electron system and briefly assume electrons to be spinless particles. Using this simplified structure allows us to understand the consequences of including physically equivalent states/configurations in our calculations. First, the probability for finding two/both electrons in some volume V_α is then given by:

$$\frac{1}{2} \int_{V_\alpha} d^3r_1 \int_{V_\alpha} d^3r_2 |\langle\mathbf{r}_1, \mathbf{r}_2|\Psi\rangle|^2 \quad (2.51)$$

Here, every contributing physical configuration contributes via two permutations. That is, the physical situation where one electron is at $\mathbf{r}_1$ and another one is at $\mathbf{r}_2$ (both $\in V_\alpha$) is included via the two equivalent states $|\mathbf{r}_1, \mathbf{r}_2\rangle$ and $|\mathbf{r}_2, \mathbf{r}_1\rangle$. Extending V_α over all space $\mathbb{R}^3$ the fact that $|\Psi\rangle$ is normalized ensures the result to be 1, that is, the probability for finding the two electrons somewhere in space is 100% (compare Eq. 2.50). Next, let us look at the probability for finding one electron in V_α and one electron in V_β , where V_α and V_β are disjoint, i.e., have no overlap. This probability can be written without repeating equivalent configurations – and thus without a prefactor – as:

$$\int_{V_\alpha} d^3r_1 \int_{V_\beta} d^3r_2 |\langle\mathbf{r}_1, \mathbf{r}_2|\Psi\rangle|^2 \quad (2.52)$$

Finally, in the most complicated case (which we do not need below), where the two volumes partially overlap, we must use the first expression for the physical situations that both electrons are in the overlap V_γ , and the second expression for the situations where one electron is in V_α/V_γ and the other is in V_β/V_γ , the situations where one is in V_α/V_γ and the other one is in V_γ and the situations where one electron is in V_β/V_γ and the other is in V_γ , which can easily be seen when drawing a Venn diagram and listing the possible distinct physical situations.

Going back to the N -electron system and including spin again, the probability of finding one electron in V_α with spin s_α , one electron in V_β with spin s_β , one electron in V_γ with spin s_γ , etc. is then, under the condition of disjoint volumes, given by:

$$\int_{V_\alpha} d^3r_1 \int_{V_\beta} d^3r_2 \dots |\langle (\mathbf{r}_1, s_\alpha), (\mathbf{r}_2, s_\beta) \dots | \Psi \rangle|^2, \quad (2.53)$$

where, as in the disjoint case before, every physically distinct state is only included once. Note that if two of the volumes are the same, but the corresponding spins are opposite, the resulting probability takes the same form. To see this, think back to the two-electron example: The probability to find both electrons in V_α , one with spin up and one with spin down is then simply given by

$$\int_{V_\alpha} d^3r_1 \int_{V_\alpha} d^3r_2 |\langle (\mathbf{r}_1, \uparrow), (\mathbf{r}_2, \downarrow) | \Psi \rangle|^2, \quad (2.54)$$

where every physically distinct configuration is only included once and thus no prefactor is needed¹².

In the extreme case of infinitesimally small volumes $\{dV_i\}$ located at positions $\{\mathbf{r}_i\}$, the probability for finding one electron in dV_1 at $\mathbf{r}_1$ with spin s_1 , one electron in dV_2 at $\mathbf{r}_2$ with spin s_2 , and so on is then given by:

$$|\langle (\mathbf{r}_1, s_1), (\mathbf{r}_2, s_2) \dots (\mathbf{r}_N, s_N) | \Psi \rangle|^2 dV_1 dV_2 \dots dV_N \quad (2.55)$$

The validity of this expression's interpretation can easily be seen by distinguishing two cases: (1) if all spin-positions are distinct, then the infinitesimal volumes are either nonoverlapping, or they are identical (meaning two positions and the corresponding infinitesimal volumes are identical), but the corresponding spins differ. Thus, the expression derived above can be used (by assuming the wave function to be approximately constant in finite volumes $\{\Delta V_i\}$ and then making the volumes infinitesimal). (2) if two spin-positions are the same, the expression vanishes due to the Pauli principle mentioned above, thus telling us that there is 0% probability to find the system in a forbidden configuration.

With this understanding of the overlap $\langle \{x\} | \Psi \rangle$, let us define the N -electron wave function as¹³:

$$\Psi(\{x\}) \equiv \frac{1}{\sqrt{N!}} \langle \{x\} | \Psi \rangle \quad (2.56)$$

¹²Within the integral $\int_{V_\alpha} d^3r_2$, for a given $\mathbf{r}_1$, the point $\mathbf{r}_2 = \mathbf{r}_1$ is of measure zero and can safely be ignored, see also Footnote 37.

¹³Throughout this text, we are occasionally sloppy in our language and use *wave function* and *state* interchangeably. This is to be excused by the fact that the two quantities contain the same information, such that no further problems should arise from this. In the presented equations, the two quantities are of course always adequately distinguished.

The $\frac{1}{\sqrt{N!}}$ is convention and is chosen for being a convenient choice in many situations. In particular, we then find that the wave function is normalized (in an expression that includes $N!$ equivalent permutations per physically distinct state):

$$\int d\{x\} |\Psi(\{x\})|^2 = 1 \quad (2.57)$$

Additionally, we find that

$$N! |\Psi((\mathbf{r}_1, s_1), (\mathbf{r}_2, s_1) \dots (\mathbf{r}_N, s_N))|^2 dV_1 dV_2 \dots dV_N \quad (2.58)$$

has the same meaning as Eq. 2.55. Note also, that we can use the antisymmetry of the spin-position state $|x_1, x_2, \dots, x_N\rangle$ with respect to coordinate swaps, to find

$$|\Psi(x_1, x_2, x_3, \dots, x_N)|^2 = |\Psi(x_2, x_1, x_3, \dots, x_N)|^2 \quad (2.59)$$

and so on, for all permutations.

Electron Density

Finally, let us now turn to the electron density n . We begin by introducing the closely related *spin density* n_s , which is defined to be the quantity that, for a given volume V and spin s , gives us via

$$\int_V d^3r n_s(\mathbf{r}) \quad (2.60)$$

the expected number of electrons with spin s in volume V , provided that our system is in some state $|\Psi\rangle$. Loosely speaking, we then say that $n_s(\mathbf{r})$ is the number of electrons at $\mathbf{r}$ with spin s . Similarly, the electron density is given by

$$n(\mathbf{r}) = n_\uparrow(\mathbf{r}) + n_\downarrow(\mathbf{r}), \quad (2.61)$$

such that

$$\int_V d^3r n(\mathbf{r}) \quad (2.62)$$

gives us the total expected number of electrons in volume V , provided, again, that our system is in some state $|\Psi\rangle$.

Our goal is now to determine how the (spin-) density of a given normalized state $|\Psi\rangle$ can be calculated from the state's N -electron wave function. To do so, we introduce the following indicator function:

$$\begin{aligned} \hat{\mathbf{N}}_{V,s} |x_1, x_2, \dots, x_N\rangle &\equiv \mathbf{N}_{V,s}(x_1, x_2, \dots, x_N) |x_1, x_2, \dots, x_N\rangle \\ \mathbf{N}_{V,s}(x_1, x_2, \dots, x_N) &\equiv \sum_{i=1}^N \mathbf{1}_{V,s}(x_i), \end{aligned} \quad (2.63)$$

where:

$$\mathbf{1}_{V,s}(\mathbf{r}, s') \equiv \begin{cases} 1 & \text{if } \mathbf{r} \in V \text{ and } s = s' \\ 0 & \text{otherwise} \end{cases} \quad (2.64)$$

For a given configuration $|x_1, x_2, \dots, x_N\rangle$, $\mathbf{N}_{V,s}(x_1, x_2, \dots, x_N)$ thus gives us the number of electrons in volume V with spin s . For a given N -electron state Ψ , the *expected* number of electrons in volume V with spin s is thus given by the expectation value of $\mathbf{N}_{V,s}$ with respect to the probability distribution given by the state. Using the above-derived interpretation of $|\langle\{x\}|\Psi\rangle|^2$ as the state's probability-density function for positions and probability-mass function for spins, we sum over all spins and integrate over all space, taking into account multi-counting via the now well-known $\frac{1}{N!}$ prefactor and find for the expectation value:

$$\begin{aligned} & \frac{1}{N!} \sum_{s_1=\uparrow,\downarrow} \sum_{s_2=\uparrow,\downarrow} \cdots \sum_{s_N=\uparrow,\downarrow} \int_{\mathbb{R}^3} d^3r_1 \int_{\mathbb{R}^3} d^3r_2 \cdots \int_{\mathbb{R}^3} d^3r_N |\langle\{x\}|\Psi\rangle|^2 \mathbf{N}_{V,s}(\{x\}) = \\ & = \sum_{s_1=\uparrow,\downarrow} \sum_{s_2=\uparrow,\downarrow} \cdots \sum_{s_N=\uparrow,\downarrow} \int_{\mathbb{R}^3} d^3r_1 \int_{\mathbb{R}^3} d^3r_2 \cdots \int_{\mathbb{R}^3} d^3r_N |\Psi(\{x\})|^2 \mathbf{N}_{V,s}(\{x\}), \end{aligned} \quad (2.65)$$

where we used the definition of the wave function in the second line. Inserting the definition of the indicator function, this becomes:

$$\begin{aligned} & \sum_{s_1=\uparrow,\downarrow} \sum_{s_2=\uparrow,\downarrow} \cdots \sum_{s_N=\uparrow,\downarrow} \int_{\mathbb{R}^3} d^3r_1 \int_{\mathbb{R}^3} d^3r_2 \cdots \int_{\mathbb{R}^3} d^3r_N |\Psi(\{x\})|^2 \sum_{i=1}^N \mathbf{1}_{V,s}(\mathbf{r}_i, s_i) = \\ & = \sum_{i=1}^N \int_V d^3r_i \prod_{j=1, j \neq i}^N \sum_{s_j=\uparrow,\downarrow} \int_{\mathbb{R}^3} d^3r_j |\Psi(\dots, (\mathbf{r}_i, s), \dots)|^2 = \\ & = N \int_V d^3r_1 \prod_{j=2}^N \sum_{s_j=\uparrow,\downarrow} \int_{\mathbb{R}^3} d^3r_j |\Psi((\mathbf{r}_1, s), \dots)|^2, \end{aligned} \quad (2.66)$$

where we used permutation symmetry Eq. 2.59 to get to the last line. Comparison with Eq. 2.60 then allows us to identify the electron spin-density as:

$$\begin{aligned} n_s(\mathbf{r}) &= N \sum_{s_2=\uparrow,\downarrow} \cdots \sum_{s_N=\uparrow,\downarrow} \int_{\mathbb{R}^3} d^3r_2 \cdots \int_{\mathbb{R}^3} d^3r_N |\Psi((\mathbf{r}, s), (\mathbf{r}_2, s_2), \dots, (\mathbf{r}_N, s_N))|^2 \\ n(\mathbf{r}) &= n_{\uparrow}(\mathbf{r}) + n_{\downarrow}(\mathbf{r}) \end{aligned} \quad (2.67)$$

Electron Density of Slater Determinants

Since we will often encounter it, let us look at the special case of an N -electron state that is a simple antisymmetrized product of N single-electron orbitals (compare Eq. A.20):

$$|\Phi\rangle = |\phi_1, \phi_2, \dots, \phi_N\rangle \quad (2.68)$$

The wave function of $|\Phi\rangle$ is a Slater determinant [42] (this holds in general, so also for non-orthonormal and even linearly dependent orbitals, see below):

$$\begin{aligned}
\Phi(\{x\}) &= \frac{1}{\sqrt{N!}} \langle \{x\} | \Phi \rangle \\
&= \frac{1}{\sqrt{N!}} \langle x_1, x_2, \dots, x_N | \phi_1, \phi_2, \dots, \phi_N \rangle \\
&= \frac{1}{\sqrt{N!}} \sum_{\Pi} (-1)^{|\Pi|} \prod_{i=1}^N \phi_{\Pi(i)}(x_i) \\
&= \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(x_1) & \phi_1(x_2) & \dots & \phi_1(x_N) \\ \phi_2(x_1) & \phi_2(x_2) & \dots & \phi_2(x_N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(x_1) & \phi_N(x_2) & \dots & \phi_N(x_N) \end{vmatrix} \tag{2.69}
\end{aligned}$$

From this form of the wave function (and using completeness of the position-spin states), it is immediately obvious that the one-electron orbitals must be linearly independent, for this state to be physically allowed (that is, not vanish). Additionally, we see that orthonormalization of the orbitals only changes the normalization and global phase of the state and that, such states are automatically normalized when they are built from orthonormal orbitals, that is $\langle \Phi | \Phi \rangle = 1$ (see Appendix A.1.2). Thus, any normalized antisymmetrized product-state, can be built from orthonormal orbitals (although of course not needed, we can even create any desired global phase by shifting the global phase of one of the orbitals appropriately)! This property will become very useful later, since, throughout this text and especially in the upcoming subsections, we will often encounter such states – where we will usually assume, without explicitly stating it, that it is normalized (and can thus be constructed from orthonormal orbitals) – and for simplicity also call the state itself a (single) *Slater determinant*.

Finally, note that the electron spin-density for such a state takes a simple form (writing $x_1 = (\mathbf{r}, s)$):

$$\begin{aligned}
n_s(\mathbf{r}) &= N \int d(x_2, \dots, x_N) |\Phi(x_1, x_2, \dots, x_N)|^2 \\
&= \frac{1}{(N-1)!} \int d(x_2, \dots, x_N) \sum_{\Pi, \Pi'} (-1)^{|\Pi|+|\Pi'|} \prod_{i=1}^N \phi_{\Pi(i)}^*(x_i) \phi_{\Pi'(i)}(x_i) \\
&= \frac{1}{(N-1)!} \sum_{\Pi, \Pi'} (-1)^{|\Pi|+|\Pi'|} \phi_{\Pi(1)}^*(x_1) \phi_{\Pi'(1)}(x_1) \prod_{i=2}^N \delta_{\Pi(i), \Pi'(i)} \\
&= \frac{1}{(N-1)!} \sum_{\Pi} |\phi_{\Pi(1)}(x_1)|^2 \\
&= \sum_{i=1}^N |\phi_i(x_1)|^2, \tag{2.70}
\end{aligned}$$

where we used orthonormality of the orbitals.

Trial Densities and N -Representability

Note that the electron density n for a given normalized state $|\Psi\rangle$ is generally a real-valued, positive semi-definite function that integrates (over all space) to N . For later use, we call a function that satisfies these conditions a *trial density* (or: density candidate):

Def. 1. An N -electron (*trial*) density is a real, positive semi-definite function that integrates (over $\mathbb{R}^3$) to N .

Note that we will often simply speak about *densities* instead of *trial densities*. Importantly, it is not trivially clear if every trial density can be derived from an N -electron state¹⁴ via Eq. 2.67. We therefore additionally define:

Def. 2. An electron (trial) density n (see Def. 1) is called N -representable if there is an (at least one) normalized N -electron state $|\Psi\rangle$ that leads to n via Eq. 2.67.

Note that if we additionally restrict ourselves to N -electron states $|\Psi\rangle$ with a finite kinetic energy expectation value – a sane assumption for physical systems – then a clearer picture emerges: We can then find that the density of such a state belongs to $H^1(\mathbb{R}^3)$ and that, conversely, every trial density n that lies in $H^1(\mathbb{R}^3)$ is N -representable by such a state $|\Psi\rangle$ with finite kinetic energy [51]. Interestingly, it can even be shown that n is in this case even *non-interacting* N -representable (more on this below), that is, representable by a Slater determinant (with, again, finite kinetic energy) [51]. Further details on these notions can also be found in Refs. [52, 53].

2.2.2 Hohenberg-Kohn Theorem I

Equipped with the definition of the electron density n , we now focus on the basic theorems of Hohenberg and Kohn [54] which underlie density functional theory. We begin with the Hamiltonian of N electrons in an arbitrary external potential v :

$$\begin{aligned}
 \hat{H}_e &= \hat{T}_e + \hat{U}_{ee} + \hat{V} \\
 \hat{T}_e &= \frac{1}{2} \sum_{i=1}^N \hat{p}_i^2 \\
 \hat{U}_{ee} &= \frac{1}{2} \sum_{i=1}^N \sum_{j=1, j \neq i}^N \frac{1}{|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|} \\
 \hat{V} &= \sum_{i=1}^N v(\hat{\mathbf{r}}_i),
 \end{aligned} \tag{2.71}$$

¹⁴Where we here and in the rest of this section always mean *pure* and *antisymmetric* N -electron states.

where $\hat{V}$ represents the external potential, for which we can easily find:

$$\langle \Psi | \hat{V} | \Psi \rangle = \int_{\mathbb{R}^3} d^3r v(\mathbf{r}) n(\mathbf{r}) \quad (2.72)$$

Comparison immediately shows that the electronic Hamiltonian Eq. 2.42 is of such form, with electron-nucleus Coulomb interactions making up the “external” potential.

In their first theorem, Hohenberg and Kohn (HK) then showed by *reductio ad absurdum* that the external potential v is (up to an additive constant) determined by the corresponding ground-state charge-density n_0 (related to the ground-state wave function Ψ_0 via Eq. 2.67). In other words, if we know the ground-state charge density of the system, we could in principle obtain the external potential from it. Note that in the original work by Hohenberg and Kohn [54] the Hamiltonian built from the potential v is assumed to have a nondegenerate ground state. This restriction can however be lifted, as is detailed in Ref. [55], such that even for a potential leading to a Hamiltonian with a degenerate ground state, the potential is uniquely determined (up to a constant) by any of the ground-state densities.

Importantly, via Eq. 2.62 the ground-state charge density also gives us the number of electrons in the system (for periodic systems the number of electrons per unit cell is the more relevant quantity, see Eq. B.9). In combination with the derived external potential, the ground-state charge-density therefore fully determines the electronic Hamiltonian Eq. 2.71 (up to an additive constant) and therefore contains in principle all information contained in the Hamiltonian¹⁵. For the case of a nondegenerate ground state, we then find a one-to-one mapping between the ground-state wave function and the ground-state density, such that all information contained in the ground-state wave function (that is, all information about the system’s state) is therefore also contained in the ground-state charge density! For a system with a degenerate ground state this simple one-to-one-mapping can break down, but an alternative mapping between a ground-state density and a manifold of ground-state wave functions can be constructed [55].

Since we will need it for the second theorem, let us introduce at this point the concept of *v-representability*. While every real, positive semi-definite function that integrates (over all space) to N may be thought of as an N -electron density (see Def. 1), the HK theorems (as presented in Ref. [54]) are concerned with *v-representable* densities, that is densities that can be derived as ground-state densities from a specific external potential v . More precisely, we define:

Def. 3. We call an N -electron density (see Def. 1) n_0 *v-representable*, when there exists an external potential v which defines an N -electron Hamiltonian H_e of the form shown in Eq. 2.71, such that H_e has a normalized ground-state wave

¹⁵ Except of course for information that changes when adding a constant to the Hamiltonian. This is the reason why we cannot derive total energies of the system’s energy eigenstates from the density alone, but only their relative energies. If one knows the external potential, we can however, use – if its functional form were known – the energy functional Eq. 2.76 to determine the ground-state energy absolutely, and therefore all other eigenenergies. Alternatively, for finite atomic systems, we may demand the potential to vanish at infinity such that the additive factor should be 0.

function Ψ_0 that leads to that density n_0 via Eq. 2.67.

The HK1 theorem (as presented in Ref. [54]) then tells us that for every v -representable density, the density uniquely determines the potential (up to an additive constant).

2.2.3 Hohenberg-Kohn Theorem II and Levy's Constrained Search

Knowing about the wealth of information stored in it, the question arises if we can determine a system's ground-state charge-density(-densities, if multiple exist) directly, that is without the many-electron ground-state wave function(s) at hand.

To answer this question, we begin by rewriting the expression for the system's ground-state energy. In terms of a ground state $|\Psi_0\rangle$ it reads:

$$E_0 = \langle \Psi_0 | \hat{H}_e | \Psi_0 \rangle = \langle \Psi_0 | \hat{T}_e | \Psi_0 \rangle + \langle \Psi_0 | \hat{U}_{ee} | \Psi_0 \rangle + \langle \Psi_0 | \hat{V} | \Psi_0 \rangle \quad (2.73)$$

In case of degeneracy, all degenerate ground-state wave functions will of course lead to the same ground-state energy E_0 .

Next, we want to express the ground-state energy in terms of a ground-state density. In the case of a degenerate ground state, there can be multiple ground-state densities, which then again should all lead to the same ground-state energy E_0 . For a given ground-state density n_0 , we can then simply pick any wave function from the corresponding manifold of ground-state wave functions mentioned above and calculate E_0 from it using Eq. 2.73. While the choice of the ground-state wave function is not unique, the resulting energy is, such that this process can be thought of as a functional of the ground-state density. For nondegenerate ground states this is of course trivially constructible via the one-to-one relation between ground-state density and ground-state wave function.

To formalize this, we first define the *universal functional* F as

$$F[n] \equiv \langle \Psi_0 | \hat{T}_e | \Psi_0 \rangle + \langle \Psi_0 | \hat{U}_{ee} | \Psi_0 \rangle, \quad (2.74)$$

where n is a v -representable density and $|\Psi_0\rangle$ is a ground state from the corresponding manifold. Note that comparison with Eqs. 2.73 and 2.72 shows that all ground states of the manifold give the same value for $\langle \Psi_0 | \hat{T}_e | \Psi_0 \rangle + \langle \Psi_0 | \hat{U}_{ee} | \Psi_0 \rangle$. Note also that F is usually called the *universal* functional because it is independent of the external potential v . For later use, we also define the kinetic-energy functional and the electron-electron interaction functionals:

$$\begin{aligned} F[n] &= T[n] + U_{ee}[n] \\ T[n] &\equiv \langle \Psi_0 | \hat{T}_e | \Psi_0 \rangle \\ U_{ee}[n] &\equiv \langle \Psi_0 | \hat{U}_{ee} | \Psi_0 \rangle \end{aligned} \quad (2.75)$$

Note that, technically, T and U_{ee} are not well-defined like this if there are multiple ground states that correspond to n . We would need some additional criterion to select one of them (for example, the one that minimizes T). We will, however, later only ever encounter the sum $T[n] + U_{ee}[n]$, where the choice of the ground state does not matter, so we do not need to further address this.

Using the universal functional and the external potential, we can then define the following energy functional as a functional of v -representable densities:

$$E_v[n] \equiv F[n] + \int_{\mathbb{R}^3} d^3r v(\mathbf{r})n(\mathbf{r}) \quad (2.76)$$

For an N -electron system with external potential v and a ground-state density n_0 , when comparing the energy functional Eq. 2.76 together with Eq. 2.72 to the system's ground-state energy E_0 , Eq. 2.73, we then immediately see, that $E_v[n_0] = E_0$. For a v -representable density corresponding to a specific potential v , the functional E_v thus gives us the ground-state energy of the Hamiltonian defined by v via Eq. 2.71.

In its original form presented in Ref. [54] the HK2 theorem is then only concerned with nondegenerate ground states, where it tells us that when taking all N -electron v -representable densities into account, the (only) one that minimizes E_v (such that it assumes the ground-state energy E_0) is the ground-state density belonging to v . Since the proof simply uses the Rayleigh-Ritz minimum principle for the ground state, it is trivially expandable to the case of a degenerate ground state, where it then tells us that when taking all N -electron v -representable densities into account, any of them that minimizes E_v – resulting again in the value E_0 – is a (possibly one of multiple) ground-state density belonging to v .

Thus, the HK2 theorem in principle tells us how to find the (or one of them if multiple exist in a degenerate case) ground-state density for a given external potential v , namely by minimizing E_v . Unfortunately, however, it is not a very practical tool, since for a direct minimization of the energy functional Eq. 2.76 we would need to know which trial densities are v -representable (such that we do not leave the domain of F) and we would need an alternative form of the universal functional really in terms of the density instead of (one of) the corresponding ground state(s) (Since knowing the/a ground state would defeat the whole point of DFT.).

At least the first of these practical concerns has been mostly alleviated by Levy in Ref [56]. To see this, let us first redefine the universal functional and the energy function in terms of N -representable densities:

$$\begin{aligned} F[n] &\equiv \min_{\Psi \rightarrow n} \left(\langle \Psi | \hat{T}_e | \Psi \rangle + \langle \Psi | \hat{U}_{ee} | \Psi \rangle \right) \\ E_v[n] &\equiv F[n] + \int_{\mathbb{R}^3} d^3r v(\mathbf{r})n(\mathbf{r}), \end{aligned} \quad (2.77)$$

where the minimum is taken with respect to all wave functions that lead to n via Eq. 2.67. Note that every v -representable density is trivially also N -representable and that for a v -representable density, the definitions Eqs. 2.74 and 2.76 coincide with Eq. 2.77. For this reason the redefinitions given here can be regarded as mere extensions (from v -representable to all N -representable densities) and we therefore do not change the functionals' symbols. Again for later use, we can in analogy with Eq. 2.75 define the kinetic energy and electron-electron interaction functionals for N -representable densities:

$$\begin{aligned} F[n] &= T[n] + U_{ee}[n] \\ T[n] &\equiv \langle \Psi | \hat{T}_e | \Psi \rangle \\ U_{ee}[n] &\equiv \langle \Psi | \hat{U}_{ee} | \Psi \rangle, \end{aligned} \quad (2.78)$$

where $|\Psi\rangle$ is the state that minimizes F in Eq. 2.77. And in analogy to Eq. 2.75, T and U_{ee} are not well-defined if there are multiple wave functions that lead to n and minimize F . As before, we can in principle add some additional selection rule to sanely define them, which is, however, again not needed, since we only encounter the sum $T[n] + U_{ee}[n]$.

Levy then showed in analogy to the original formulation of HK2 that when taking all N -representable densities into account, the energy functional E_v is minimized by the ground-state density (ground-state densities, if there are multiple) of the system and assumes the ground-state energy E_0 . Note that every N -representable density that minimizes E_v (i.e. every solution) is also v -representable and is a ground-state density¹⁶ with respect to v . Thus, in order to obtain the ground-state density (densities) of the system, instead of using v -representable densities and HK2, we can minimize Levy's energy functional E_v , Eq. 2.77, with respect to N -representable densities. Put simply, the two minimization approaches work with different domains, but they give the same solutions¹⁷! In the following we will refer to the minimization approach that utilizes Levy's functional Eq. 2.77 as *Levy's constrained search* (LCS).

2.2.4 Kohn-Sham Approach

We have now mostly alleviated the first of the two concerns given above Eq. 2.77: instead of minimizing E_v with respect to v -representable densities, we can minimize it with respect to N -representable densities, which form a greater set of densities such that the risk of exiting the domain of E_v during minimization is reduced (see also comments below Def. 2). If we knew the functional form of F in terms of n , we could then directly minimize E_v (while making sure not to leave its domain) to find a ground-state density of the system under study. Unfortunately, however, the functional dependence of F on n is not known and simple approximations are accompanied by a rather large loss in accuracy [47]. The trick of Kohn-Sham DFT [57] is then to investigate an alternative system of non-interacting electrons, whose ground-state density is by construction the same as that of the interacting system. For this system the kinetic energy can readily be calculated, thereby heavily reducing the size of the unknown functional in the theory (which in KS-DFT is called the *exchange-correlation functional*) and thus decreasing errors made due to approximations of the unknown functional [47]! This way, the second concern given above Eq. 2.77 is addressed.

¹⁶ A density n is N -representable if there is an N -electron wave function Ψ that is related to n via Eq. 2.67. If n minimizes the energy functional E_v for some v , then this means that Ψ minimizes the expectation value of $\hat{H}_e$ (see Eq. 2.73) and is therefore by Rayleigh-Ritz a ground-state wave function. Thus, n is v -representable and is a ground-state density with respect to v .

¹⁷ All solutions of HK2 (i.e. finding minima w.r.t. v -representable densities) are also solutions of LCS (i.e. finding minima w.r.t. N -representable densities), because all v -representable densities (with energy E_0) are also N -representable densities (with energy E_0). All solutions of LCS are also solutions of HK2, because they then are also v -representable densities (with energy E_0), as shown in Footnote 16.

HK and LCS for a Non-Interacting System

Similarly to HK1, let us start with the Hamiltonian of N electrons in an arbitrary external potential v . In contrast to HK1, however, we drop the electron-electron Coulomb repulsion, such that the Hamiltonian can be understood as the Hamiltonian of a fictitious type of *non-interacting* electrons:

$$\begin{aligned}\hat{H}_e &= \hat{T}_e + \hat{V} \\ \hat{T}_e &= \frac{1}{2} \sum_{i=1}^N \hat{p}_i^2 \\ \hat{V} &= \sum_{i=1}^N v(\hat{\mathbf{r}}_i)\end{aligned}\tag{2.79}$$

Next, we define the non-interacting analog of v -representability:

Def. 4. We call an N -electron density (see Def. 1) n_0 *non-interacting v -representable*, when there exists an external potential v which defines an N -electron Hamiltonian H_e of the form shown in Eq. 2.79, such that H_e has a normalized ground-state wave function Φ_0 that leads to that density n_0 via Eq. 2.67.

At this point it is important to note that the (normalized) eigenstates – and thus also the ground state(s) – of such a non-interacting system Eq. 2.79 can always be written, without approximation, as (single) Slater determinants of N orthonormalized one-electron orbitals (see also Eq. 2.69). Every non-interacting v -representable density is therefore related to a (at least one) (single) Slater determinant ground-state wave function via Eq. 2.67.

The argumentations in Refs. [54, 55] do not depend on the form of the electron-electron interaction and can therefore be transferred over to the non-interacting system. We thus find in analogy to HK1, that for every non-interacting v -representable density, the density uniquely determines the potential (up to an additive constant). Secondly, in analogy to before, we can define the non-interacting kinetic energy functional

$$T^{(s)}[n] \equiv \langle \Phi_0 | \hat{T}_e | \Phi_0 \rangle, \tag{2.80}$$

where n is a non-interacting v -representable density and $|\Phi_0\rangle$ is a ground state (whose wave function can be written as a Slater determinant) from the corresponding manifold¹⁸. The energy functional of non-interacting v -representable densities then becomes

$$E_v^{(s)}[n] \equiv T^{(s)}[n] + \int_{\mathbb{R}^3} d^3r v(\mathbf{r})n(\mathbf{r}) \tag{2.81}$$

and in analogy to HK2, we find that when taking all non-interacting v -representable densities into account, $E_v^{(s)}$ assumes a minimal value of E_0 (the ground-state energy of the corresponding non-interacting Hamiltonian), which it (only) assumes for the ground-state density(-densities, if multiple exist) related to v .

Finally, also LCS in terms of N -representable densities can be transferred over. We first define:

¹⁸ Comparison with Eqs. 2.79 and 2.72 shows that all ground states of the manifold give the same value for $\langle \Phi_0 | \hat{T}_e | \Phi_0 \rangle$.

Def. 5. An electron density n (see Def. 1) is called *non-interacting N -representable* if there is a (at least one) normalized N -electron (single) Slater determinant $|\Phi\rangle$ that leads to n via Eq. 2.67.

Additionally, in analogy to Eq. 2.77, we define the non-interacting energy functionals in terms of non-interacting N -representable densities as

$$\begin{aligned} T^{(s)}[n] &\equiv \min_{\Phi \rightarrow n} \left(\langle \Phi | \hat{T}_e | \Phi \rangle \right) \\ E_v^{(s)}[n] &\equiv T^{(s)}[n] + \int_{\mathbb{R}^3} d^3r v(\mathbf{r})n(\mathbf{r}), \end{aligned} \quad (2.82)$$

which again can be understood as a simple extension of the domain of those functionals. Note that the minimization here runs over all Slater determinants that lead to n via Eq. 2.67. Thus, in analogy to before, in order to obtain the ground-state density (densities) of the non-interacting system, instead of using non-interacting v -representable densities and HK2, we can minimize Levy's energy functional $E_v^{(s)}$, Eq. 2.82, with respect to non-interacting N -representable densities¹⁹.

Connection between Interacting and Non-Interacting Systems

Until now, all we have achieved is to transfer the HK theorems and LCS over to the more simple system of non-interacting electrons. The key assumption of the Kohn-Sham approach to DFT (KS-DFT) now is that for every physically relevant system of *interacting* electrons Eq. 2.71, the ground-state density is (densities are) not only v -representable (which is of course always true, by definition), *but also non-interacting v -representable!* In other words, we assume that for every ground-state density n of every (physical) interacting system Eq. 2.71, there exists an effective, “external” potential $v^{(s)}$, such that for a non-interacting system Eq. 2.79 with that potential $v^{(s)}$, n is also a ground-state density. The idea of KS-DFT then is to use the adequate potential $v^{(s)}$ and solve the simpler non-interacting problem (see below). Leaving aside that the set of v -representable densities and the set of non-interacting v -representable densities are not the same [51, 53] (we simply assume that in our interacting physical systems, the ground-state density belongs to both sets), we have to take into account the additional complication that this potential $v^{(s)}$ will in general be different for different densities n . To address these points we introduce the potential functional $v^{(s)}[\cdot]$ (domain: non-interacting N -representable densities, see below) which is a functional of a density and demand:

$$\begin{aligned} G_v &= \{n_i \mid n_i \text{ is interacting ground-state density at } v\} \\ G_v^{(s)}[n] &= \{n_i^{(s)} \mid n_i^{(s)} \text{ is non-interacting ground-state density at } v^{(s)}[n]\} \\ \forall n_i \in G_v : n_i &\in G_v^{(s)}[n_i] \end{aligned} \quad (2.83)$$

¹⁹ Note that taking only non-interacting N -representable densities into account and formulating the minimization in Eq. 2.82 only with respect to Slater determinants suffices, because (each of) the ground-state wave function(s) of the non-interacting Hamiltonian can be expressed as such a (single) Slater determinant. Therefore, Levy's argumentation (notably Eq. (17) in Ref. [56]) still holds, as does the Rayleigh-Ritz minimization argument (in terms of non-interacting N - and v -representability) of Footnote 16.

In words: we want to construct $v^{(s)}[\cdot]$ in such a way, that every solution n of the interacting problem with external potential v can in principle be found as the solution of a non-interacting problem with potential²⁰ $v^{(s)}[n]$. This way, if we can somehow construct this functional $v^{(s)}[\cdot]$, then the solutions of the interacting problem are *self-consistent* solutions of the non-interacting problem, where we call a density n a self-consistent solution if it is a ground-state density of the non-interacting system with potential $v^{(s)}[n]$.

To proceed, we should now think about how the potential functional $v^{(s)}[\cdot]$ should look like to satisfy the above-mentioned behavior. We start by explicitly stating the interacting and non-interacting minimization problems:

For the interacting problem with external potential v and Hamiltonian Eq. 2.71 our goal is to find an N -electron N -representable density n_0 that minimizes E_v , Eq. 2.77. Instead of allowing only for variations δn that do not change the number of electrons (such that $n + \delta n$ remains an N -electron density), it is more convenient to allow for arbitrary variations (or in other words: densities of an arbitrary number of electrons) and add the constraint on the number of electrons as a Lagrange multiplier to the optimization problem. Thus, allowing for N -representable densities of an arbitrary number of electrons, we are searching for a density n_0 that satisfies (where F is now a functional of N -representable densities of an arbitrary number of electrons²¹):

$$\delta \left\{ F[n] + \int_{\mathbb{R}^3} d^3r v(\mathbf{r}) n(\mathbf{r}) + \mu \left(N - \int_{\mathbb{R}^3} d^3r n(\mathbf{r}) \right) \right\} = 0 \quad (2.84)$$

Assuming that the functional derivative of F exists at every n , we can equivalently search for a density n_0 such that:

$$\begin{aligned} \left. \frac{\delta F}{\delta n(\mathbf{r})} \right|_{n_0} + v(\mathbf{r}) &= \mu \\ \int_{\mathbb{R}^3} d^3r n_0(\mathbf{r}) &= N \end{aligned} \quad (2.85)$$

On a sidenote, there can in principle be multiple such critical points and we have to choose the one density (or the ones, if there are multiple) from them that (globally) minimizes E_v . Note that if n_0 is a ground-state density then μ can be identified as the *chemical potential* of the ground state [53].

Similarly, for the non-interacting problem with the potential $v^{(s)}$ ($v^{(s)}[\tilde{n}]$ for some fixed density $\tilde{n}$), allowing for non-interacting N -representable densities of an arbitrary number of electrons, we are searching for a density $n_0^{(s)}$ that satisfies:

$$\delta \left\{ T^{(s)}[n] + \int_{\mathbb{R}^3} d^3r v^{(s)}(\mathbf{r}) n(\mathbf{r}) + \mu^{(s)} \left(N - \int_{\mathbb{R}^3} d^3r n(\mathbf{r}) \right) \right\} = 0 \quad (2.86)$$

²⁰Note that for every non-interacting Hamiltonian with potential $v^{(s)}[n]$ (where n is some fixed density!), the HK theorems and LCS again hold in the way detailed before.

²¹This, in principle, necessitates a deviation from the normalized N -electron pure states we used until now when talking about N -representability. While details can be found in Ref. [53], we do not go into details here, since the final density satisfying the stationarity condition is again, thanks to the Lagrange multiplier, a density that integrates (over all space) to an integer number N .

Assuming that the functional derivative of $T^{(s)}$ exists at every n , we can equivalently search for a density $n_0^{(s)}$ such that:

$$\begin{aligned} \left. \frac{\delta T^{(s)}}{\delta n(\mathbf{r})} \right|_{n_0^{(s)}} + v^{(s)}(\mathbf{r}) &= \mu^{(s)} \\ \int_{\mathbb{R}^3} d^3r n_0^{(s)}(\mathbf{r}) &= N \end{aligned} \quad (2.87)$$

As before, there can in principle be multiple critical points besides the global minimum.

Via comparison, we then construct the potential functional as:

$$v^{(s)}[n](\mathbf{r}) = v(\mathbf{r}) + \left. \frac{\delta F}{\delta n(\mathbf{r})} \right|_n - \left. \frac{\delta T^{(s)}}{\delta n(\mathbf{r})} \right|_n, \quad (2.88)$$

with its domain being the non-interacting N -representable densities²². Now, suppose n_0 is a ground-state density of the interacting problem. Thus, it satisfies:

$$\left. \frac{\delta F}{\delta n(\mathbf{r})} \right|_{n_0} + v(\mathbf{r}) = \mu \quad (2.89)$$

Let us now additionally assume (as stated above) that n_0 is non-interacting v -representable. Thus, n_0 lies in the domain of $v^{(s)}[\cdot]$ and (the derivative of) $T^{(s)}$ and we find that it satisfies:

$$\left. \frac{\delta T^{(s)}}{\delta n(\mathbf{r})} \right|_{n_0} + v^{(s)}[n_0](\mathbf{r}) = \mu \quad (2.90)$$

Further, since n_0 is non-interacting v -representable there exists some potential w such that n_0 is the global minimum of $E_w^{(s)}$ and satisfies:

$$\left. \frac{\delta T^{(s)}}{\delta n(\mathbf{r})} \right|_{n_0} + w(\mathbf{r}) = \mu^{(s)} \quad (2.91)$$

Comparison thus gives us:

$$w(\mathbf{r}) = v^{(s)}[n_0](\mathbf{r}) + (\mu^{(s)} - \mu) \quad (2.92)$$

Thus, $v^{(s)}[n_0]$ is the (by HK1, up to an additive constant²³) unique external potential with respect to which n_0 is a non-interacting ground-state density! In other

²²Note that every non-interacting N -representable density is trivially also an N -representable density, such that both $T^{(s)}$ and F (and their derivatives, which we assume to exist at all non-interacting N -representable densities) are well-defined here.

²³Note that, in order to satisfy Eq. 2.85 for a given external potential v of the interacting system, the additive constant $\mu^{(s)} - \mu$ must be absorbed into $v^{(s)}[\cdot]$ [49], thus rigidly shifting Kohn-Sham energies (see below). Instead of doing this, we can however cleverly choose the non-interacting potential: starting from $w(\mathbf{r}) = v^{(s)}[n_0](\mathbf{r}) + (\mu^{(s)} - \mu)$ we find, using Eq. 2.98 that $w(\mathbf{r}) = v(\mathbf{r}) + v_J[n_0](\mathbf{r}) + v_{xc}[n_0](\mathbf{r}) + (\mu^{(s)} - \mu)$. For finite systems, the sum of the potentials on the right-hand side should vanish at infinity, while for repeated-slab calculations it should (approximately) vanish in the vacuum region. Thus, $w(\mathbf{r}) \rightarrow (\mu^{(s)} - \mu)$ in said region. By demanding w to vanish in said region, we thus obtain $\mu^{(s)} - \mu = 0$ and $w(\mathbf{r}) = v^{(s)}[n_0](\mathbf{r})$. From now on, we can thus continue by using $v^{(s)}[n_0]$ as the external potential in the non-interacting problem.

words, n_0 is a ground-state density of $v^{(s)}[n_0]$ and the functional $v^{(s)}[\cdot]$ Eq. 2.88 thus satisfies the demand Eq. 2.83. Thus, if n_0 is a ground-state density of the interacting system it is a *self-consistent* solution of the potential functional $v^{(s)}[\cdot]$ and therefore²⁴ a *fixed point* in the iterative scheme $n_i \rightarrow v^{(s)}[n_i] \rightarrow n_{i+1} \rightarrow \dots$, where n_{i+1} is the non-interacting ground-state density at $v^{(s)}[n_i]$ [58, 59]. Of course, there can in principle be additional self-consistent solutions to $v^{(s)}[\cdot]$ which are not ground-state densities of the interacting system, such that, for a given starting density in this chain, we cannot be sure that the density we converge at is really a ground-state density of the interacting system²⁵ [60, 61]! In practice, we assume however that with a reasonable starting density we will obtain a fixed point that is “close-enough” to a true ground-state density of the interacting system [61] such that this point can be neglected in the following. For simplicity, instead of saying that we get a density close to it, we will in the following thus simply write that this iterative scheme gives us the/an interacting ground-state density.

Kohn-Sham Equations

The last thing to do now is to find solutions (i.e. ground-state densities) of the non-interacting problem, given a fixed potential $v^{(s)}$. This is however a very simple task, since the system is non-interacting: instead of finding ground-state densities via minimization of the energy functional²⁶, Eq. 2.86, we can just directly solve the eigenvalue problem of the non-interacting Hamiltonian Eq. 2.79. From the obtained ground-state wave function we can then simply calculate the ground-state density of the system (if there are multiple ground-state wave functions, care must be taken, for example by choosing one of them). From there we can then calculate the next potential in our iterative scheme and repeat until we achieve self-consistency. Let us formalize this:

For a non-interacting Hamiltonian of the form Eq. 2.79, finding the ground state(s) can be reduced to finding solutions of the one-particle equation

$$\left(\frac{1}{2} \hat{p}^2 + v^{(s)}(\hat{\mathbf{r}}) \right) |\phi_i\rangle = \varepsilon_i |\phi_i\rangle, \quad (2.93)$$

or in position-spin representation:

$$\left(-\frac{1}{2} \nabla^2 + v^{(s)}(\mathbf{r}) \right) \phi_i(x) = \varepsilon_i \phi_i(x) \quad (2.94)$$

Since the one-electron Hamiltonian is Hermitian, the solutions of this eigenvalue problem can be chosen orthonormal (see Appendix A.1.1). From this set of orthonormal orbitals, we then take the N with the lowest energies $\{\varepsilon_i\}$ (this means

²⁴Every self-consistent solution is a fixed point in such a chain and every fixed point of such a chain is a self-consistent solution.

²⁵To avoid this, we would need to additionally demand in Eq. 2.83 that: $n \in G_v^{(s)}[n] \Rightarrow n \in G_v$ for all non-interacting N -representable densities n .

²⁶Note that the stationarity condition in Eq. 2.86 is performed in terms of non-interacting N -representable densities. Based on Eq. 2.82 it can thus also be formulated as a stationarity condition in terms of Slater determinants (where LCS for the non-interacting system shows its usefulness), or, in fact, orthonormal orbitals (see text below Eq. 2.69) and yields the same global minimum for the energy functional. As can be seen by following Sec. 7.2 in Ref. [47] and simply removing J and E_{xc} and replacing v by $v^{(s)}$ this leads to Eq. 2.94.

that the ground state can be degenerate, if the highest of those orbitals is degenerate) to form the (one of them, if it is degenerate) N -electron ground state. We call these orbitals the *occupied orbitals* and the resulting wave function is a Slater determinant, see Eq. 2.69. And from this ground-state wave function, the corresponding ground-state density can simply be calculated via Eq. 2.70.

In principle, we now know everything we need: we know how to solve the non-interacting problem, and we know how we must construct the potential functional $v^{(s)}[\cdot]$, such that the obtained (self-consistent) solution is also ground-state density of the interacting problem. In our last step, to arrive at the most commonly used form of KS-DFT, we follow Kohn and Sham [57] and split the universal functional F of Eq. 2.77 up²⁷:

$$F[n] = T^{(s)}[n] + J[n] + E_{xc}[n], \quad (2.95)$$

where $T^{(s)}$ is the non-interacting kinetic energy defined in Eq. 2.82 and J is the well-known Hartree energy:

$$J[n] = \frac{1}{2} \int_{\mathbb{R}^3} d^3r \int_{\mathbb{R}^3} d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (2.96)$$

Having split off two familiar terms, all further effects contributing to the universal functional must then be contained in E_{xc} , the *exchange-correlation energy* functional, for which we find (using Eq. 2.78):

$$E_{xc}[n] = T[n] - T^{(s)}[n] + U_{ee}[n] - J[n] \quad (2.97)$$

As a small sidenote, it may not be immediately clear that T of Eq. 2.78 and $T^{(s)}$ of Eq. 2.82 lead to different energies for the same (non-interacting N -representable) density n . However, comparing Eqs. 2.77 and Eq. 2.78 with Eq. 2.82 it is clear that they in general are based on different wave functions (leading to the same density) and can thus yield different values for the same density.

Remembering the constructed potential functional Eq. 2.88, we can insert Eq. 2.95 to find²⁸:

$$v^{(s)}[n](\mathbf{r}) = v(\mathbf{r}) + \left. \frac{\delta J}{\delta n(\mathbf{r})} \right|_n + \left. \frac{\delta E_{xc}}{\delta n(\mathbf{r})} \right|_n = v(\mathbf{r}) + v_J[n](\mathbf{r}) + v_{xc}[n](\mathbf{r}), \quad (2.98)$$

with the Hartree potential $v_J[n]$ and the exchange-correlation potential $v_{xc}[n]$. While the latter depends on the until now not explicitly defined exchange correlation energy functional, the former has a well-known form [47]:

$$v_J[n](\mathbf{r}) = \int_{\mathbb{R}^3} d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (2.99)$$

²⁷Note that, split up like this, the universal functional is now only defined for non-interacting N -representable densities, since this is the domain of $T^{(s)}$. So, compared to Eq. 2.77, we have shrunk its domain. However, the non-interacting N -representable densities are precisely what we need to find solutions, see text above, and we therefore abstain for readability from introducing a new symbol for F on this smaller domain.

²⁸Where we assume that the functional derivative of E_{xc} exists at every non-interacting N -representable density n .

Eqs. 2.94, 2.70 and 2.98 together then form the Kohn-Sham scheme:

$$\begin{aligned} \left(-\frac{1}{2}\nabla^2 + v^{(s)}(\mathbf{r})\right)\phi_i(x) &= \varepsilon_i\phi_i(x) \\ n(\mathbf{r}) &= \sum_{s=\uparrow,\downarrow} \sum_{i=1}^N |\phi_i(\mathbf{r}, s)|^2 \\ v^{(s)}[n](\mathbf{r}) &= v(\mathbf{r}) + \int_{\mathbb{R}^3} d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}[n](\mathbf{r}) \end{aligned} \quad (2.100)$$

We can in principle start the loop from any of the three involved quantities, orbitals, density or potential. Say we start from an initial guess for the density, then we first calculate the KS potential from it. This potential is then inserted into the eigenvalue equation, which we then solve. Then we take the N lowest-energy solutions (where degeneracy in orbitals can lead to a possible free choice of orbitals, as mentioned above) and construct a new density from them. This process is repeated, until the density does not change anymore²⁹. And finally, thanks to the way the potential functional is constructed, the density is then a ground-state density of the interacting Hamiltonian. On a sidenote, we can see from Eq. 2.100 that changing the global phase of any KS orbital does not change the density and that the KS orbital remains a solution of the Schrödinger equation in the first line. Consequently, the global phases of the KS orbitals we obtain from this iterative scheme are in principle arbitrary (this also holds when including the exact exchange via the GKS scheme – see below – since the exchange operator is also invariant under phase-rotations of orbitals and is linear [47]).

Occupying Orbitals and Electronic Spin

Note that the one-particle Hamiltonian of Eq. 2.100 is spin-independent! As a consequence, its solutions can be chosen as position-spin product states with one spin-up and one spin-down orbital per *spatial orbital* φ_i [47, 53] (compare Appendix A.1.1). Further, these two orbitals then have the same orbital energy and the full set $\{\phi_i\}$ of KS orbitals can thus be written as:

$$\begin{aligned} \{\phi_i\} &= \{\phi_{j,s}\} \\ |\phi_{j,s}\rangle &= |\varphi_j\rangle \otimes |s\rangle \\ \varepsilon_{j,\uparrow} &= \varepsilon_{j,\downarrow} \end{aligned} \quad (2.101)$$

Occasionally the KS orbitals $\{\phi_i\}$ are then called *spin-orbitals* to distinguish them from the spatial orbitals $\{\varphi_i\}$. Note that this form of the KS orbitals is not (as in restricted Hartree-Fock theory) an approximation but simply a consequence of the construction of the non-interacting problem based on a spin-independent external potential [47]. We will occasionally call orbital (sets) that satisfy Eq. 2.101 *spin-unpolarized* orbitals. (Note also, that the exact exchange operator that can occur in the GKS formalism (see below) is generally not spin-independent, see Ref. [47]. In our practical calculations we will use the GKS formalism only for systems with an even number N of electrons. Additionally, we will use *restricted (G)KS* which

²⁹Convergence in this iterative scheme can be improved by using more sophisticated iteration schemes based on density-mixing [59].

enforces spin-unpolarized orbitals. For each system under study we then find our GKS ground state to be closed shell (see below), such that the exchange operator becomes spin-independent.)

Assuming that the number of electrons N in our system is even and that the $\frac{N}{2}$ -th and $\frac{N}{2} + 1$ -th spatial orbitals (sorted by energy) are not degenerate, every spatial orbital (up to the $\frac{N}{2}$ -th) is occupied twice in the constructed (non-interacting) ground-state wave function and we find:

$$n(\mathbf{r}) = 2n_{\uparrow}(\mathbf{r}) = 2n_{\downarrow}(\mathbf{r}) \quad (2.102)$$

We then say that every electron is *spin-paired* and that the system has a *closed shell* KS ground state or simply, that *the system is closed shell*. Alternatively, if the number of electrons is odd and the $\frac{N}{2}$ -th spatial orbital is not degenerate with any other orbital, we can either occupy its spin-up or the spin-down version, thus leading to different spin-densities, but, with either occupation, leading to the same total density n . In the remaining scenarios the situation is accordingly more complicated and of no further relevance to us (see below).

Note that in *spin-density functional theory*, an extension of DFT that also allows for external magnetic fields besides the scalar external potential of Eq. 2.72 [47], the electronic orbitals are in general spinors (compare Eq. A.16). Calculations that allow for such general spinor-orbitals are termed *non-collinear spin-polarized* while calculations that restrict orbitals to pure spin-up and spin-down states – however without the degeneracy described above and with in principle different spatial orbitals for the spin-up and spin-down states – are called *collinear spin-polarized*. In contrast, we refer to the formalism shown in this section as *spin-unpolarized* KS-DFT. Note that spin-density functional theory is needed if *spin-orbit coupling* is to be included in the Hamiltonian [47]. Further details on spin-density functional theory can for example be found in Ref. [62].

In our practical calculations later in this text we solely use spin-unpolarized KS-DFT (and spin-restricted GKS-DFT) such that we always obtain spin-unpolarized orbitals. Additionally, we will only encounter closed-shell systems, namely closed-shell isolated molecules and clusters as well as semiconducting 2D systems.

Summary of KS Derivation

Note that – starting from typical approximations used in solid state physics and quantum chemistry (Born-Oppenheimer approximation, nonrelativistic treatment) – we formulated the general DFT formalism, as well as the KS scheme, based on a couple of assumptions (e.g. the non-interacting v -representability assumption), but we did not introduce any additional approximations! Under the condition that these assumptions are correct, KS-DFT can therefore be understood as an exact method and if we knew the form of the exchange-correlation energy functional, we would obtain exact ground-state densities from it [59]. And from this density, a wealth of information about the system (see Footnote 15) is in principle obtainable thanks to HK1. While this is an intriguing property of the method, the exact form of the exchange correlation functional to date unfortunately remains unknown. To use KS-DFT for practical calculations, we therefore need to use approximative forms of the exchange correlation energy functional, where approximations on varying levels of sophistication exist and are arranged on the so-called *Jacob's ladder* of exchange-correlation functionals.

2.2.5 Jacob's Ladder of Exchange-Correlation Functionals

Details on a large set of commonly used exchange-correlation functionals and their arrangement in the Jacob's ladder can be found in Ref. [63]. We will restrict ourselves in the following to a brief description of the different levels of Jacob's ladder given in Ref. [63] and list the specific functionals which will be used in practical calculations in later chapters of this text.

Separation into Exchange and Correlation Functionals

First, note that the exact exchange-correlation functionals E_{XC} of KS-DFT is often separated into two parts, namely the *KS exchange functional* E_X^{KS} and the *KS correlation functional* E_C^{KS} :

$$E_{XC}[n] = E_X^{KS}[n] + E_C^{KS}[n] \quad (2.103)$$

As explained before, E_{XC} is defined for non-interacting N -representable densities. On this domain we can then go ahead and define its constituents.

First let us define the generic exchange functional of *Slater determinants* as:

$$E_X[\Phi] = \langle \Phi | \hat{U}_{ee} | \Phi \rangle - J[n[\Phi]] \quad (2.104)$$

In words, it is the difference between the expectation value of the electron-electron interaction in terms of the Slater determinant $|\Phi\rangle$, and the Hartree energy derived from the density that is obtained from said Slater determinant.

The exact KS exchange functional is then defined as [49]

$$E_X^{KS}[n] = \langle \Phi_0 | \hat{U}_{ee} | \Phi_0 \rangle - J[n], \quad (2.105)$$

where $|\Phi_0\rangle$ is (one of – see below) the Slater determinant that leads to n and minimizes the kinetic-energy expectation value, see Eq. 2.82. The exact KS correlation functional then becomes

$$\begin{aligned} E_C^{KS}[n] &= E_{XC}[n] - E_X^{KS}[n] = \\ &= T[n] - T^{(s)}[n] + U_{ee}[n] - J[n] - \langle \Phi_0 | \hat{U}_{ee} | \Phi_0 \rangle + J[n] \\ &= \langle \Psi_0 | \hat{U}_{ee} + \hat{T}_e | \Psi_0 \rangle - \langle \Phi_0 | \hat{U}_{ee} + \hat{T}_e | \Phi_0 \rangle \\ &= \langle \Psi_0 | \hat{H}_e | \Psi_0 \rangle - \langle \Phi_0 | \hat{H}_e | \Phi_0 \rangle, \end{aligned} \quad (2.106)$$

where $|\Psi_0\rangle$ is the state that leads to n and that minimizes the universal functional³⁰, see Eq. 2.77. Note that we used Eqs. 2.97, 2.75 and 2.80 to get to the third line and the fact that both states correspond to the same ground-state density together with Eqs. 2.72 and 2.71 to get to the last line.

Note that we have omitted a subtlety in the definition of the exact KS exchange energy functional! It may occur that there are multiple Slater determinants $\{|\Phi_{0,i}\rangle\}$

³⁰Note that $|\Psi_0\rangle$ is in general not a single Slater determinant, see Eq. 2.176! Even though we restrict ourselves here to non-interacting N -representable densities, the wave function that leads to this density and minimizes the universal functional will in principle be a correlated wave function. Note also, that, as stated before, every non-interacting N -representable density is trivially also N -representable, which is why Levy's universal functional is well-defined on the non-interacting N -representable densities.

that lead to n and minimize the kinetic energy expectation value. And while they all lead to the same kinetic-energy expectation value, the expectation values of the electron-electron interaction $\{\langle \Phi_{0,i} | \hat{U}_{ee} | \Phi_{0,i} \rangle\}$ will in general be different, such that E_X^{KS} is not well-defined if multiple such determinants exist. As a result, also E_C^{KS} is then not well-defined! To end up with a well-defined functional, we may add some selection scheme, that chooses one of the determinants. Alternatively, in a more neutral scheme, we may also just take the average over the determinants. Then, also $\langle \Phi_0 | \hat{H}_e | \Phi_0 \rangle$ in E_C^{KS} can be understood as an average over these determinants, since $\langle \Phi_0 | \hat{T}_e | \Phi_0 \rangle$ is per construction the same for all the determinants, as is $\langle \Phi_0 | \hat{V} | \Phi_0 \rangle$, which is the same for all states leading to n , see Eq. 2.72. With this small point fixed, E_X^{KS} and E_C^{KS} are again well-defined for all non-interacting N -representable densities.

The names of these functionals are chosen in analogy to Hartree-Fock (HF) theory (see e.g. Ref. [47]): Assume n is the ground-state density for some given external potential, obtained through the KS scheme. This means that n is v -representable (w.r.t. that one specific potential, see HK1) and $|\Psi_0\rangle$ is a ground state of the interacting system (see above). Additionally, it is also non-interacting v -representable (w.r.t. the corresponding unique KS potential, see HK1 for non-interacting systems) and $|\Phi_0\rangle$ is a ground state of the non-interacting system (see above). Then E_X^{KS} has the same form as the exact exchange of HF theory. Both methods can be understood to use the same functional Eq. 2.104, just with the difference that we here use (a Slater determinant constructed from) Kohn-Sham orbitals, while HF uses orbitals obtained through solution of the HF equations [49]. Additionally, remember that in HF theory, the system's ground-state wave function is approximately written as a single Slater determinant (which constitutes the only approximation made in HF, besides the typically used BOA and nonrelativistic treatment) and the resulting expression for the systems energy contains the HF kinetic energy, the energy due to the external potential, the Hartree term, and the exchange term. All neglected energy terms, or, conversely, the difference between the exact ground-state energy $\langle \Psi_0 | \hat{H}_e | \Psi_0 \rangle$ obtained for (one of) the exact ground state(s) and the HF ground-state energy $\langle \Phi_0^{\text{HF}} | \hat{H}_e | \Phi_0^{\text{HF}} \rangle$ of (one of) the HF Slater determinant ground state(s) is then termed correlation. Similarly, the correlation energy of KS-DFT is the difference between the exact ground-state energy $\langle \Psi_0 | \hat{H}_e | \Psi_0 \rangle$ and the expectation value $\langle \Phi_0 | \hat{H}_e | \Phi_0 \rangle$ using the KS ground state.

When approximating the exchange-correlation functional, we often use separate approximations, one for the exact KS exchange functional and one for the exact KS correlation functional and use their sum as the approximated exchange-correlation functional. We will get back to this separation below, in the context of hybrid functionals.

Rung 1: Local Density Approximation (LDA)

Functionals of this rung have the following generic form [64]:

$$E_{XC}^{\text{LDA}}[n] = \int_{\mathbb{R}^3} d^3r \, n(\mathbf{r}) e_{XC}(n(\mathbf{r})) \quad (2.107)$$

This expression can be understood as a restriction of the functional dependence of the exchange-correlation functional. That is, the functional (integrand) only

depends locally on the density, or in other words, densities at different positions contribute independently to the exchange-correlation energy. This is of course a rather crude approximation and leads to large errors in many systems. After all, the real electronic system consists of interacting particles such that the relation of densities at different positions in space are crucial for the total energy of the system. To give examples, this is why local (and semi-local, see below) functionals fail to properly account for London dispersion interactions (where positions far apart are correlated in the ground-state wave function [65], such that they have to be accounted for together – otherwise minimization of the energy will lead to a wrong ground-state density that does not account for this correlation) or why TDDFT with such functionals fails to properly describe CT or Wannier excitons, where the nonlocal correlation between an electron and a hole becomes crucial (and thus the relative position of the two must be taken into account).

Note that though LDA is in general a class of functionals defined by the functional form Eq. 2.107, it is in practice often synonymously used for expressions based on the exchange-correlation energy of the homogeneous electron gas (see e.g. Ref. [63]).

Rung 2: Generalized Gradient Approximation (GGA)

Functionals of the second rung additionally depend on the local gradient of the density (*local* gradient meaning: same position as density itself) [64]:

$$E_{XC}^{\text{GGA}}[n] = \int_{\mathbb{R}^3} d^3r \, n(\mathbf{r}) e_{XC}(n(\mathbf{r}), \nabla n(\mathbf{r})) \quad (2.108)$$

They are termed *semi*-local because information of the density at some point $\mathbf{r}$ is mixed with information on how the density changes around $\mathbf{r}$, thus the relation between the density at $\mathbf{r}$ and the density in the immediate neighborhood of $\mathbf{r}$ is included.

For our practical calculations of extended systems we will use the *PBE* functional [66], a – if not *the* – standard GGA functional for solid-state physics.

Rung 3: Meta-Generalized Gradient Approximation (mGGA)

In the third rung, additional dependence on the local Laplacian $\nabla^2 n$ of the density and/or on the *local kinetic energy density* τ (see Ref. [47]) is included,

$$E_{XC}^{\text{mGGA}}[n, \tau] = \int_{\mathbb{R}^3} d^3r \, n(\mathbf{r}) e_{XC}(n(\mathbf{r}), \nabla n(\mathbf{r}), \nabla^2 n(\mathbf{r}), \tau(\mathbf{r}))$$

$$\tau(\mathbf{r}) = \sum_{i=1}^N \langle \phi_i | \frac{\hat{p}^2}{2} | \phi_i \rangle, \quad (2.109)$$

where a dependence on τ is most common [63, 64]. Based on the specific structure of the shown functional, mGGAs are, as GGAs before, termed semi-local functionals.

Since we will not use this kind of functional, we will not further elaborate on it. Just note that the explicit dependence on (G)KS orbitals via the local kinetic energy density complicates the formalism (while the dependence on the Laplacian is unproblematic), when compared to GGA functionals. While we could in principle

treat the orbitals as functionals of the density and then use the normal KS scheme (minimizing w.r.t. the density), mGGAs are in practice typically used within the framework of GKS theory (see below), where the total energy is minimized with respect to (GKS) orbitals.

Rung 4: Hybrid Functionals

The idea of hybrid functionals – the fourth rung of Jacob’s ladder – is to partially include the exact exchange interaction of the electrons. Instead of directly including our expression Eq. 2.105 in the exchange-correlation functional of KS-DFT, hybrid functionals are typically used within the framework of the *generalized Kohn-Sham* (GKS) approach³¹.

Details on the GKS approach can be found in Refs. [67, 68], but to briefly summarize, the general idea is to partially reintroduce electronic interactions into the auxiliary electron system: the interaction is introduced as part of a functional S of Slater determinants. In addition, we then introduce a density functional F^S via the Slater determinant(s) that minimizes S and leads to the density (thus the domain of F^S is given by the non-interacting N -representable densities):

$$F^S[n] = \min_{\Phi \rightarrow n} (S[\Phi]) \quad (2.110)$$

The difference between Levy’s universal functional Eq. 2.77 of the fully interacting system and F^S of the partially interacting system is then called the *remainder energy* functional R^S :

$$F[n] = F^S[n] + R^S[n] \quad (2.111)$$

This is then used to express the total energy of the interacting system for a given external potential as a functional of non-interacting N -representable densities³². This minimization is then carried out in terms of Slater determinants, that is, in terms of their one-electron orbitals, leading to the GKS equations³³.

As a special case of the GKS formalism, we define S as:

$$S[\Phi] = \langle \Phi | \hat{T}_e + \alpha \hat{U}_{ee} | \Phi \rangle \quad (2.112)$$

Here, $0 \leq \alpha \leq 1$ such that we quite literally have partially interacting electron. The corresponding density functional then becomes:

$$F^S[n] = \min_{\Phi \rightarrow n} \left(\langle \Phi | \hat{T}_e + \alpha \hat{U}_{ee} | \Phi \rangle \right) \quad (2.113)$$

³¹As is commonly done, we may at other points in the text simply refer to *KS* orbitals, *KS* energies and so on and implicitly also mean *GKS* orbitals, *GKS* energies, etc.

³²Compare Eqs. 2.77 and 2.84, where we still used N -representable densities. Just like KS theory assumes that the (all if many) ground-state density n of the interacting problem for the given external potential is also non-interacting v -representable, and thus non-interacting N -representable, (exactness of the) GKS theory assumes that for the chosen S , the density n can be constructed from GKS orbitals obtained from the formalism explained here (we may define something like “ S -interacting- v -representability”), and thus also assumes that the density is non-interacting N -representable.

³³When instead minimizing with respect to densities, we end up with a nontrivial integro-differential equation known as the *optimized effective potential* (OEP) [68].

Denoting one of the minimizing determinants by Φ_0^S and using Eq. 2.104, this can be written as:

$$F^S[n] = \langle \Phi_0^S | \hat{T}_e | \Phi_0^S \rangle + \alpha E_X[\Phi_0^S] + \alpha J[n] \quad (2.114)$$

Three comments are adequate here: first, note that while the total value of $F^S[n]$ does not depend on the chosen minimizing orbital, the individual contributions $\langle \Phi_0^S | \hat{T}_e | \Phi_0^S \rangle$ and $\alpha E_X[\Phi_0^S]$ will in general depend on this choice, i.e., be different, for a different minimizing orbital, assuming multiple exist. This is analogous to the discussion of E_X^{KS} given below Eq. 2.105. Second, if we define E_X^{GKS} via $E_X^{GKS}[n] = E_X[\Phi_0^S]$ (and assume problems related to the existence of multiple minimizing determinant have been alleviated as for E_X^{KS} , which we will do from now on), then for a given density n , we will in general find $E_X^{GKS}[n] \neq E_X^{KS}[n]$, because they use Eq. 2.104 in terms of differing Slater determinants. Similarly, $\langle \Phi_0^S | \hat{T}_e | \Phi_0^S \rangle$ may be called the GKS kinetic energy, and will for a given density in general be different from the KS kinetic energy of Eq. 2.82 and the exact kinetic energy of Eq. 2.77. Third, the GKS exchange E_X^{GKS} leads to the occurrence of the nonmultiplicative Fock exchange operator in the GKS equations (in contrast, R^S , see below, leads to a multiplicative potential.).

Continuing with the GKS formalism for the special case of Eq. 2.112, the remainder energy functional is then usually approximated as [68]

$$R^S[n] = (1 - \alpha)J[n] + (1 - \alpha)V_X^{\text{approx}}[n] + V_C^{\text{approx}}[n], \quad (2.115)$$

where V_X^{approx} and V_C^{approx} are approximative density functionals for exchange and correlation, taken from the lower rungs of Jacob’s ladder, typically a GGA functional³⁴. In analogy to KS-DFT (see Eq. 2.95), we may write

$$\begin{aligned} F[n] &= F^S[n] + R^S[n] \\ &= \langle \Phi_0^S | \hat{T}_e | \Phi_0^S \rangle + J[n] + E_{XC}[n] \\ E_{XC}^S[n] &= \alpha E_X[\Phi_0^S] + (1 - \alpha)V_X^{\text{approx}}[n] + V_C^{\text{approx}}[n] \end{aligned} \quad (2.116)$$

and call E_{XC}^S a *global hybrid (GKS) exchange-correlation functional* – “hybrid”, because it mixes the exact GKS exchange with an approximative exchange functional, and “global”, because the same fraction of exact exchange is used at all electron-electron distances, that is S was constructed as shown in Eq. 2.112, with a global scaling factor α applied onto the Coulomb electron-electron interaction. In contrast to such global hybrid functionals, there are also *range-separated hybrid functionals*, where the Coulomb interaction is split into a short range and a long range part, that are then treated differently [63]. We will not get into these, because they are not used later.

For our calculations of isolated molecules and clusters later, we will use the *B3LYP* functional [69, 70], a global Hybrid functional. Note that B3LYP mixes exchange and correlation functionals of both LDA- and GGA-kind, and deviates in how it mixes them from the generic form for the GKS exchange correlation

³⁴Note that if we take a meta-GGA functional, then the kinetic-energy density is expressed in terms of the GKS orbitals and leads to a nonmultiplicative term in the GKS equations. In contrast, using GGA functionals simply leads to multiplicative potential terms, one for the exchange and one for the correlation part.

functional given in Eq. 2.116. Simply adapting the remainder functional R^S accordingly via the desired combination of approximative exchange and correlation functionals, compare Eq. 2.115, however does not change anything in the formalism and then gives us B3LYP in Eq. 2.116.

Rung 5: Double Hybrids

Finally, the exchange-correlation functionals of rung five are known as double-hybrids and additionally depend on unoccupied orbitals [63, 64]. These functionals are very expensive and rarely used as of writing, so we will not go into further detail here.

Dispersion Corrections

Though they are not part of Jacob’s ladder, this is also the right time to introduce *dispersion corrections* (commonly called *van-der-Waals corrections* [71]). As mentioned above, local and semi-local exchange-correlation functionals do not properly describe London dispersion interactions. In scenarios where these interactions become important (for example when calculating adsorption heights of molecules on some crystalline substrate), a dispersion correction can be incorporated into the exchange-correlation functional.

Details on common dispersion corrections can be found in Ref. [72]. While more sophisticated dispersion corrections in terms of nonlocal density functionals exist, they are less widely used than simple *atom-pairwise methods*. Importantly, the atom-pairwise methods we will use in practice (see below) give an energy contribution to the total energy that does not depend on the density and therefore does not affect KS orbitals and orbital energies, since they drop out after performing the functional derivative w.r.t. the density (same for GKS, when minimizing w.r.t. the orbitals). Thus, they are not relevant for a single solution of the (G)KS equations for a given external potential, but become relevant when performing geometry optimizations, where the total energy of different nuclear configurations is compared.

For our practical calculations we will either not use any dispersion correction, or use the *Becke-Johnson (BJ) damping variant of the Grimme D3 correction* [73, 74], which is an atom-pairwise method.

2.2.6 Kohn-Sham DFT in Practice

We conclude this section on density functional theory by focusing on the parts we need for our photoemission simulations. In brief, all we need to do is to solve the Kohn-Sham equations Eq. 2.100, where we need to settle on a nuclear geometry that defines the “external” potential v and choose an exchange-correlation functional from Jacob’s ladder (alternatively: use hybrids and GKS theory). There are of course many more practical issues in such calculations. While a treatment of those goes beyond the scope of this text, a rather practical introduction to KS-DFT calculations can be found in Ref. [46].

Having solved the Kohn-Sham equations, we then use the obtained orbitals and orbital energies (in Eq. 2.178 we also use the exchange-correlation energy of the orbitals) in the upcoming theoretical frameworks as well as directly in our

photoemission simulations. Note that we can in principle obtain a complete set of one-electron orbitals by first converging the ground-state density and then solving the KS Schrödinger equation (first line in Eq. 2.100) for all solutions, that is, bound and scattering states (see Appendix A.1.1). While this is in principle needed for completeness (for example when expanding L in the Bethe-Salpeter equations, see Appendix C.1.1) and while the scattering states could in principle be used as final states in our photoemission simulations (see Sec. 3.3.4), we will in practice only ever solve the KS equations for bound orbitals, namely its valence and (part of its) conduction orbitals.

Note also, that throughout this section – and including the Kohn-Sham equations Eq. 2.100 – we assumed that we are working with a physical, that is, finitely sized atomic system. As explained in Sec. 2.1.1 we however routinely perform calculations for a model system that is an infinitely extended thin atomic plane. Such a system can be thought of as the *thermodynamic limit* of a finite crystal (see Appendix A.1.1). Note that extensive quantities diverge in this limit and must be renormalized (for example to “per-unit-cell” quantities). A discussion of DFT for infinite crystals can for example be found in Ref. [37]. We focus in the following on the ingredients we need in practice for our photoemission simulations, namely the KS orbitals and energies as well as the KS equations, which all stay well-defined in the thermodynamic limit and only change minimally. Translational symmetry of the surface tells us that the ground-state density (an observable quantity), must also be surface-periodic. As a result of the system’s translational symmetry, also the effective potential $v^{(s)}$ is surface-periodic (while omitting a proof of this intuitive result, note that this is trivially the case for v and v_J). Note that the ionic potential v and the Hartree potential v_J are strictly speaking ill-defined by themselves, due to the long-range Coulomb interaction and the infinite system size. For charge-neutral systems (where the ionic and electronic charges in a unit-cell sum up to 0), their sum is however finite (intuitively: a far-away unit cell looks essentially like an uncharged area, see also Appendix F in Ref. [59]). We additionally – of course – assume that v_{xc} is constructed in such a way that it is well-defined everywhere, such that the full KS potential $v^{(s)}$ is then well-defined. As detailed in Appendix A.1.1, the KS orbitals obtained with this periodic potential are then in-plane *Bloch orbitals*, with bound states $\{\phi_{n,\mathbf{q}}\}$ being indexed by a *band index* n and a *Bloch momentum* $\mathbf{q}$ (from the surface Brillouin-zone). Lastly, as detailed in Appendix B.1, the electron density is then obtained by integrating over the Brillouin zone:

$$n(\mathbf{r}) = \sum_{s=\uparrow,\downarrow} \sum_n^{occ.} \int_{\text{BZ}} d^2q |u_{n,\mathbf{q}}(\mathbf{r}, s)|^2, \quad (2.117)$$

where $\{u_{n,\mathbf{q}}\}$ are the unit-cell-periodic parts of the Bloch functions – thus making the periodicity of the density directly visible – which have to be normalized according to Eq. B.6. This normalization is essential to ensure that integration of n over a single unit cell gives us the number of electrons in the unit cell (as demanded from the density in Eq. 2.60). Of course, integrating n over all space gives us a divergence – after all, there is an infinite number of electrons in an infinite surface. Note that this expression for n assumes a gapped system, that is, a system with only completely filled or completely empty bands. When performing spin-unpolarized calculations (KS-DFT as outlined above) where spin-up and

spin-down orbitals have the same spatial wave function and the same energies, this additionally means that the sum over spins can be replaced by a factor of 2 (with n then indexing spatial bands). This is the type of system we will meet later in our practical calculations (free-standing layer of 6T and free-standing layer of hBN). For metallic systems, the sum must run over all – at least partially occupied – bands and include the occupation number $f_n(\mathbf{q})$ in the integrand. In practice, the integral is then evaluated using quadrature. Usually we sample the Brillouin zone via a regular (usually rectilinear in coordinates of the reciprocal unit-cell-vectors) grid of discrete Bloch momenta, N_1 and N_2 in each respective surface direction, and calculate the density as (see Appendix B.3):

$$n(\mathbf{r}) \approx \frac{(2\pi)^2}{N_1 N_2 A_c} \sum_{s=\uparrow, \downarrow} \sum_n^{occ.} \sum_{\mathbf{q}}^{BZ} |u_{n,\mathbf{q}}(\mathbf{r}, s)|^2, \quad (2.118)$$

where A_c is the area of the surface unit cell. Trivially, N_1 and N_2 must then be increased until the so-obtained electron density is converged.

Lastly, note that we often split DFT calculations into two parts, where we first converge the density as described above. In a second step, we can then solve the (G)KS equation (without updating the (G)KS potential/operator) to obtain (G)KS orbitals and energies at any desired Bloch momentum. Importantly, we can this way calculate solutions at any Bloch momentum independently (that is, the solutions at $\mathbf{q}_i$ do only depend on the density/KS operator we start with, but not on which other Bloch momenta we solve for in the second step) [46]! This is particularly useful in the context of our photoemission simulations, where the resolution of, for example, momentum maps is determined by the Bloch-momentum-grid of available KS orbitals and -energies – a consequence of in-plane crystal-momentum conservation, see Appendix D.2.1.

2.3 MBPT I: GW and Quasiparticle Approximation

Die Galoschen konnten, wie jeder, der etwas gründlich machen will, nur eine Sache auf einmal tun. Er wollte Dichter sein, das wurde er. Nun wollte er ein kleiner Vogel sein, aber als er dies wurde, hörte die vorige Eigentümlichkeit auf.

— Hans Christian Andersen, *Die Galoschen des Glücks* [insel taschenbuch 133. Insel Verlag, 1992, S. 166.]

Having introduced Kohn-Sham density functional theory (KS-DFT) as our go-to method for calculating ground-state properties, the next step is to focus on excited states. For this we use *many-body perturbation theory* (MBPT) and first focus on *charged excitations*, where we focus on excitations that change the number of electrons in our system from N to $N \pm 1$. Later, in our photoemission formalism, we will use these states (the $N - 1$ -electron ones) to describe the remaining electronic system after the emission of a photoelectron. As in Sec. 2.2 we generally assume systems to be finitely sized and only return to intricacies of infinitely sized systems briefly around the end of this section.

2.3.1 Quantum Field Operators

Since we will need them repeatedly later in this section, we start by introducing the so-called *quantum field operators*.

Say $\{|\phi_i\rangle\}$ is an orthonormal and complete set of one-electron states (ONB, see Appendix A.1.1) with corresponding wave functions $\{\phi_i\}$ and (second quantization) annihilation operators $\{\hat{a}_i\}$ and creation operators $\{\hat{a}_i^\dagger\}$. Then we define the quantum field annihilation operator $\hat{\Psi}(x)$ and creation operator $\hat{\Psi}^\dagger(x)$ as (for some position and spin, $x = (\mathbf{r}, s)$):

$$\begin{aligned}\hat{\Psi}(x) &= \sum_i \phi_i(x) \hat{a}_i \\ \hat{\Psi}^\dagger(x) &= \sum_i \phi_i^*(x) \hat{a}_i^\dagger\end{aligned}\tag{2.119}$$

Note that this is simply the equation for expressing annihilation and creation operators belonging to the position-spin basis $\{|x\rangle\}$ in terms of the above-chosen one-electron basis $\{|\phi_i\rangle\}$ [75]. The field operators $\hat{\Psi}(x)$ and $\hat{\Psi}^\dagger(x)$ are independent of the chosen one-electron basis $\{|\phi_i\rangle\}$ and represent respectively the annihilation and creation of an electron at position $\mathbf{r}$ with spin s . As is commonly done in solid-state physics, removing an electron from a system can be thought of as adding an *electron-hole* – simply called a *hole* – to it, such that $\hat{\Psi}(x)$ is said to *create a hole at x* . It can also easily be shown (see Ref. [75]) that the following

anticommutation³⁵ relations hold:

$$\begin{aligned}\{\hat{\Psi}(x), \hat{\Psi}(x')\} &= 0 \\ \{\hat{\Psi}^\dagger(x), \hat{\Psi}^\dagger(x')\} &= 0 \\ \{\hat{\Psi}(x), \hat{\Psi}^\dagger(x')\} &\equiv \delta(x - x')\end{aligned}\tag{2.120}$$

We can also use the quantum field operators (just like any other set of annihilation and creation operators), to express one-electron and two-electron operators (see Appendix A.1.4). Most notably, the time-independent electronic Hamiltonian Eq. 2.42 becomes:

$$\begin{aligned}\hat{H}_e &= \int dx \hat{\Psi}^\dagger(x) \left[-\frac{\nabla_{\mathbf{r}}^2}{2} + V(\mathbf{r}) \right] \hat{\Psi}(x) \\ &\quad + \frac{1}{2} \int dx dx' \hat{\Psi}^\dagger(x) \hat{\Psi}^\dagger(x') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \hat{\Psi}(x') \hat{\Psi}(x) \\ V(\mathbf{r}) &= - \sum_{k=1}^K \frac{Z_k}{|\mathbf{r} - \mathbf{R}_k|}\end{aligned}\tag{2.121}$$

With this we can also compactly write the time-dependent quantum field operators as (assuming the Heisenberg picture):

$$\begin{aligned}\hat{\Psi}(x, t) &= e^{i\hat{H}_e t} \hat{\Psi}(x) e^{-i\hat{H}_e t} \\ \hat{\Psi}^\dagger(x, t) &= e^{i\hat{H}_e t} \hat{\Psi}^\dagger(x) e^{-i\hat{H}_e t}\end{aligned}\tag{2.122}$$

Note that the field operators are operators in Fock space and change the number of electrons in a state they act on (see also Appendix A.1.3). While our electronic Hamiltonian Eq. 2.42 was initially restricted to the domain of N -electron states, the second-quantized version of Eq. 2.121 takes the same form on the whole Fock space (see Eq. A.28) such that Eq. 2.122 is well-defined on all Fock space.

2.3.2 One-Particle Green's Function

With the N -electron quantum field operators $\hat{\Psi}(x, t)$ and $\hat{\Psi}^\dagger(x, t)$ at hand and writing the (normalized) ground state³⁶ of the N -electron Hamiltonian Eq. 2.42 as $|N, 0\rangle$, we define the (time-ordered) *one-particle Green's function* G_1 as [77]:

$$\begin{aligned}G_1(x, t, x', t') &= -i \langle N, 0 | \hat{\Psi}(x, t) \hat{\Psi}^\dagger(x', t') | N, 0 \rangle \theta(t - t') \\ &\quad + i \langle N, 0 | \hat{\Psi}^\dagger(x', t') \hat{\Psi}(x, t) | N, 0 \rangle \theta(t' - t),\end{aligned}\tag{2.123}$$

³⁵With $\{\hat{A}, \hat{B}\} = \hat{A}\hat{B} + \hat{B}\hat{A}$.

³⁶ For degenerate ground states, we may additionally average over them, see Ref. [76]. This is however not needed for the systems we meet in Chapters 4, 5 and 6 – which all exhibit non-degenerate ground states – and an explicit treatment of systems with a degenerate ground state is thus omitted for simplicity.

where we use the Heaviside step function³⁷:

$$\theta(t) = \begin{cases} 1, & \text{if } t > 0 \\ 0, & \text{if } t < 0 \end{cases} \quad (2.124)$$

Note that there is a very intuitive meaning to the one-particle Green's function. Using Eq. 2.122, we find that in $\langle N, 0 | \hat{\Psi}(x, t) \hat{\Psi}^\dagger(x', t') | N, 0 \rangle$, we first propagate the ground state to t' , then add an electron at x' and then propagate from t' to t . There, we then calculate the overlap with a state that started from the ground state, was directly propagated to t and then had an electron added at x . In the case $t > t'$, $|G_1(x, t, x', t')|^2$ is therefore the probability³⁸ of finding the system in a state that is the ground state with an additional electron at x , if we started from the ground state with an added electron at x' and then propagated for $t - t'$ time³⁹. Or, speaking more loosely, it is the probability of finding an electron at x , if it was $t - t'$ time ago added at x' . Similarly, for $t' > t$, $|G_1(x, t, x', t')|^2$ is the probability of finding the system in a state that is the ground state with an electron removed at x' , if we initially started from the ground state, removed an electron at x and then propagated for $t' - t$ time. A removed or “missing” electron may also be interpreted as a hole (see above), such that, loosely speaking, $|G_1(x, t, x', t')|^2$ for $t' > t$ is the probability of finding a hole at x' , if it was $t' - t$ time ago added at x .

Since we will use it later, and since this is how the time-ordering is usually introduced, $G_1(x, t, x', t')$ shall also be expressed in terms of a *time-ordered product* $T[\dots]$ of field operators, where it takes the form [76, 77, 81, 82]:

$$G_1(x, t, x', t') = -i \langle N, 0 | T \left[\hat{\Psi}(x, t) \hat{\Psi}^\dagger(x', t') \right] | N, 0 \rangle \quad (2.125)$$

³⁷ Note that we did not specify $\theta(0)$ and therefore also $G_1(x, t, x', t')$ was not defined for equal times $t = t'$. This is commonly done, see e.g. Ref. [78], but may be a bit unsatisfactory at first sight. We may for example write $\theta(0) = 1$, such that $G_1(x, t, x', t) = -i \langle N, 0 | e^{i\hat{H}_e t} \left[\hat{\Psi}(x), \hat{\Psi}^\dagger(x') \right] e^{-i\hat{H}_e t} | N, 0 \rangle$, where we used Eq. 2.122. Using the interpretations given below, $G_1(x, t, x', t)$ is the probability amplitude for finding an electron at x at time t , if it was added at x' at time t , minus the same expression for a hole (with x and x' swapped). Being a mixture of electron and hole probability amplitudes makes this a less appealing quantity than $G_1(x, t, x', t')$ for $t \neq t'$, which can instead be used to obtain solely the electron- or hole probability amplitudes at (almost) equal time by taking $t' = t^-$ and $t' = t^+$, respectively. This is for example used in Eq. 2.137. Additionally, whenever $G_1(x, t, x', t)$ is integrated over, for example in Hedin's equations Eq. 2.159, or when Fourier-transforming over $t - t'$, see Eq. 2.134, it is important to remember that the result of such an integration does not change when changing the integrand at isolated points (Thus the integral in Footnote 42 does not depend on the value at 0.), see e.g. Refs. [79, 80]. In these contexts, we may thus simply set $G_1(x, t, x', t)$ to any value we like, without affecting the result, which is why it is usually not discussed.

³⁸ Assuming, of course, additional normalization of those states for the probability interpretation to be valid throughout this paragraph. See Eq. 2.137, where the normalization of these states can be read off as $n(x')$ and $n(x)$ (using that time-evolution is unitary).

³⁹ Note that, at first sight, $|G_1(x, t, x', t')|^2$ is strictly speaking the probability of ending up in a state that is the ground state, *propagated to t* and then has an electron added at x , when starting from the ground state, *propagating to t'* , adding an electron at x' and then *propagating to t* . However, since our electronic Hamiltonian is time-independent, the time-evolution operator takes the simple exponential form shown in Eq. 2.122 and $\langle N, 0 | e^{i\hat{H}_e t} = e^{iE(N,0)t} \langle N, 0 |$, where we used the notation of Eq. 2.126. But since $|e^{iE(N,0)t}|^2 = 1$, the time-evolution of the ground-state bra drops out. The same holds for the time-evolution of the ground-state ket, such that $|G_1(x, t, x', t')|^2$ is simply the probability of ending up in a state that is the ground state with an electron added at x , i.e. $\hat{\Psi}^\dagger(x) | N, 0 \rangle$, when starting from $\hat{\Psi}^\dagger(x') | N, 0 \rangle$ and propagating for $t - t'$ time.

The time-dependent field operators inside the brackets are ordered from right to left in ascending time, where a factor of -1 is applied for every needed permutation of two operators⁴⁰. This way, we retrieve Eq. 2.123.

To see why the one-particle Green's function (one-particle GF) is of interest to us, let us rewrite it a bit to see its connection to charged excitations. Looking at its definition, Eq. 2.123, we first note that in the first term, $\langle N, 0 | \hat{\Psi}(x, t)$ and $\hat{\Psi}^\dagger(x', t') | N, 0 \rangle$ both describe (one as a bra and one as a ket) $N + 1$ -electron states. Similarly, in the second term, $\langle N, 0 | \hat{\Psi}^\dagger(x', t')$ and $\hat{\Psi}(x, t) | N, 0 \rangle$ describe $N - 1$ -electron states. Denoting the eigenstates and eigenenergies of the N -electron Hamiltonian as $\{|N, S\rangle\}$ and $\{E(N, S)\}$, respectively,

$$\hat{H}_e |N, S\rangle = E(N, S) |N, S\rangle, \quad (2.126)$$

we can expand $\hat{\Psi}^\dagger(x', t') | N, 0 \rangle$ in the $\{|N + 1, S\rangle\}$ (orthonormal basis of the $N + 1$ -electron Hilbert space) and $\hat{\Psi}(x, t) | N, 0 \rangle$ in the $\{|N - 1, S\rangle\}$ (orthonormal basis of the $N - 1$ -electron Hilbert space). Using the time-dependent field operators of Eq. 2.122 we find:

$$\begin{aligned} \hat{\Psi}^\dagger(x', t') | N, 0 \rangle &= \sum_S |N + 1, S\rangle \langle N + 1, S | \hat{\Psi}^\dagger(x', t') | N, 0 \rangle \\ &= \sum_S |N + 1, S\rangle \langle N + 1, S | e^{i\hat{H}_e t'} \hat{\Psi}^\dagger(x') e^{-i\hat{H}_e t'} | N, 0 \rangle \\ &= \sum_S |N + 1, S\rangle e^{iE(N+1, S)t'} \langle N + 1, S | \hat{\Psi}^\dagger(x') | N, 0 \rangle e^{-iE(N, 0)t'} \\ &= \sum_S |N + 1, S\rangle e^{i(E(N+1, S) - E(N, 0))t'} \langle N + 1, S | \hat{\Psi}^\dagger(x') | N, 0 \rangle \end{aligned} \quad (2.127)$$

Using additionally

$$\begin{aligned} \langle N, 0 | \hat{\Psi}(x, t) | N + 1, S \rangle &= \langle N, 0 | e^{i\hat{H}_e t} \hat{\Psi}(x) e^{-i\hat{H}_e t} | N + 1, S \rangle \\ &= e^{iE(N, 0)t} \langle N, 0 | \hat{\Psi}(x) | N + 1, S \rangle e^{-iE(N+1, S)t} \\ &= e^{-i(E(N+1, S) - E(N, 0))t} \langle N, 0 | \hat{\Psi}(x) | N + 1, S \rangle, \end{aligned} \quad (2.128)$$

we find:

$$\begin{aligned} \langle N, 0 | \hat{\Psi}(x, t) \hat{\Psi}^\dagger(x', t') | N, 0 \rangle &= \\ &= \sum_S \langle N, 0 | \hat{\Psi}(x) | N + 1, S \rangle \langle N + 1, S | \hat{\Psi}^\dagger(x') | N, 0 \rangle e^{-i(E(N+1, S) - E(N, 0))(t - t')} \end{aligned} \quad (2.129)$$

Similarly:

$$\begin{aligned} \langle N, 0 | \hat{\Psi}^\dagger(x', t') \hat{\Psi}(x, t) | N, 0 \rangle &= \\ &= \sum_S \langle N, 0 | \hat{\Psi}^\dagger(x') | N - 1, S \rangle \langle N - 1, S | \hat{\Psi}(x) | N, 0 \rangle e^{i(E(N-1, S) - E(N, 0))(t - t')} \end{aligned} \quad (2.130)$$

⁴⁰Note that we leave $T[\dots]$ undefined for situations where not all operators are at different times, see also Footnote 37.

Using the fact that the field operators $\hat{\Psi}(x)$ and $\hat{\Psi}^\dagger(x)$ are adjoint operators of one another and using $\langle u | \hat{A}^\dagger | v \rangle = \langle v | \hat{A} | u \rangle^*$, we can then write the one-particle GF as⁴¹

$$G_1(x, t, x', t') = -i \sum_S f_S^+(x) f_S^{+*}(x') e^{-i\varepsilon_S^+(t-t')} \theta(t-t') \\ + i \sum_S f_S^-(x) f_S^{-*}(x') e^{-i\varepsilon_S^-(t-t')} \theta(t'-t), \quad (2.131)$$

where we have defined the Lehmann amplitudes

$$f_S^+(x) = \langle N, 0 | \hat{\Psi}(x) | N+1, S \rangle \\ f_S^-(x) = \langle N-1, S | \hat{\Psi}(x) | N, 0 \rangle \quad (2.132)$$

and the electron addition and removal energies

$$\varepsilon_S^+ = E(N+1, S) - E(N, 0) \\ \varepsilon_S^- = E(N, 0) - E(N-1, S). \quad (2.133)$$

Notice, that $G_1(x, t, x', t')$ only depends on the difference $t - t'$, as we would expect with a time-independent Hamiltonian. Fourier-transforming with respect to $t - t'$ we find⁴²:

$$G_1(x, x', \omega) = \sum_S \frac{f_S^+(x) f_S^{+*}(x')}{\omega - \varepsilon_S^+ + i\eta} + \sum_S \frac{f_S^-(x) f_S^{-*}(x')}{\omega - \varepsilon_S^- - i\eta}, \quad (2.134)$$

with $\eta = 0^+$. This is the *Lehmann representation* of the one-particle GF. It tells us that, $G_1(x, x', \omega)$ is – as a function of ω – a sum of poles, where the poles are located at the positions $\{\varepsilon_S^-\}$ and $\{\varepsilon_S^+\}$ (and are independent of x and x'). And from Eq. 2.133, we can see that these pole positions are actually the electron addition and electron removal energies relative to the N -electron ground state! That is, ε_S^+ gives us the change in energy when adding an electron to the N -electron ground state, such that we end up in the S -th eigenstate (ground state $S = 0$ or excited state $S = 1, 2, \dots$) of the $N+1$ -electron Hamiltonian. The electron addition energies $\{\varepsilon_S^+\}$ are the negative of what is typically called the ground state's *electron affinities*. Similarly, ε_S^- gives us the change in energy when removing an electron to the N -electron ground state, such that we end up in the S -th eigenstate of the $N-1$ -electron Hamiltonian. The electron removal energies $\{\varepsilon_S^-\}$ are the negative of what is typically called the ground state's *ionization energies*.

⁴¹Note that the two sums run over different states, the first over eigenstates of the $N+1$ -electron Hamiltonian and the second over those of the $N-1$ -electron Hamiltonian.

⁴²Here we used the “limes-expression” for the Fourier-transform Eq. A.60 of the (exponentially damped) Heaviside function $\theta(t)$: as can be seen in Refs. [77, 83], $\int_{\mathbb{R}} dt \theta(t) e^{i\omega t - \eta t} = \frac{i}{\omega + i\eta}$, such that the Fourier transform is obtained via $\lim_{\eta \rightarrow 0^+} \int_{\mathbb{R}} dt \theta(t) e^{i\omega t - \eta t}$ and is written as $\frac{i}{\omega + i\eta}$, where $\eta = 0^+$. For the second term we similarly use $\int_{\mathbb{R}} dt \theta(-t) e^{i\omega t + \eta t} = \frac{-i}{\omega - i\eta}$. The electron addition and removal energies $\varepsilon_S^\pm$ then trivially enter the denominator in Eq. 2.134 and determine the pole positions. Note that when the pole positions acquire imaginary parts (negative for electron addition, positive for electron removal), see quasiparticle Green's function in Sec. 2.3.6, our convergence problems (and the remaining problem at $\omega = \Re \varepsilon_S^\pm$) disappear and we can set $\eta = 0$ for $\omega \in \mathbb{R}$.

We will later assume the ionization energies to be larger than the electron affinities (as is commonly done, see e.g. Ref. [84]), which follows from the intuition that it takes less energy to remove an electron from an $N + 1$ -electron state than from an N -electron state, since the nuclei (whose positions we take to be the same for the N - and $N \pm 1$ -electron states, as we do throughout this text) are more screened by the other electrons in the $N + 1$ -electron case than in the N -electron case. Consequently, we find for any S and S' :

$$\varepsilon_S^+ \geq E(N + 1, 0) - E(N, 0) > E(N, 0) - E(N - 1, 0) \geq \varepsilon_{S'}^- \quad (2.135)$$

When written as $E(N + 1, 0) + E(N - 1, 0) > 2E(N, 0)$, this is known as the *convexity of the ground-state energy* with respect to the number of electrons. While this assumption is normally safe to use for systems typical in solid-state physics and quantum chemistry, note that it lacks a rigorous proof and recently even a counter-example has been claimed to have been found [85]. Assuming Eq. 2.135, we will later also use the chemical potential

$$\mu \equiv \frac{\varepsilon_0^+ + \varepsilon_0^-}{2} = \frac{E(N + 1, 0) - E(N - 1, 0)}{2} \quad (2.136)$$

to separate the electron addition and electron removal part of the one-particle GF and related quantities.

Finally, note that G_1 is also closely related to the ground-state electron spin-density:

$$\begin{aligned} -iG_1(x, t, x, t^+) &= \langle N, 0 | \hat{\Psi}^\dagger(x, t^+) \hat{\Psi}(x, t) | N, 0 \rangle \\ &= \langle N, 0 | \hat{\Psi}^\dagger(x) \hat{\Psi}(x) | N, 0 \rangle \\ &= \frac{1}{(N!)^2} \int d\{x'\} d\{x''\} \langle N, 0 | \{x'\} \rangle \\ &\quad \langle \{x'\} | \hat{\Psi}^\dagger(x) \hat{\Psi}(x) | \{x''\} \rangle \langle \{x''\} | N, 0 \rangle \\ &= \frac{1}{(N!)^2} \int d\{x'\} d\{x''\} \langle N, 0 | \{x'\} \rangle \\ &\quad \langle \{x'\} | \{x''\} \rangle \sum_{i=1}^N \delta(x - x_i'') \langle \{x''\} | N, 0 \rangle \\ &= \frac{1}{N!} \int d\{x'\} \sum_{i=1}^N \delta(x - x_i') |\langle \{x'\} | N, 0 \rangle|^2 \\ &= \int d\{x'\} \sum_{i=1}^N \delta(x - x_i') |\Psi_0(\{x'\})|^2 \\ &= N \int d\{x_2, x_3, \dots, x_N\} |\Psi_0(\{x, x_2, x_3, \dots, x_N\})|^2 \\ &= n(x), \end{aligned} \quad (2.137)$$

where we used that the electronic Hamiltonian is time-independent to get to the second line (otherwise the bra and ket would need to be propagated to t and we would get a time-dependent spin-/density, which is what happens in the Hedin equations), expressed the field operators in terms of Dirac deltas in line four (compare Ref. [75]), used Eq. 2.56 to get to line six, used Eq. 2.59 to get to line seven

and identified the result with the electron spin-density of Eq. 2.67, which we now write as:

$$n(x) = n(\mathbf{r}, s) \equiv n_s(\mathbf{r}) \quad (2.138)$$

The Hartree potential of Eq. 2.99 can thus also be written as:

$$\begin{aligned} v_J[n](\mathbf{r}) &= -i \int_{\mathbb{R}^3} d^3r' \sum_{s'=\uparrow,\downarrow} \frac{G_1(x', t, x', t^+)}{|\mathbf{r} - \mathbf{r}'|} \\ &= -i \int dx' \frac{G_1(x', t, x', t^+)}{|\mathbf{r} - \mathbf{r}'|} \end{aligned} \quad (2.139)$$

2.3.3 Spectral Function and Relation to Photoemission

A quantity closely related to the one-particle GF is the *spectral function* A , formally defined as [84]:

$$A(x, x', \omega) = \sum_S f_S^+(x) f_S^{+*}(x') \delta(\omega - \varepsilon_S^+) + \sum_S f_S^-(x) f_S^{-*}(x') \delta(\omega - \varepsilon_S^-) \quad (2.140)$$

There is a very intuitive meaning to $A(x, x, \omega)$, which can be seen when inserting Eq. 2.132:

$$\begin{aligned} A(x, x, \omega) &= \sum_S |\langle N+1, S | \hat{\Psi}^\dagger(x) | N, 0 \rangle|^2 \delta(\omega - \varepsilon_S^+) \\ &\quad + \sum_S |\langle N-1, S | \hat{\Psi}(x) | N, 0 \rangle|^2 \delta(\omega - \varepsilon_S^-) \end{aligned} \quad (2.141)$$

Remembering that the field operators add/remove an electron at x , $A(x, x, \omega)$ tells us how likely it is to end up in state $|N \pm 1, S\rangle$ if an electron is added/removed at x , and it gives us the associated change in the system's energy. Or, stated differently, for a given x and ω , $A(x, x, \omega)$ tells us if there is any (possibly multiple) $N \pm 1$ -electron state available at this energy change ω , and if so, how likely it is to end up in this state(s), if an electron is added to/removed from the ground state at x . It may in this sense therefore be regarded as a local density of $N \pm 1$ -electron states and it is already clear from this definition that there must be a close relation between A and photoemission experiments.

Note that the spectral function is closely related to the one-particle GF via [84]

$$G_1(x, x', \omega) = \int_{\mathbb{R}} d\omega' \frac{A(x, x', \omega')}{\omega - \omega' + i\eta \operatorname{sgn}(\omega' - \mu)}, \quad (2.142)$$

where we used Eqs. 2.135 and 2.136. It is trivial to verify this by inserting Eq. 2.140 and evaluating the delta functions. Alternatively, we can also use the *Sokhotski–Plemelj theorem* to rewrite the poles in the Green's function [83, 86] and extract the imaginary part as a sum over delta functions to find (for $x = x'$):

$$A(x, x, \omega) = \frac{1}{\pi} \Im \{ G_1(x, x, \omega) \} \operatorname{sgn}(\mu - \omega) \quad (2.143)$$

Having these relations at hand, we can now show that the spectral function, just like G_1 , is closely related to photoemission experiments. Details on photoemission

simulations can be found in Sec. 3.3. For our present purposes, it is enough to remember that in a typical photoemission experiment an external light source is applied onto an atomic system, which then leads to the emission of electrons via the photoelectric effect. The emitted electrons then reach a detection device and thereby reveal information about the atomic system via the *photoemission intensity* (distribution). As shown in Sec. 3.3, the ground-state photoemission intensity for a photoelectron state $|\gamma\rangle$ is then given by (compare Eq. 3.35 and use $E(N, 0) - E(N - 1, S) = \varepsilon_S^-$):

$$I_{0,\gamma} \propto \sum_S |\langle \gamma | \mathbf{A} \cdot \hat{\mathbf{p}} | d_{0,S} \rangle|^2 \delta(\omega + \varepsilon_S^- - E_{\text{kin}})$$

$$d_{0,S}(x) = \langle x | d_{0,S} \rangle = \langle N - 1, S | \hat{\Psi}(x) | N, 0 \rangle, \quad (2.144)$$

where $\mathbf{A}$ is the amplitude of the electromagnetic vector potential (in dipole approximation), E_{kin} is the kinetic energy of the photoelectron and the sum runs over the exact eigenstates of the $N - 1$ -electron system. Expanding the Dyson orbital state $|d_{0,S}\rangle$ in one-electron (typically Kohn-Sham) orbitals using Eq. 2.119,

$$|d_{0,S}\rangle = \sum_m |\phi_m\rangle \langle N - 1, S | \hat{a}_m | N, 0 \rangle, \quad (2.145)$$

we find:

$$I_{0,\gamma} \propto \sum_S \left| \sum_m \langle \gamma | \mathbf{A} \cdot \hat{\mathbf{p}} | \phi_m \rangle \langle N - 1, S | \hat{a}_m | N, 0 \rangle \right|^2 \delta(\omega + \varepsilon_S^- - E_{\text{kin}}) \quad (2.146)$$

Defining

$$M_{\gamma,m} = \langle \gamma | \mathbf{A} \cdot \hat{\mathbf{p}} | \phi_m \rangle \quad (2.147)$$

and simply using $|z|^2 = zz^*$, we find (compare Ref. [82]):

$$I_{0,\gamma} \propto \sum_S \sum_{m,n} M_{\gamma,m} M_{\gamma,n}^* \langle N, 0 | \hat{a}_n^\dagger | N - 1, S \rangle \langle N - 1, S | \hat{a}_m | N, 0 \rangle \delta(\omega + \varepsilon_S^- - E_{\text{kin}})$$

$$= \sum_{m,n} M_{\gamma,m} M_{\gamma,n}^* A_{m,n}^<(E_{\text{kin}} - \omega), \quad (2.148)$$

where we introduced⁴³ the *lesser* spectral function

$$A^<(x, x', \omega) = A(x, x', \omega) \theta(\mu - \omega) = \sum_S f_S^-(x) f_S^{-*}(x') \delta(\omega - \varepsilon_S^-) \quad (2.149)$$

and (using Eq. 2.119 and orthonormality of the one-electron orbitals)

$$A_{m,n}^<(\omega) = \int dx \int dx' \phi_m^*(x) \phi_n(x') A^<(x, x', \omega)$$

$$= \sum_S \langle N, 0 | \hat{a}_n^\dagger | N - 1, S \rangle \langle N - 1, S | \hat{a}_m | N, 0 \rangle \delta(\omega - \varepsilon_S^-), \quad (2.150)$$

⁴³The Heaviside function $\theta(\mu - \omega)$ removes the poles at $\{\varepsilon_S^+\}$ in the sense that $\int_{\mathbb{R}} d\omega f(\omega) \delta(\omega - \varepsilon_S^+) \theta(\mu - \omega) = f(\varepsilon_S^+) \theta(\mu - \varepsilon_S^+) = 0$.

whose diagonal elements are again directly related to the Green's function⁴⁴:

$$A_{n,n}^<(\omega) = \frac{1}{\pi} \Im \{G_{1;n,n}(\omega)\} \theta(\mu - \omega) \quad (2.151)$$

On a sidenote, we find that $A_{m,n}^<(\omega)$ is diagonal for a non-interacting system (whose one-electron Hamiltonian is the Hamiltonian with regard to which we choose the one-electron orbitals), which follows from the $N - 1$ -electron eigenstates simply being single Slater determinants built from the one-electron orbitals (see also Sec. 2.2.4). Thus, also for a weakly correlated system, we can expect the photoemission intensity $I_{0,\gamma}$ to be dominated by the diagonal matrix elements $\{A_{n,n}^<(E_{\text{kin}} - \omega)\}_n$ [87].

Within the approximations underlying Eq. 2.144, we have thus shown via Eq. 2.148 that the photoemission intensity from the ground state to (the set of N -electron final states with) a scattering state $|\gamma\rangle$ is given by the matrix elements of the light-matter interaction Hamiltonian and by the matrix-elements of the lesser spectral function⁴⁵.

To conclude, note that it is a widespread approximation to simulate photoemission based purely on the (diagonal elements) of the lesser spectral function, thereby also neglecting effects of the matrix elements $\{M_{\gamma,m}\}$ [82]. In Sec. 3.3 we will go beyond this approximation and include these so-called *matrix-element effects*. Importantly, we should not get confused about what kind of matrix element we are talking about: in the derivation shown above, the matrix elements $\{M_{\gamma,m}\}$ referred to matrix elements of $\mathbf{A} \cdot \hat{\mathbf{p}}$ between $\langle\gamma|$ and the one-electron basis orbitals $\{|\phi_m\rangle\}$ (usually Kohn-Sham orbitals) and we needed to (double-) sum over those orbitals to get the photoemission intensity. In contrast, in POT – compare Eq. 3.32 – we use a (single) sum over matrix element of the same operator and bra, however using the Dyson orbitals $\{|d_{i,f}\rangle\}$ as kets. These matrix elements then already contain the necessary information that is otherwise stored in the spectral function. For the POT formalism, as presented in Sec. 3.3, the spectral function is thus of no particular relevance and we will continue with the closely related one-particle Green's function G_1 , which not only contains the electron removal energies $\{\varepsilon_S^-\}$ needed for ground-state- and excited-state photoemission but also contains the ground-state Dyson orbitals $\{d_{0,S}\}$ (which are simply its Lehmann amplitudes, see Sec. 3.3.9) needed for ground-state photoemission simulations, see Eq. 2.144. Additionally, G_1 itself will be relevant for the derivation of the *Bethe-Salpeter equation* (via L_0 , see Sec. 2.4.4) underlying our excited-state photoemission formalism.

2.3.4 Hedin's Equations

Having seen the close relation between the one-particle Green's function G_1 and photoemission, the question now arises how we can calculate G_1 and obtain the Lehmann amplitudes and electron addition/removal energies. The commonly used approach to achieve this is to solve a set of integro-differential equations known as

⁴⁴This is a special case of $A_{n,n}(\omega) = \frac{1}{\pi} \Im \{G_{1;n,n}(\omega)\} \text{sgn}(\mu - \omega)$ (see also Ref. [77]), where we define the matrix elements as in Eq. 2.150, which again easily be seen by explicitly writing the matrix elements on both sides and using the Sokhotski–Plemelj theorem. See also Eq. 2.143.

⁴⁵We could have, of course, also stuck with the “normal” spectral function by replacing $A_{m,n}^<(E_{\text{kin}} - \omega)$ in Eq. 2.148 with $A_{m,n}(E_{\text{kin}} - \omega)\theta(\mu - E_{\text{kin}} + \omega)$.

Hedin's equations. For their derivation, a small external time-dependent perturbation φ is introduced and added to the Hamiltonian. This potential is only used for variational calculations and is ultimately (for example for the evaluation of the occurring functional derivatives) set to zero again [82] (we omit writing $|\varphi=0$ next to each functional derivative for readability, compare Appendix A.3). At given points 1 and 2, the Green's function of the perturbed system is then denoted as $G_1(1, 2; \varphi)$ and can be understood as a functional of the perturbing potential φ . For the remainder of this section, we drop the explicit functional dependence on φ for readability.

Based on Ref. [82], let us now introduce a couple of new quantities: The *self-energy* Σ is formally defined as (see Sec. 2.1 for an explanation of the used notation):

$$\Sigma(1, 2) \equiv -i \int d(3, 4) v(1, 3) G_1(1, 4) \frac{\delta G_1^{-1}(4, 2)}{\delta \varphi(3)}, \quad (2.152)$$

where we used the *inverse Green's function*:

$$\int d(3) G_1(1, 3) G_1^{-1}(3, 2) = \delta(1, 2) \quad (2.153)$$

This definition of the self-energy is rather abstract. Its physical meaning will however become very clear in the context of quasiparticle equation of motion (see Eq. 2.177). With the definition of the total potential (time-(but not spin-)dependent Hartree potential of perturbed system plus perturbation itself)

$$V(1) \equiv v_J(1) + \varphi(1), \quad (2.154)$$

we then define the *vertex function*

$$\Gamma(1, 2, 3) \equiv -\frac{\delta G_1^{-1}(1, 2)}{\delta V(3)}, \quad (2.155)$$

the *inverse dielectric function*

$$\varepsilon^{-1}(1, 2) \equiv \frac{\delta V(1)}{\delta \varphi(2)}, \quad (2.156)$$

the *screened Coulomb interaction*

$$W(1, 2) \equiv \int d(3) \varepsilon^{-1}(1, 3) v(3, 2) \quad (2.157)$$

and finally the *irreducible polarizability*

$$P(1, 2) \equiv \frac{\delta n(1)}{\delta V(2)}, \quad (2.158)$$

for which we may also use Eq. 2.137 (modified for a time-dependent Hamiltonian) to express it as functional derivatives of the Green's function.

Hedin's equations [81, 82] are then a set of five equations that relate these quantities:

$$\begin{aligned}
G_1(1, 2) &= G_1^{(0)}(1, 2) + \int d(3, 4) G_1^{(0)}(1, 3) \Sigma(3, 4) G_1(4, 2) \\
\Gamma(1, 2, 3) &= \delta(1, 2) \delta(1, 3) + \int d(4, 5, 6, 7) \frac{\delta \Sigma(1, 2)}{\delta G_1(4, 5)} G_1(4, 6) G_1(7, 5) \Gamma(6, 7, 3) \\
P(1, 2) &= -i \int d(3, 4) G_1(4, 2) G_1(2, 3) \Gamma(3, 4, 1) \\
W(1, 2) &= v(1, 2) + \int d(3, 4) v(1, 3) P(3, 4) W(4, 2) \\
\Sigma(1, 2) &= i \int d(3, 4) G_1(1, 4) W(1^+, 3) \Gamma(4, 2, 3)
\end{aligned} \tag{2.159}$$

Note that $G_1^{(0)}$ denotes the Hartree-level Green's function, whose Lehmann representation can be seen in Eq. 2.169. These five equations can then be solved self-consistently, thereby yielding the (in principle exact) self-energy Σ and one-particle Green's function G_1 .

The first line of Eq. 2.159 is known as the *Dyson equation* of G_1 [82]. Using the equation of motion of $G_1^{(0)}$, this can also be written as [76, 81, 82]:

$$\begin{aligned}
\left[i \frac{\partial}{\partial t} - h(\mathbf{r}) - v_J(\mathbf{r}) \right] G_1(x, t, x', t') &= \delta(t - t') \delta(x - x') \\
&+ \int_{\mathbb{R}} dt'' \int x'' \Sigma(x, t, x'', t'') G_1(x'', t'', x', t'),
\end{aligned} \tag{2.160}$$

where h is the one-electron Hamiltonian of Eq. 2.43 Fourier transforming (see Eq. A.60) with respect to $t - t'$ (using time-translation invariance) and using the Lehmann representation of the one-particle GF, Eq. 2.134, we then find that the Lehmann amplitudes and the corresponding electron addition/removal energies solve the following equation of motion [19, 81]:

$$[h(\mathbf{r}) + v_J(\mathbf{r})] f_S^\pm(x) + \int dx' \Sigma(x, x', \varepsilon_S^\pm) f_S^\pm(x') = \varepsilon_S^\pm f_S^\pm(x) \tag{2.161}$$

As noted in Ref. [81], the derivation of this equation assumed that the (real-valued, exact) electron addition/removal energy $\varepsilon_S^\pm$ is (related to an $N \pm 1$ -electron state that is) part of the discrete spectrum of the $N \pm 1$ -electron Hamiltonian, thus forming a discrete pole of G_1 . If it is part of the continuous spectrum (see Appendix A.1.1), the situation is more complicated [81]. We will get back to this equation in the context of the quasiparticle approximation, where G_1 is written in terms of a small number of discrete poles (in the complex plane), each satisfying an equation like Eq. 2.161, see Eqs. 2.168 and 2.177.

We will now introduce two approximations, namely the GW approximation and the quasiparticle approximation. While these approximations can be applied independently, we will in practice always use both of them.

2.3.5 GW Approximation

As can be easily guessed from looking at Hedin's equations Eq. 2.159, the equation for the vertex function $\Gamma(1, 2, 3)$ poses a particular problem in practical calculations, since it involves the complicated functional derivative of the self-energy with respect to the Green's function. Fortunately, in many practical calculations, the vertex function can be approximated as $\Gamma(1, 2, 3) = \delta(1, 2)\delta(1, 3)$, yielding Hedin's equations in the *GW approximation* [82]:

$$\begin{aligned} G_1(1, 2) &= G_1^{(0)}(1, 2) + \int d(3, 4) G_1^{(0)}(1, 3) \Sigma(3, 4) G_1(4, 2) \\ P(1, 2) &= -i G_1(1, 2) G_1(2, 1) \\ W(1, 2) &= v(1, 2) + \int d(3, 4) v(1, 3) P(3, 4) W(4, 2) \\ \Sigma(1, 2) &= i G_1(1, 2) W(1^+, 2) \end{aligned} \quad (2.162)$$

As can be seen from the last line, the GW approximation derives its name from the simple form that the self-energy takes. Comparison with Eq. 2.159 shows that the GW approximation significantly simplifies the set of equations to be solved self-consistently.

2.3.6 Quasiparticle Approximation

In practice, we almost never work with the exact Green's function G_1 in terms of exact eigenstates of the $N \pm 1$ -electron states, but instead use the *quasiparticle* (QP) approximation (QPA) for a cheap and effective description of the Green's function in terms of particle-like charged excitations. In the following, we will first derive an exact alternative representation of the Green's function and then introduce the QPA.

Besides the references used throughout this subsection, additional details on the QPA can also be found in Refs. [88–90]

Complex-Pole Representation of G_1

In preparation for the QPA, we first focus on an alternative representation of G_1 which we will call the *complex-pole representation*. While the Lehmann representation Eq. 2.134 takes real energies ω as its third argument, G_1 can also be extended to complex arguments z by analytic continuation. We denote the analytic continuation by $\tilde{G}_1$ and it can be shown that [76, 91] the complex-pole representation

$$\tilde{G}_1(x, x', z) = \sum_n \frac{\tilde{\phi}_n(x, z) \tilde{\psi}_n^*(x', z)}{z - E_n(z)}, \quad (2.163)$$

with (z serves as a parameter)

$$\begin{aligned} [h(\mathbf{r}) + v_J(\mathbf{r})] \tilde{\phi}_n(x, z) + \int dx' \Sigma(x, x', z) \tilde{\phi}_n(x', z) &= E_n(z) \tilde{\phi}_n(x, z) \\ \left[[h(\mathbf{r}) + v_J(\mathbf{r})] \tilde{\psi}_n(x, z) \right]^* + \int dx' \Sigma(x', x, z) \tilde{\psi}_n^*(x', z) &= E_n(z) \tilde{\psi}_n^*(x, z), \end{aligned} \quad (2.164)$$

satisfies

$$\tilde{G}_1(x, x', \omega) = G_1(x, x', \omega) \quad (2.165)$$

for real $z = \omega$.

QPA

Until now, we have made no approximations, that is, $\tilde{G}_1$ still satisfies Eq. 2.165 exactly. While $\tilde{G}_1$ may in general be a complicated function of z , we are in principle only interested in its values on the real axis. In the *quasiparticle approximation*, we then assume that $\tilde{G}_1$ around the real axis is dominated by complex poles which arise from the denominators vanishing (see Ref. [76] for details) and are thus located at (close to the real axis):

$$z = E_n(z) \quad (2.166)$$

Assuming that there is only one *quasiparticle energy* z_n per n (or: neglecting additional solutions of $z = E_n(z)$, see Ref. [76, 91]), we then find $\tilde{G}_1$ within the QPA [76] (abbreviating $\tilde{\phi}_n(x, z_n)$ by $\tilde{\phi}_n(x)$ and $\tilde{\psi}_n(x', z_n)$ by $\tilde{\psi}_n(x')$):

$$\begin{aligned} \tilde{G}_1^{QP}(x, x', z) &\approx \tilde{G}_1(x, x', z) \\ \tilde{G}_1^{QP}(x, x', z) &= \sum_n g_n \frac{\tilde{\phi}_n(x) \tilde{\psi}_n^*(x')}{z - z_n} \\ g_n &= \left(1 - \left. \frac{\partial E_n(z)}{\partial z} \right|_{z=z_n} \right)^{-1}, \end{aligned} \quad (2.167)$$

where the *quasiparticle renormalization factor* g_n arises from a linear Taylor expansion of $(z - E_n(z))^{-1}$ around z_n (while the *quasiparticle orbitals* $\tilde{\phi}_n(x)$ and $\tilde{\psi}_n(x')$ are assumed to be approximately constant around z_n), which is assumed to be valid for z close to z_n . In the QPA, the equations Eq. 2.164 become:

$$\begin{aligned} [h(\mathbf{r}) + v_J(\mathbf{r})] \tilde{\phi}_n(x) + \int dx' \Sigma(x, x', z_n) \tilde{\phi}_n(x') &= z_n \tilde{\phi}_n(x) \\ \left[[h(\mathbf{r}) + v_J(\mathbf{r})] \tilde{\psi}_n(x) \right]^* + \int dx' \Sigma(x', x, z_n) \tilde{\psi}_n^*(x') &= z_n \tilde{\psi}_n^*(x) \end{aligned} \quad (2.168)$$

While G_1 in the Lehmann representation Eq. 2.134 is a sum of real poles ($\mp i\eta$), whose positions correspond to the exact eigenenergies of the $N \pm 1$ -electron system (relative to $E(N, 0)$) and whose residues are given by the corresponding Lehmann amplitudes (Dyson orbitals), $\tilde{G}_1^{QP}$ is a sum over *quasiparticle poles* located at the complex quasiparticle energies with residues given by the quasiparticle orbitals (and g_n). As is detailed below (via comparison to a non-interacting system), the benefit of the QPA Green's function $\tilde{G}_1^{QP}$ is that it often reproduces G_1 reasonably well on the real axis, while needing far fewer poles in the summation! In that sense, each quasiparticle pole can then be thought of as replacing many real poles located at exact eigenenergies, as detailed below (this interpretation of course becomes slightly problematic if two quasiparticle energies are very close such that the poles overlap and “share” real poles).

Experimental Support for the QPA

We have already seen in Sec. 2.3.3 that there is a very close relationship between experimental ground-state photoemission intensities, the spectral function A (via Eq. 2.148) and the one-particle Green's function G_1 (via Eq. 2.144). We have seen in particular that the pole-positions of the Green's function determine the kinetic energies at which photoemission can occur (while the current argument is performed based on ground-state photoemission, this point also holds in our excited-state photoemission formalism).

Now, the experimentally obtained ground-state photoemission spectra of many systems look exactly as what is predicted by the Green's function within the QPA! That is, when plotting the photoemission intensity as a function of kinetic energy for a fixed photoemission in-plane direction (k_x, k_y) , they show dominant broadened photoemission peaks (see also comments below Eqs. 3.39 and 3.45), accompanied by a much smaller background signal and possibly additional, smaller peaks (called satellites) [82, 87]. This dominant broadened peaks can be understood as corresponding to the quasiparticle poles and their dominance over other features in the photoemission spectrum tells us that performing the QPA, which means neglecting the remaining structure of the Green's function, is well-justified (at least in the context of photoemission). Thus, we find that the QPA can be expected to be a good approximation to the Green's function of many physical systems and that we are justified to use it for the simulation of photoemission experiments.

Interpretation of the QPA

To understand why we identified each pole in Eq. 2.163 with a *quasiparticle*, we follow Refs. [82, 87] and first take a step back to analyze a system of non-interacting electrons (e.g. electrons in an external+Hartree potential, or the non-interacting electrons of KS-DFT). When we solve the corresponding single-electron eigenvalue equation we obtain one-electron orbitals $\{\phi_i\}$ (forming an orthonormal one-electron basis) and one-electron energies $\{\varepsilon_i\}$. The ground state (single Slater determinant of *valence* orbitals) and all excited states of an N - and $N \pm 1$ -electron system of such non-interacting electrons can then be written exactly as single Slater determinants of these orbitals and their energies are simply the sums of the orbital energies belonging to the orbitals from which the determinants were built. Let us now choose these orbitals $\{\phi_i\}$ and the corresponding creation and annihilation operators to construct the quantum field operators $\hat{\Psi}(x)$ and $\hat{\Psi}^\dagger(x)$. Remembering the definition of the Lehmann amplitudes, Eq. 2.132, and using the orthogonality of Slater determinants built from different orthonormal orbitals (see Ref. [42]), we then immediately see that the Lehmann amplitudes of most $N \pm 1$ eigenstates vanish! In fact, the only $N + 1$ ($N - 1$) -electron eigenstates with nonvanishing Lehmann amplitudes are the ones that differ from the N -electron ground state by a single creation (annihilation) operator, that is, they represent the ground state with simply an electron added in (removed from) some orbital ϕ_i . Trivially (using the fact that all eigenstates are normalized to one⁴⁶), the Lehmann amplitude of

⁴⁶Which of course does not hold for $N \pm 1$ -electron scattering states, compare Appendix A.1.1. These states however lie energetically beyond the applicability of the QPA, so the argument holds within the valid energetic range of the QPA and we do not need to dive any deeper into the influence of Dirac delta normalization here.

such a remaining state is then simply given by the orbital ϕ_i . The corresponding poles are then located at the orbital energies $\{\varepsilon_i\}$ and the one-particle GF of such a system takes the form

$$G_1^{(0)}(x, x', \omega) = \sum_i^{\text{occ.}} \frac{\phi_i(x)\phi_i^*(x')}{\omega - \varepsilon_i - i\eta} + \sum_i^{\text{unocc.}} \frac{\phi_i(x)\phi_i^*(x')}{\omega - \varepsilon_i + i\eta}, \quad (2.169)$$

where the first sum runs over the N orbitals with the lowest energy (which are occupied in the non-interacting N -electron ground state) and the second sum runs over the remaining orbitals. Note that all $N \pm 1$ -electron states that contribute to the Green's function can therefore be understood by the addition or removal of a single electron from the ground state and thus by the properties of said electron (its wave function and its orbital energy). Using Eq. 2.144 to calculate the ground-state photoemission intensity from such a non-interacting system, we find:

$$I_{0,\gamma} \propto \sum_i^{\text{occ.}} |\langle \gamma | \mathbf{A} \cdot \hat{\mathbf{p}} | \phi_i \rangle|^2 \delta(\omega + \varepsilon_i - E_{\text{kin}}) \quad (2.170)$$

So, only the states $\{\hat{a}_v | N, 0 \rangle\}$ (one per occupied/valence orbital) can contribute to the ground-state photoemission signal! That is, the possible system states after photoemission are each fully described (relative to the ground state) by a missing electron, that is, a photohole in orbital ϕ_v . Moreover, we see that the system's Green's function exhibits poles at the orbital energies and that – exactly as described in the previous section (where we talked about “dominant” poles) – photoemission from such an idealized system is sharply peaked, namely around the orbital energies (precisely: around $E_{\text{kin}} = \omega + \varepsilon_v = (k_x^2 + k_y^2 + k_z^2)/2$, when plotting the photoemission intensity as a function of E_{kin} for a given in-plane direction (k_x, k_y) , see comments below Eqs. 3.39 and 3.45).

The interpretation of $\tilde{G}_1^{QP}$ in terms of *quasiparticles* now arises if the poles of $\tilde{G}_1^{QP}$ can be identified⁴⁷ (one-to-one) with the poles of the non-interacting Green's function $G_1^{(0)}$ (usually from KS-DFT) [87, 92]. The quasiparticle Green's function $\tilde{G}_1^{QP}$ can then be thought of as originating from $G_1^{(0)}$ by having switched on the electron-electron interaction⁴⁸. For each quasiparticle pole, its energy ε_i^{QP} (which was called z_i in Eq. 2.167) can be thought of as a “corrected” orbital energy ε_i and the (left and right) quasiparticle wave function as a corrected wave function. Remember now, that $\tilde{G}_1^{QP}$ is the (approximated) Green's function of a system of *interacting* electrons and that in the Lehmann representation Eq. 2.134 of the exact G_1 , each pole corresponds to an exact charged excitation of the system (where exact here means that it is a transition to an eigenstate: $|N, 0\rangle \rightarrow |N \pm 1, S\rangle$). We have thus achieved an effective description of the interacting system (or at least G_1) in terms of effective excitations that have particle-like character but also take into account the interactions in the system (see also Refs. [93, 94]). Each of these excitations is then called a *quasiparticle* (-excitation) of the system and can be

⁴⁷In practice, this one-to-one identification is usually not given for all orbitals of the non-interacting system, but restricted to orbitals around the Fermi level [19]. In other words, we usually only have a one-to-one identification of these orbitals and the low-energy part of the Green's function in terms of quasiparticle poles.

⁴⁸Strictly speaking, this interaction is of course already partially accounted for in the Hartree/-Fock and (G)KS schemes.

thought of as an added “bare”⁴⁹ electron (or hole) that is “dressed” by a *polarization cloud*, which describes the way the other electrons in the system are affected by its presence/addition. The bare electron (or hole) and the polarization cloud together form a cohesive entity, thus allowing for the interpretation as a (quasi-) *particle* [82]. In analogy to $G_1^{(0)}$, the quasiparticle Green’s function can then be thought of as a sum over possible states (see below) of the added electron/hole, with the quasiparticle (one-particle) orbitals in place of the Lehmann amplitudes and with the poles being located at the energy of the quasiparticle (-state). Using the QPA for the description of photoemission, the ionized system (with one removed electron) can then be described in this effective single-particle way as a *photohole* (via one of the quasihole states and the corresponding properties). And – within the confines of the QPA’s applicability (see below) – the dominant peaks observed in ground-state photoemission then correspond to the different quasiparticle (quasihole when talking about direct photoemission) states (in our excited-state photoemission formalism this is also the case, since we also describe the final state of the remaining system via these quasihole states, see Sec. 3.3.10 and below).

Quasiparticle States

Using the similarities between the exact Lehmann representation of G_1 and the quasiparticle approximation $\tilde{G}_1^{QP}$ we can go a step further and assign a many-electron state $|N + / - 1, c/v\rangle_{QP}$ to each quasiparticle pole. As noted above, each pole of the non-interacting Green’s function corresponds to a state that can be understood by the addition or removal of a single electron from the ground state. Similarly, each of these *quasiparticle states* $|N + / - 1, c/v\rangle_{QP}$ can then be understood by the addition or removal of a *quasielectron*. To get to these states, remember that for the exact Green’s function, the numerator in the Lehmann representation contains the Lehmann amplitudes, which are connected to the system’s exact charged excitations via Eq. 2.132:

$$\begin{aligned} f_S^-(x) &= \langle N - 1, S | \hat{\Psi}(x) | N, 0 \rangle \\ f_S^+(x) &= \langle N, 0 | \hat{\Psi}(x) | N + 1, S \rangle \end{aligned} \quad (2.171)$$

In contrast, for $\tilde{G}_1^{QP}$, the numerator is given by the right and left quasiparticle wave function of the pole. Using that the quasiparticle orbitals are usually very similar to the Kohn-Sham (KS) orbitals [36, 95], we can replace them by the KS orbitals and can then identify the *quasiparticle states* of the system as effective states satisfying the conditions (one QP state per KS orbital):

$$\begin{aligned} \phi_v(x) &\stackrel{!}{=} \langle N - 1, v |_{QP} \hat{\Psi}(x) | N, 0 \rangle \\ \phi_c(x) &\stackrel{!}{=} \langle N, 0 | \hat{\Psi}(x) | N + 1, c \rangle_{QP} \end{aligned} \quad (2.172)$$

⁴⁹A *bare* electron or hole is what we have seen in the non-interacting case: the particle is added to the system in a given orbital and the other electrons are unaffected by it. The difference between a bare particle and a quasiparticle can also be nicely contrasted in terms of the *people in a crowd* example of Ref. [82], where a “bare person” would walk through the crowd without affecting others while creating a “bare person-hole” would correspond to removing a person from the crowd without others reacting to it, that is, without others “filling up” the created empty space.

Expanding the field operators in KS orbitals using Eq. 2.119, this becomes:

$$\begin{aligned}\phi_v(x) &\stackrel{!}{=} \sum_i \phi_i(x) \langle N-1, v |_{QP} \hat{a}_i | N, 0 \rangle \\ \phi_c(x) &\stackrel{!}{=} \sum_i \phi_i(x) \langle N, 0 | \hat{a}_i | N+1, c \rangle_{QP}\end{aligned}\quad (2.173)$$

We then introduce the ansatz

$$\begin{aligned}|N-1, v\rangle_{QP} &= \hat{a}_v |N, 0\rangle \\ |N+1, c\rangle_{QP} &= \hat{a}_c^\dagger |N, 0\rangle,\end{aligned}\quad (2.174)$$

where the first/second line shows how a QP state belonging to a valence/conduction KS orbital looks like, where $\hat{a}_v$ is the annihilation operator for KS orbital v , $\hat{a}_c^\dagger$ is the creation operator for KS orbital c and $|N, 0\rangle$ is the system's exact ground state. In particular, the first state can be interpreted as a *quasihole* state and the second one as a *quasielectron* state. Inserting this ansatz into Eq. 2.173 we find:

$$\begin{aligned}\phi_v(x) &\stackrel{!}{=} \langle N-1, v |_{QP} \hat{\Psi}(x) | N, 0 \rangle \\ &= \sum_i \phi_i(x) \langle N, 0 | \hat{a}_v^\dagger \hat{a}_i | N, 0 \rangle \\ &= \phi_v(x) \langle N, 0 | \hat{n}_v | N, 0 \rangle + \sum_{i \neq v} \phi_i(x) \langle N, 0 | \hat{a}_v^\dagger \hat{a}_i | N, 0 \rangle \\ \phi_c(x) &\stackrel{!}{=} \langle N, 0 | \hat{\Psi}(x) | N+1, c \rangle_{QP} \\ &= \sum_i \phi_i(x) \langle N, 0 | \hat{a}_i \hat{a}_c^\dagger | N, 0 \rangle \\ &= \phi_c(x) \langle N, 0 | (1 - \hat{n}_c) | N, 0 \rangle + \sum_{i \neq c} \phi_i(x) \langle N, 0 | \hat{a}_i \hat{a}_c^\dagger | N, 0 \rangle\end{aligned}\quad (2.175)$$

These equations do not hold exactly in general, since the exact ground state expressed in KS orbitals is a linear combination of the ground-state determinant $|0\rangle$ (built from valence orbitals only), and singly, doubly, etc. excited determinants⁵⁰:

$$|N, 0\rangle = c_0 |0\rangle + \sum_{v_1, c_1} c_{v_1, c_1} \hat{a}_{c_1}^\dagger \hat{a}_{v_1} |0\rangle + \sum_{v_1 < v_2, c_1 < c_2} c_{v_1, v_2, c_1, c_2} \hat{a}_{c_2}^\dagger \hat{a}_{v_2} \hat{a}_{c_1}^\dagger \hat{a}_{v_1} |0\rangle + \dots\quad (2.176)$$

Assuming that the system's ground state is not highly correlated, the ground-state determinant dominates, that is, c_0 is rather close to 1 and the remaining coefficients are small (assuming normalization of the ground state to 1). In that case, the equations are sufficiently well satisfied, thus justifying, for such systems, the ansatz Eq. 2.174 for the *quasiparticle states* of the system (after all we were simply searching for states that satisfy Eq. 2.173). Note that, under this assumption, the QP states are also automatically (approximately) normalized to 1.

Thus, we see that the one-particle Green's function (in the low-energy domain) can be obtained via an effective description of the system in terms of the

⁵⁰This is the basis of *configuration interaction* methods, see Ref. [96].

quasiparticle states/excitations Eq. 2.174 and the corresponding complex charged excitation energies $\{\varepsilon_i^{QP}\}$. Note that the quasiparticle states are not exact eigenstates of the $N \pm 1$ -electron system, but rather a linear combination of energetically almost degenerate (or fully degenerate) exact eigenstates [97], spread around the real part of the quasiparticle energy. This is also reflected in the fact that the QP states' "energies" are complex-valued, so they are not energy eigenstates of the system. Additionally, they are not stable states of the system. In particular, the lifetime of a quasiparticle is determined by the imaginary part of its energy, where larger imaginary parts (more precisely, larger $|\Im(\varepsilon_i^{QP})|$) correspond to a smaller lifetime of the quasiparticle state [82]. This can be understood conceptually as follows: imagine, a system is prepared in a quasiparticle state. This state is a superposition of exact eigenstates, each of which evolves over time based on its energy (assuming a time-independent Hamiltonian). Since the states in the superposition have slightly different energies, their phases evolve differently over time. As a result, the overlap of the time-evolved state with the initial state shrinks and the quasiparticle-nature is lost. Trivially, the larger the imaginary part and thus (see below) the larger the spread of energies of the contributing states is, the faster this process takes place. See also Ref. [98] for a study of different influences on the quasiparticle lifetimes. Without going into detail, the QP energies are also necessarily complex from the point of view of the spectral function, where each exact excitation contributes a delta-peak on the real axis. To replace multiple (possibly infinitely many, in thermodynamic limit) closely packed delta-peaks by a single QP peak, the QP peak must be located in the complex plane off the real axis, leading to a broadened structure on the real axis [87, 99] (this also explains why a larger $|\Im(\varepsilon_i^{QP})|$ corresponds to a larger energetic spread of eigenstates making up the quasiparticle).

We conclude with two remarks: first, note that we did not include states like $\hat{a}_c |N, 0\rangle$ and $\hat{a}_v^\dagger |N, 0\rangle$ in the set of quasiparticle states Eq. 2.174. Even though these states are in general allowed – remembering that the ground state is generally not a single Slater determinant – they are not expected to contribute significantly to photoemission from the system, since the ground state is often (we also use this approximation routinely in Sec. 3.3) still close to a single Slater determinant. Thus, they are not expected to contribute dominant poles to the quasiparticle Green's function. Second, going from the description of the one-particle Green's function in terms of the quasiparticle poles to the effective description of the system in terms of the quasiparticle states Eq. 2.174 may be seen as a conceptual leap, and it is not immediately clear, how far this description can be taken. Based on the close relation between G_1 and photoemission (see Sec. 2.3.3), it is however natural to assume that these states can be used for an effective description and simulation of photoemission experiments (compare Sec. 3.3.9 and Sec. 3.3.10, where the effective states are used as final states describing the $N - 1$ -electron system after photoemission in terms of a quasihole).

Quasiparticle Equation of Motion

As mentioned before, the quasiparticle orbitals $\{\tilde{\phi}_i\}$ and $\{\tilde{\psi}_i\}$ are typically very close to the orbitals obtained from a KS-DFT calculation and are thus in practice usually replaced by those. It is then sufficient to focus on the first equation in

Eq. 2.168, which reads⁵¹:

$$[h(\mathbf{r}) + v_J(\mathbf{r})] \phi_i(x) + \int dx' \Sigma(x, x', \varepsilon_i^{QP}) \phi_i(x') = \varepsilon_i^{QP} \phi_i(x), \quad (2.177)$$

where ϕ_i is the KS orbital related to the (complex) quasiparticle energy ε_i^{QP} . Note that in analogy to the Kohn-Sham equations Eq. 2.100, the *quasiparticle equation*⁵² Eq. 2.177 is again an effective one-electron Schrödinger equation (see also 2.168 which can also be interpreted in that way). In comparison to the KS equations, the local and energy-independent exchange-correlation potential⁵³ is replaced by the nonlocal and energy-dependent self-energy, which can then again be understood as an effective (nonlocal, energy-dependent) potential. As mentioned before, a quasi-electron (similarly for quasiholes) can be understood as a cohesive entity composed of a bare electron and a *polarization cloud*, which encompasses the response of the other electrons to its presence/addition and acts back on the bare electron. This interaction is incorporated in the self-energy, whose name can then be understood as originating from the fact that it describes the interaction between the bare electron and the polarization cloud that it (the bare electron) itself created [82].

Since we already know the KS orbitals from the preceding DFT calculation, we do not need to solve Eq. 2.177 for them. We can then instead find a more useful equation for obtaining the QP energies by adding and subtracting the exchange-correlation energy⁵⁴ ε_i^{xc} of orbital i , projecting from the left onto ϕ_i and using the orthonormality of KS orbitals⁵⁵, to find (compare Eq. 2.100) the quasiparticle equation in alternative form [19, 36, 82]:

$$\varepsilon_i^{QP} = \varepsilon_i^{KS} - \varepsilon_i^{xc} + \int dx dx' \phi_i^*(x) \Sigma(x, x', \varepsilon_i^{QP}) \phi_i(x'), \quad (2.178)$$

where ε_i^{KS} refers to the KS energy of orbital i . This equation is typically used in practical calculations, see below. Note that Eq. 2.178 can be understood as a first-order perturbative energy correction with the perturbation being the corrected electron-electron interaction, that is, the difference between the self-energy and the exchange-correlation energy [19].

Limitations of the Quasiparticle Approximation

While the quasiparticle approximation is highly useful for many systems, we have to keep its limitations in mind before using it.

⁵¹The Hartree potential is evaluated at the ground-state density of the unperturbed system, compare notes in Sec. 2.3.4

⁵²Following Ref. [19], we will refer to Eqs. 2.177 and 2.178 as the *quasiparticle equation*. Some authors instead call Eq. 2.168 the *quasiparticle equation*, see for example Ref. citeGolze2019.

⁵³Compare also the GKS scheme, see Sec. 2.2.5.

⁵⁴Formulated like this Eq. 2.178 is compatible with both, the KS and GKS schemes. In the KS scheme, using the exchange-correlation potential v_{xc} (at the unperturbed ground-state density), we simply have $\varepsilon_i^{xc} = \int dx v_{xc}(\mathbf{r}) |\phi_i(x)|^2$ (for infinite surfaces the integration runs only over the surface unit-cell, see Footnote 55), while, in GKS, we must use the expectation value of the nonlocal exchange-correlation operator, see e.g. Eq. (14) in Ref. [68]. Note that in spin-density functional theory, the exchange-correlation “potential” additionally acts nontrivially in spin-space, see text around Eq. 2.102. The same generally goes for the GKS scheme, see text below Eq. 2.101.

⁵⁵For infinite surfaces only integrate over the surface unit-cell and use Eq. B.19.

First, we have already mentioned above, that the QPA breaks down for high-energy excitations, which would be identified with KS orbitals far from the Fermi level [19] (similarly, the quasiparticles of Fermi liquid theory lie near the Fermi surface Ref. [77]).

Even at low energies, the quasiparticle poles do not incorporate all details observed experimentally. In particular, photoemission experiments show an incoherent background signal (which arises from complicated many-electron excitations) and satellite peaks (which can be understood in a quasiparticle picture as a quasi-hole plus additional quasiparticles, for example plasmons or phonons) which are missing in the QPA spectral function [82, 87]. The fact that these additional features are missing can also clearly be seen from the states Eq. 2.174 that we identified with the QPA. When working with these states in our photoemission formalism we thus neglect this additional structure in the photoemission intensity distribution (a justifiable approximation, as long as the QP contribution is dominant).

Lastly, note that the spectral weights $\{g_i\}$ serve as a measure for how well the system can be described in terms of quasiparticle poles [19]. If they are close to 1 (up to a certain energy), then the experimental spectrum will (up to that energy) be dominated by the quasiparticle peaks and other structures may be neglected safely⁵⁶. Conversely, if no dominant poles can be found via Eq. 2.166 (above some energy or at all), the experimental spectrum can be expected to feature no dominant poles, with small spectral weights indicating satellite features [82].

2.3.7 GW in Practice

Starting from the one-particle Green's function, we have now introduced a lot of quantities and approximations. To not lose sight of our goals, a brief overview of which of these quantities is needed for the photoemission simulation of Sec. 3.3 shall now be given, as well as an outline of how we calculate them in practice.

For ground-state POT, Sec. 3.3.9, we will need Kohn-Sham (KS) orbitals and KS energies or quasiparticle (QP) energies in the GW approximation (we will not perform QP calculations, Eq. 2.178, beyond the GW approximation). Similarly, for exciton POT, Sec. 3.3.10, we will need to additionally solve the Bethe-Salpeter equation (BSE; Sec. 2.4.4) to obtain the BSE eigenvectors and eigenvalues.

Having obtained the KS orbitals and energies (with exchange-correlation energies explicitly calculated) from a preceding DFT calculation and assuming the QP wave functions to be close to the KS wave functions, we can find the QP energies from Eq. 2.178. Note that in this equation, the self-energy is evaluated at the searched QP energy and there can in principle be multiple solutions (as mentioned below Eq. 2.166), from which a dominant one (with a large quasiparticle renormalization factor) has to be chosen [19], which – as mentioned before – may not be possible for orbitals far from the Fermi level [19, 100]. Assuming these difficulties to be addressed, there are then various ways in which Eq. 2.178 can be

⁵⁶We can get some insight into why this is the case: from Eq. 2.167 we have $g_n = \left(1 - \frac{\partial E_n(z)}{\partial z}\bigg|_{z=z_n}\right)^{-1}$. Thus, $g_n = 1$ means $\frac{\partial E_n(z)}{\partial z}\bigg|_{z=z_n} = 0$. Conversely, $g_n \rightarrow 0$ means $\left|\frac{\partial E_n(z)}{\partial z}\bigg|_{z=z_n}\right| \rightarrow \infty$. Trivially, replacing $E_n(z)$ by z_n is not well justified in the latter case since $E_n(z)$ rapidly changes in the region around z_n . The converse holds in the case $g_n = 1$.

solved, with G_0W_0 and $evGW$ being two widespread approaches, both based on the GW approximation for the self-energy [101]: in G_0W_0 , the Green's function $G_1^{(0)}$ is constructed from the KS orbitals and energies, see Eq. 2.169, and never updated. Similarly, W_0 is built from the KS orbitals and -energies⁵⁷ and also not updated. Using this expression for Σ , Eq. 2.178 can then be solved iteratively until convergence is achieved and the QP energies have been found (see also Figure 10 in Ref. [82] for a flowchart of a G_0W_0 calculation). To reduce computational costs, the self-energy may be linearized around the KS energies, see Refs. [82, 102] for details. In *eigenvalue-self-consistent GW*, $evGW$, the above approach is repeated multiple times by updating the one-particle energies in the Green's function after every iteration. That is, we start with $G_1^{(0)}$ and W_0 based on KS energies and calculate a set of QP energies, which are then QP energies on the G_0W_0 level (which is why G_0W_0 is also termed *single-shot GW*). Then, we replace the KS energies in the Green's function by these new energies⁵⁸ and also recalculate W based on this new Green's function. With the so-obtained new self-energy, we then again solve Eq. 2.178 as described before (where we may again use the linearization of Σ) and we obtain a new set of QP energies. This process is then iterated until convergence is achieved.

Note that the so-obtained spectrum of quasiparticle energies $\{\varepsilon_i^{(QP)}\}$ often closely resembles the KS-energy spectrum $\{\varepsilon_i\}$. This can be seen as a consequence of KS-DFT being a sophisticated effective one-electron theory, where much of the electron-electron interaction is already accounted for via the exchange-correlation potential and motivates the use of KS energies in ground-state POT thus allowing us to avoid expensive GW calculations. Note, however, that this is not a general rule and KS energies cannot be blindly trusted for the calculation of photoemission spectra [103]. This is not a surprise, since KS energies do in general *not* represent the system's ionization energies and electron affinities (exception: the highest occupied orbital, see *Janak's theorem* in Ref. [49]).

With regard to the BSE (needed for exciton POT), construction of the BSE Hamiltonian in the GW/BSE approach (see Appendix C.1.1 and Sec. 2.4.4 for details) presumes knowledge of the KS orbitals, QP energies and the screened Coulomb interaction W . Using again KS orbitals from a preceding calculation, the QP energies and W can then be calculated as described in the previous paragraph.

Note that we typically restrict ourselves to G_0W_0 for periodic systems. In analogy to the ground-state electron density of an infinite surface (see Appendix B.1), the KS Green's function $G_1^{(0)}$ (see of Eq. 2.169) based on KS orbitals – in this case Bloch orbitals – of an infinite surface contains an integral over the in-plane Brillouin zone (compare also Eqs. 2.137 and 2.131 with Eq. B.8). As with the density,

⁵⁷Which can be done by calculating P in the GW approximation, see Eq. 2.162 based on the KS-Green's function $G_1^{(0)}$, then calculating the dielectric function via (written symbolically) $\varepsilon = 1 - vP$ [82, 87] and inverting it to finally calculate W via Eq. C.129. Note also, that W is frequency-dependent and for the calculation of Σ this frequency is integrated over, see Eq. (10)/Eq. (23) in Refs. [95, 102] (which can easily be derived from Eq. 2.162 and the convolution theorem). In practice, we often only calculate the static interaction $W(\omega = 0)$ explicitly and use a *plasmon-pole* model to extend it to finite frequencies [95].

⁵⁸As can also be explicitly seen from Eq. (8) in Ref. [101], this slightly deviates from the QP Green's function Eq. 2.167 (even after replacing QP orbitals by KS orbitals), since the quasiparticle renormalization factors are omitted/ set to 1 (which may be justified by the fact that the QPA is anyway only valid in the energetic domain where the $\{g_i\}$ are close to 1).

this integral is in practice performed using quadrature (compare Appendix B.3), where the number of used Bloch momenta must be converged to obtain a converged screened Coulomb interaction W_0 and G_0W_0 self-energy. Additionally, $G_1^{(0)}$ contains a sum over the unoccupied KS bands, where in principle all of them must be included. In practice, this turns into an additional convergence parameter (where in principle different values can be used for “the $G_1^{(0)}$ ” used in the calculation of W_0 and “the $G_1^{(0)}$ ” that directly enters G_0W_0). The resulting converged self-energy can then be used in the quasiparticle equation Eq. 2.178 which can then be solved independently for any desired Bloch momentum $\mathbf{q}$ and band index n (based on the KS wave function and -energy at that momentum and band index) to obtain the QP energy $\varepsilon_{n,\mathbf{q}}^{(\text{QP})}$. This is similar to the behavior of KS-DFT when using a converged density (see Sec. 2.2.6) and can, as mentioned there, be used to easily increase the resolution of photoemission distribution plots.

With this overview in mind, note that we have of course omitted many additional details needed for an efficient implementation of the GW (and BSE) method – which depend heavily on the system type (gas-phase versus periodic calculations, see Sec. 2.1.1). See, for example, Ref. [104] on the implementation of GW (and BSE) in the BERKELEYGW code [36, 95, 104] and subtleties that occur when applying the GW (and BSE) formalism to periodic systems (where surface-periodicity is used to perform calculations in Fourier space).

2.4 MBPT II: BSE and Excitons

Having introduced basic concepts of many-body perturbation theory (MBPT) with a focus on charged excitations in the previous section, we now focus on the MBPT description of N -electron excitations, that is, (*charge- neutral excited states* (i.e. solutions of the N -electron Schrödinger equation that lie energetically above the ground state). We are in particular interested in a specific type of excited states, namely *excitons*, that is, excited states described (in an approximative fashion) by a correlated electron-hole pair, which will then serve as the basis of our excited-state photoemission formalism in Sec. 3.3.10. In particular, we are interested in excitons across all ranges of electron-hole separations, that is, Frenkel excitons (small separation), charge-transfer excitons (medium separation) and Wannier excitons (large separation), see Ref. [19] for details on this classification. Note that there again exists a range of available methods for calculating excited states [45]. Since we perform our ground-state calculations using Kohn-Sham density functional theory (KS-DFT), an obvious choice would be KS-time-dependent DFT (KS-TDDFT), where in particular the Casida formalism [105, 106] can be used to calculate excitons. However, as of writing, KS-TDDFT remains a computationally demanding method, which in practical calculations would often limit us to the use of adiabatic LDA/GGA (ALDA/AGGA, see [107]) exchange-correlation functionals (see Sec. 2.2.5 on typical approximations of the exchange-correlation functional used in DFT). With such a semi-/ local exchange-correlation functional, the long-range correlated nature of the electron-hole pair forming a charge-transfer or Wannier exciton is often not captured sufficiently [19] (see also Ref. [108]). We therefore instead continue along the route of MBPT and use the Bethe-Salpeter equation (BSE), in combination with the GW approximation (thus called the GW/BSE method), where the long-range interaction between electron and hole in charge-transfer and Wannier excitons is sufficiently accounted for [19].

As usual, systems are initially assumed to be finitely sized, see Appendix C.1.4 for details.

2.4.1 Two-Particle Green's Function

We start by introducing the *two-particle Green's function* G_2 as defined in Ref. [109]:

$$G_2(1, 2, 1', 2') = - \langle N, 0 | T \left[\hat{\Psi}(1) \hat{\Psi}(2) \hat{\Psi}^\dagger(2') \hat{\Psi}^\dagger(1') \right] | N, 0 \rangle, \quad (2.179)$$

where we made use of the notation introduced in the beginning of Sec. 2.1. Depending on the four time-arguments, the field operators in $G_2(1, 2, 1', 2')$ can be arranged by the time-ordering in $4! = 24$ distinct ways, each of which can be interpreted in a way analogous to the interpretation of the two terms of the one-particle Green's function given below Eq. 2.123. Out of all these terms, we will focus on two, which are extracted via the conditions $t_{1'} = t_1^+$, $t_{2'} = t_2^+$ and the condition that either $t_1 > t_{2'}$ or $t_2 > t_{1'}$. The Green's function $G_2(1, 2, 1', 2')$ can then be

written as⁵⁹⁶⁰:

$$\begin{aligned} G_2(x_1, x_2, x_{1'}, x_{2'}, t_1, t_2) = \\ = - \langle N, 0 | \hat{\Psi}^\dagger(x_{1'}, t_1) \hat{\Psi}(x_1, t_1) \hat{\Psi}^\dagger(x_{2'}, t_2) \hat{\Psi}(x_2, t_2) | N, 0 \rangle \theta(t_1 - t_2) \\ - \langle N, 0 | \hat{\Psi}^\dagger(x_{2'}, t_2) \hat{\Psi}(x_2, t_2) \hat{\Psi}^\dagger(x_{1'}, t_1) \hat{\Psi}(x_1, t_1) | N, 0 \rangle \theta(t_2 - t_1), \end{aligned} \quad (2.180)$$

where we – as usual – abstain from introducing a new symbol for G_2 with this specific time-ordering. Inserting Eq. 2.122, we get (using that $\hat{H}_e$ is time-independent):

$$\begin{aligned} G_2(x_1, x_2, x_{1'}, x_{2'}, t_1, t_2) = \\ = - \langle N, 0 | e^{i\hat{H}_e t_1} \hat{\Psi}^\dagger(x_{1'}) \hat{\Psi}(x_1) e^{-i\hat{H}_e(t_1-t_2)} \hat{\Psi}^\dagger(x_{2'}) \hat{\Psi}(x_2) e^{-i\hat{H}_e t_2} | N, 0 \rangle \theta(t_1 - t_2) \\ - \langle N, 0 | e^{i\hat{H}_e t_2} \hat{\Psi}^\dagger(x_{2'}) \hat{\Psi}(x_2) e^{-i\hat{H}_e(t_2-t_1)} \hat{\Psi}^\dagger(x_{1'}) \hat{\Psi}(x_1) e^{-i\hat{H}_e t_1} | N, 0 \rangle \theta(t_2 - t_1) \end{aligned} \quad (2.181)$$

At $t_1 > t_2$, $G_2(x_1, x_2, x_{1'}, x_{2'}, t_1, t_2)$ gives us (minus) the overlap between two states: in the first one (ket), we start from the ground state, propagate it to t_2 , then add a hole (remove an electron) at x_2 and an electron at $x_{2'}$ and then propagate from t_2 to t_1 . In the second state (bra), we directly propagate to t_1 and then add a hole at $x_{1'}$ and an electron at x_1 (which can be seen when looking at the ket belonging to the bra). At $t_1 > t_2$, the absolute square $|G_2(x_1, x_2, x_{1'}, x_{2'}, t_1, t_2)|^2$ thus is the probability⁶¹ to end up in a state that is the ground state with an added hole at $x_{1'}$ and electron at x_1 , when starting from the ground state, adding a hole at x_2 and an electron at $x_{2'}$ and propagating for the time $t_1 - t_2$. Or, loosely speaking, it is the probability to find a hole and an electron at $x_{1'}$ and x_1 respectively, if $t_1 - t_2$ time ago they were inserted at x_2 and $x_{2'}$ (respectively). For $t_2 > t_1$ the interpretation is precisely the same, just with swapped coordinates. In short, $|G_2(x_1, x_2, x_{1'}, x_{2'}, t_1, t_2)|^2$ then is (loosely speaking) the probability to find a hole and an electron at $x_{2'}$ and x_2 respectively, if $t_2 - t_1$ time ago they were inserted at x_1 and $x_{1'}$ (respectively).

Continuing the analogy to G_1 , G_2 in the chosen time-ordering also admits a Lehmann representation similar to Eq. 2.134. To see this, we first use the com-

⁵⁹ Note that $t_{1'} = t_1^+$, $t_{2'} = t_2^+$ and $t_1 > t_{2'}$ or $t_2 > t_{1'}$ was needed to get a time-ordering of the field operators which allows for a clear interpretation of G_2 in terms of an electron and a hole (see below). In the upcoming discussion of G_2 we can then set $t_i = t_i^+$ without harm. In other words: except for the fact that G_2 as defined in Eq. 2.179 is strictly speaking undefined at $t_{i'} = t_i$ ($i = 1, 2$), the limit $t_i^+ \rightarrow t_i$ can be performed within G_2 without a problem, once the time-ordering has been performed (i.e., once the related θ -functions have been evaluated, compare Eq. 2.124). For example, we can simply write $\theta(t_1 - t_2)$ instead of $\theta(t_1 - t_2^+)$. The resulting Green's function G_2 is then a function of $t_1 - t_2$ (see below) and defined everywhere except for the set of measure zero given by the limit $|t_1 - t_2| \rightarrow 0$, compare Footnote 37.

⁶⁰See also Footnote 36.

⁶¹Compare Footnotes 39 and 38.

pleteness of the eigenstates $\{|N, S\rangle\}$ of the N -electron Hamiltonian to find:

$$\begin{aligned}
G_2(x_1, x_2, x_{1'}, x_{2'}, t_1, t_2) &= - \sum_S \langle N, 0 | e^{i\hat{H}_e t_1} \hat{\Psi}^\dagger(x_{1'}) \hat{\Psi}(x_1) e^{-i\hat{H}_e(t_1-t_2)} | N, S \rangle \\
&\quad \langle N, S | \hat{\Psi}^\dagger(x_{2'}) \hat{\Psi}(x_2) e^{-i\hat{H}_e t_2} | N, 0 \rangle \theta(t_1 - t_2) \\
&\quad + \langle N, 0 | e^{i\hat{H}_e t_2} \hat{\Psi}^\dagger(x_{2'}) \hat{\Psi}(x_2) e^{-i\hat{H}_e(t_2-t_1)} | N, S \rangle \\
&\quad \langle N, S | \hat{\Psi}^\dagger(x_{1'}) \hat{\Psi}(x_1) e^{-i\hat{H}_e t_1} | N, 0 \rangle \theta(t_2 - t_1) \\
&= - \sum_S \langle N, 0 | e^{iE(N,0)t_1} \hat{\Psi}^\dagger(x_{1'}) \hat{\Psi}(x_1) e^{-iE(N,S)(t_1-t_2)} | N, S \rangle \\
&\quad \langle N, S | \hat{\Psi}^\dagger(x_{2'}) \hat{\Psi}(x_2) e^{-iE(N,0)t_2} | N, 0 \rangle \theta(t_1 - t_2) \\
&\quad + \langle N, 0 | e^{iE(N,0)t_2} \hat{\Psi}^\dagger(x_{2'}) \hat{\Psi}(x_2) e^{-iE(N,S)(t_2-t_1)} | N, S \rangle \\
&\quad \langle N, S | \hat{\Psi}^\dagger(x_{1'}) \hat{\Psi}(x_1) e^{-iE(N,0)t_1} | N, 0 \rangle \theta(t_2 - t_1) \\
&= - \sum_S e^{-i(E(N,S)-E(N,0))(t_1-t_2)} \langle N, 0 | \hat{\Psi}^\dagger(x_{1'}) \hat{\Psi}(x_1) | N, S \rangle \\
&\quad \langle N, S | \hat{\Psi}^\dagger(x_{2'}) \hat{\Psi}(x_2) | N, 0 \rangle \theta(t_1 - t_2) \\
&\quad + e^{-i(E(N,S)-E(N,0))(t_2-t_1)} \langle N, 0 | \hat{\Psi}^\dagger(x_{2'}) \hat{\Psi}(x_2) | N, S \rangle \\
&\quad \langle N, S | \hat{\Psi}^\dagger(x_{1'}) \hat{\Psi}(x_1) | N, 0 \rangle \theta(t_2 - t_1) \tag{2.182}
\end{aligned}$$

In analogy to Eq. 2.133, we define the *excitation energies* (often also called *charge-neutral* excitation energies, because we do not change the number of electrons):

$$\Omega_S = E(N, S) - E(N, 0) \geq 0, \tag{2.183}$$

where the equality is only given at the ground state $S = 0$. And in accordance with the Lehmann amplitudes of Eq. 2.132, we define:

$$\chi_S(x, x') = \langle N, 0 | \hat{\Psi}^\dagger(x') \hat{\Psi}(x) | N, S \rangle \tag{2.184}$$

Using additionally

$$\chi_S^*(x, x') = \langle N, S | \hat{\Psi}^\dagger(x) \hat{\Psi}(x') | N, 0 \rangle, \tag{2.185}$$

we find:

$$\begin{aligned}
G_2(x_1, x_2, x_{1'}, x_{2'}, t_1, t_2) &= \\
&= - \sum_S e^{-i\Omega_S(t_1-t_2)} \chi_S(x_1, x_{1'}) \chi_S^*(x_{2'}, x_2) \theta(t_1 - t_2) \\
&\quad + e^{-i\Omega_S(t_2-t_1)} \chi_S(x_2, x_{2'}) \chi_S^*(x_{1'}, x_1) \theta(t_2 - t_1) \tag{2.186}
\end{aligned}$$

Note that $G_2(x_1, x_2, x_{1'}, x_{2'}, t_1, t_2)$ only depends on the difference $t_1 - t_2$ as expected with a time-independent Hamiltonian. Fourier-transforming (see Eq. A.60) with respect to $t_1 - t_2$ we find⁶²:

$$\begin{aligned}
G_2(x_1, x_2, x_{1'}, x_{2'}, \omega) &= \\
&= -i \sum_S \frac{\chi_S(x_1, x_{1'}) \chi_S^*(x_{2'}, x_2)}{\omega - \Omega_S + i\eta} - \frac{\chi_S(x_2, x_{2'}) \chi_S^*(x_{1'}, x_1)}{\omega + \Omega_S - i\eta}, \tag{2.187}
\end{aligned}$$

⁶²Compare Footnotes 42, 37 and 59.

with $\eta = 0^+$. So, $G_2(x_1, x_2, x_{1'}, x_{2'}, \omega)$ as a function of ω is a sum of poles with the poles located at (plus/minus) the excitation energies $\{\Omega_S\}$ (shifted by minus/plus $i\eta$). Note that also the ground state $S = 0$ with energy $\Omega_0 = 0$ is contained in the sum! Instead of further evaluating this contribution, we will now get rid of it, so we are left with a sum over excited states only (i.e. starting at $S = 1$).

2.4.2 Two-Particle Correlation Function

To get to an expression that excludes the ground state from the summation, we use the one-particle Green's function G_1 of Eq. 2.125 and define the *two-particle correlation function* as:

$$L(1, 2, 1', 2') = -G_2(1, 2, 1', 2') + G_1(1, 1')G_1(2, 2') \quad (2.188)$$

Using the conditions $t_{1'} = t_1^+$, $t_{2'} = t_2^+$ and Eq. 2.122, we find

$$G_1(1, 1')G_1(2, 2') = -\langle N, 0 | \hat{\Psi}^\dagger(x_{1'})\hat{\Psi}(x_1) | N, 0 \rangle \langle N, 0 | \hat{\Psi}^\dagger(x_{2'})\hat{\Psi}(x_2) | N, 0 \rangle \quad (2.189)$$

and therefore

$$\begin{aligned} G_1(1, 1')G_1(2, 2') &= -\chi_0(x_1, x_{1'})\chi_0^*(x_{2'}, x_2) \\ &= -\chi_0(x_2, x_{2'})\chi_0^*(x_{1'}, x_1). \end{aligned} \quad (2.190)$$

Together with Eq. 2.186, we then get (using the same time-condition as for G_2)

$$\begin{aligned} L(x_1, x_2, x_{1'}, x_{2'}, t_1, t_2) &= \\ &= \sum_{S=1} e^{-i\Omega_S(t_1-t_2)} \chi_S(x_1, x_{1'})\chi_S^*(x_{2'}, x_2)\theta(t_1 - t_2) \\ &\quad + e^{-i\Omega_S(t_2-t_1)} \chi_S(x_2, x_{2'})\chi_S^*(x_{1'}, x_1)\theta(t_2 - t_1), \end{aligned} \quad (2.191)$$

where we used $\Omega_0 = 0$ and $\theta(t_1 - t_2) + \theta(t_2 - t_1) = 1$ (except for $t_1 = t_2$, where G_2 and thus also L are undefined anyway) to cancel out the $S = 0$ -part of the sum with $G_1(1, 1')G_1(2, 2')$. While we denoted it here explicitly, it will later be understood implicitly that the sum over S making up the two-particle correlation function L starts at $S = 1$ (while that of G_2 starts at $S = 0$) and therefore only runs over excited states, thereby excluding the ground state. For the Lehmann representation of L we then find (compare Ref. [36]):

$$\begin{aligned} L(x_1, x_2, x_{1'}, x_{2'}, \omega) &= \\ &= i \sum_{S=1} \frac{\chi_S(x_1, x_{1'})\chi_S^*(x_{2'}, x_2)}{\omega - \Omega_S + i\eta} - \frac{\chi_S(x_2, x_{2'})\chi_S^*(x_{1'}, x_1)}{\omega + \Omega_S - i\eta} \end{aligned} \quad (2.192)$$

To summarize $L(x_1, x_2, x_{1'}, x_{2'}, \omega)$ as a function of ω is therefore a sum over the (charge-neutral) excited states of the N -electron system with each excited state contributing a pole at $\pm(\Omega_S - i\eta)$.

Having seen the close relation between L and the charge-neutral excited states we are interested in, we now introduce the *independent-electron-hole propagator* L_0 , which will then be used for calculating L .

2.4.3 Independent-Electron-Hole Propagator

We start by introducing the *independent-electron-hole propagator* L_0 , which is defined as [36]:

$$L_0(1, 2, 1', 2') = G_1(1, 2')G_1(2, 1') \quad (2.193)$$

$L_0(1, 2, 1', 2')$ and $|L_0(1, 2, 1', 2')|^2$ can then be interpreted for a given time-ordering⁶³ of t_1 relative to $t_{2'}$ and of t_2 relative to $t_{1'}$, by remembering the interpretation of G_1 (and $|G_1|^2$), which is given below Eq. 2.123. As detailed above, we are especially interested in the situation $t_{1'} = t_1^+$, $t_{2'} = t_2^+$ and $t_1 > t_{2'}$ or $t_2 > t_{1'}$, where $L_0(1, 2, 1', 2')$ becomes⁶⁴:

$$\begin{aligned} L_0(x_1, x_2, x_{1'}, x_{2'}, t_1, t_2) = & \\ & \langle N, 0 | \hat{\Psi}(x_1, t_1) \hat{\Psi}^\dagger(x_{2'}, t_2) | N, 0 \rangle \langle N, 0 | \hat{\Psi}^\dagger(x_{1'}, t_1) \hat{\Psi}(x_2, t_2) | N, 0 \rangle \theta(t_1 - t_2) \\ & + \langle N, 0 | \hat{\Psi}^\dagger(x_{2'}, t_2) \hat{\Psi}(x_1, t_1) | N, 0 \rangle \langle N, 0 | \hat{\Psi}(x_2, t_2) \hat{\Psi}^\dagger(x_{1'}, t_1) | N, 0 \rangle \theta(t_2 - t_1) \end{aligned} \quad (2.194)$$

For $t_1 > t_2$, $|L_0(x_1, x_2, x_{1'}, x_{2'}, t_1, t_2)|^2$ is then (loosely speaking) the probability for finding an electron at x_1 , if $t_1 - t_2$ time ago it was added at $x_{2'}$, multiplied with the probability for finding a hole at $x_{1'}$, if $t_1 - t_2$ time ago (at the same time) it was added at x_2 . It can thus also be understood as the probability of finding a hole and an electron at $x_{1'}$ and x_1 respectively, if $t_1 - t_2$ time ago they were (at the same time) inserted at x_2 and $x_{2'}$ (respectively), under the assumption that they do not at all influence one another. Similarly, for $t_2 > t_1$, $|L_0(x_1, x_2, x_{1'}, x_{2'}, t_1, t_2)|^2$ is then the probability of finding a hole and an electron at $x_{2'}$ and x_2 respectively, if $t_2 - t_1$ time ago they were (at the same time) inserted at x_1 and $x_{1'}$ (respectively), under the assumption that they do not at all influence one another. Comparing this to the interpretation of G_2 given below Eq. 2.179, we can see that L_0 is the equivalent to G_2 , under the assumption that the electron and the hole are *independent particles*, which is the origin of L_0 's name.

Starting from Eq. 2.194 we can again derive a Lehmann representation. Using Eqs. 2.129 and 2.130, we find

$$\begin{aligned} L_0(x_1, x_2, x_{1'}, x_{2'}, t_1, t_2) = & \\ = \sum_{S, S'} f_S^+(x_1) f_{S'}^-(x_2) (f_{S'}^-(x_{1'}))^* (f_S^+(x_{2'}))^* e^{-i(\varepsilon_S^+ - \varepsilon_{S'}^-)(t_1 - t_2)} \theta(t_1 - t_2) \\ & + f_{S'}^-(x_1) f_S^+(x_2) (f_S^+(x_{1'}))^* (f_{S'}^-(x_{2'}))^* e^{-i(\varepsilon_{S'}^- - \varepsilon_S^+)(t_1 - t_2)} \theta(t_2 - t_1) \end{aligned} \quad (2.195)$$

Once again performing the Fourier-transform Eq. A.60 with respect to $t_1 - t_2$, we

⁶³ As detailed below, the cases $t_1 > t_{2'}, t_{1'} > t_2$ and $t_{2'} > t_1, t_2 > t_{1'}$ correspond to (independent) electron-hole propagation. The remaining cases $t_1 > t_{2'}, t_2 > t_{1'}$ and $t_{2'} > t_1, t_{1'} > t_2$ describe the (independent) propagation of two electrons and two holes, respectively. See for example Ref. [110] for an analysis of the two-electron or two-hole Bethe-Salpeter equation.

⁶⁴ Here and in the discussion below, we set $t_2^+ = t_2$ and $t_1^+ = t_1$, which can be done without harm since, within L_0 , these times do not occur together inside a time-ordering bracket and because of the conditions $t_1 > t_2^+$ or $t_2 > t_1^+$. See also Footnote 59.

find:

$$L_0(x_1, x_2, x_{1'}, x_{2'}, \omega) = i \sum_{S, S'} \frac{f_S^+(x_1) f_{S'}^-(x_2) (f_{S'}^-(x_{1'}))^* (f_S^+(x_{2'}))^*}{\omega - (\varepsilon_S^+ - \varepsilon_{S'}^-) + i\eta} - \frac{f_{S'}^-(x_1) f_S^+(x_2) (f_S^+(x_{1'}))^* (f_{S'}^-(x_{2'}))^*}{\omega + (\varepsilon_S^+ - \varepsilon_{S'}^-) - i\eta} \quad (2.196)$$

Comparison with the Lehmann representation Eq. 2.187 of G_2 , we can see that when neglecting the interaction of electron and hole, the poles occur at the energies $\{\pm(\varepsilon_S^+ - \varepsilon_{S'}^-)\}$ and the amplitudes become products of an electron- and a hole-part. This can very clearly be understood in the quasiparticle picture of Sec. 2.3.6, with L_0 being constructed from the quasiparticle one-particle Green's function, where – neglecting the interaction of quasielectron and quasihole – excitation energies are then simply given by the energies of the created quasiparticles (see also L_0 in Appendix C.1.1).

2.4.4 Bethe-Salpeter Equation

Just like the Dyson equation in the first line of Eq. 2.159 relates the one-particle Green's function G_1 with its non-interacting counterpart $G_1^{(0)}$, we can find an equation that connects the two-particle correlation function L to the independent-electron-hole propagator L_0 , the *Bethe-Salpeter equation* (BSE) [19, 36]:

$$L(1, 2, 1', 2') = L_0(1, 2, 1', 2') + \int d(3, 4, 5, 6) L_0(1, 4, 1', 3) K(3, 5, 4, 6) L(6, 2, 5, 2'), \quad (2.197)$$

where we introduced the *electron-hole interaction kernel*⁶⁵:

$$K(3, 5, 4, 6) = \frac{\delta[v_J(3)\delta(3, 4) + \Sigma(3, 4)]}{\delta G_1(6, 5)}, \quad (2.198)$$

where v_J is the Hartree potential and Σ the self-energy⁶⁶ as defined in Eq. 2.152.

As a sidenote, it is interesting to see that while the first term, $L_0(1, 2, 1', 2')$, on the right-hand-side of the BSE is subject to the time-conditions $t_{1'} = t_1^+$, $t_{2'} = t_2^+$ and $t_1 > t_{2'}$ or $t_2 > t_{1'}$, we find that $L_0(1, 4, 1', 3)$ inside the integral is only subject to $t_{1'} = t_1^+$. It does therefore not admit such a simple Lehmann-representation as $L_0(1, 2, 1', 2')$ (Eq. 2.196) and also contains two-electron or two-hole propagation terms (see Footnote 63). The same holds for the additional occurrences of L_0 under the integral (the one on the very right is subject to $t_{2'} = t_2^+$, the others are completely free), which we get when re-entering the BSE into itself. This issue is taken care of through our use of the *static-screening GW*-kernel, see below (in particular Eq. 2.208).

⁶⁵The functional derivative is evaluated at G_1 as defined in Eq. 2.123, which we omit to write for readability, compare Appendix A.3.

⁶⁶Note that, as in Ref. [36], we chose to exclude the Hartree potential from the self energy, which then leads to the sum of the two quantities here. Others include the Hartree potential in the self-energy, see e.g. Ref. [109]. See also Appendix B.2 in Ref. [82] on this.

GW/BSE

Since we typically use the GW approximation to calculate the one-particle Green's function, it is not only practical but also consistent to again use the self-energy in the GW approximation when solving the BSE. Using $\Sigma(1, 2) = iG_1(1, 2)W(1^+, 2)$ from Eq. 2.162, we thus write the electron-hole interaction kernel as:

$$K(3, 5, 4, 6) = \frac{\delta [v_J(3)\delta(3, 4) + iG_1(3, 4)W(3^+, 4)]}{\delta G_1(6, 5)} \quad (2.199)$$

Using Eq. 2.139 to express the Hartree potential in terms of G_1 , we get [36] (using the notation of Eq. 2.7):

$$\begin{aligned} K(3, 5, 4, 6) = & -i\delta(3, 4)\delta(5, 6^+)v(3, 6) \\ & + i\delta(3, 6)\delta(4, 5)W(3^+, 4) \\ & + iG_1(3, 4)\frac{\delta W(3^+, 4)}{\delta G_1(6, 5)} \end{aligned} \quad (2.200)$$

The third term is usually neglected, thereby significantly reducing complexity of the BSE [19, 36]. This then leads to the commonly used form of the electron-hole interaction kernel:

$$\begin{aligned} K(3, 5, 4, 6) &= K^x(3, 5, 4, 6) + K^d(3, 5, 4, 6) \\ K^x(3, 5, 4, 6) &= -i\delta(3, 4)\delta(5, 6^+)v(3, 6) \\ K^d(3, 5, 4, 6) &= i\delta(3, 6)\delta(4, 5)W(3^+, 4), \end{aligned} \quad (2.201)$$

where we introduced the *exchange term* K^x and the *direct interaction term* K^d , whose names are explained later in Sec. 2.4.4 in the context of *excitons*.

BSE in the Static Screening Approximation

The Bethe-Salpeter equation in Eq. 2.197 is formulated in real-time and shall now be transformed to the frequency/energy domain which is where calculations are usually performed.

For simplicity, we will adopt the *static screening approximation* for W ⁶⁷. From translational symmetry in time, we already know that $W(1, 2)$ can only depend on $t_1 - t_2$. Thus, we can Fourier-transform (see Eq. A.60) it with respect to $t_1 - t_2$ and write the result as $W(x_1, x_2, \omega)$. In the static screening approximation we then assume that the frequency-dependence of W can be neglected, that is:

$$W(x_1, x_2, \omega) \approx W(x_1, x_2, 0) \equiv W(x_1, x_2) \quad (2.202)$$

This corresponds to the real-time form:

$$W(1, 2) = W(x_1, x_2)\delta(t_1 - t_2) \quad (2.203)$$

Thus, we assume $W(1, 2)$ to be an instantaneous interaction (like $v(1, 2)$ in Eq. 2.7) and neglect retardation effects. A discussion of the static approximation can for example be found in Ref. [112].

⁶⁷Taking the frequency-dependency into account leads to the more complicated *dynamical BSE* (DBSE), see Ref. [111].

Entering the kernel Eq. 2.201 into the BSE Eq. 2.197 and using the static screening approximation we get for our time-ordering $t_{1'} = t_1^+$, $t_{2'} = t_2^+$ with $t_1 > t_{2'}$ or $t_2 > t_{1'}$:

$$\begin{aligned}
L(1, 2, 1', 2') &= L_0(1, 2, 1', 2') \\
&\quad - i \int d(3, 4) L_0(1, 3, 1', 3) v(x_3, x_4) \delta(t_3 - t_4) L(4, 2, 4^+, 2') \\
&\quad + i \int d(3, 4) L_0(1, 4, 1', 3) W(x_3, x_4) \delta(t_3^+ - t_4) L(3, 2, 4, 2') \\
&= L_0(1, 2, 1', 2') - i \int d(x_3, x_4) \int dt_3 \\
&\quad L_0(x_1, x_3, x_{1'}, x_3, t_1 - t_3) v(x_3, x_4) L(x_4, x_2, x_4, x_{2'}, t_3 - t_2) \\
&\quad - L_0(x_1, x_4, x_{1'}, x_3, t_1 - t_3) W(x_3, x_4) L(x_3, x_2, x_4, x_{2'}, t_3 - t_2)
\end{aligned} \tag{2.204}$$

For the last line, we used that

$$\begin{aligned}
&L_0((x_1, t_1), (x_3, t_3), (x_{1'}, t_1^+), (x_3, t_3)) \\
&L_0((x_1, t_1), (x_4, t_3^+), (x_{1'}, t_1^+), (x_3, t_3)) \\
&L((x_4, t_3), (x_2, t_2), (x_4, t_3^+), (x_{2'}, t_2^+)) \\
&L((x_3, t_3), (x_2, t_2), (x_4, t_3^+), (x_2, t_2^+))
\end{aligned} \tag{2.205}$$

all only depend on the respective time-differences⁶⁸. We can then perform a variable transformation $t_3 \rightarrow t_3 - t_2$ and perform the Fourier-transform (see Eq. A.60) with respect to $t_1 - t_2$ (keeping in mind our conditions on $t_1, t_{1'}, t_2, t_{2'}$). Using the convolution theorem for the integral, we find:

$$\begin{aligned}
L(x_1, x_2, x_{1'}, x_{2'}, \omega) &= L_0(x_1, x_2, x_{1'}, x_{2'}, \omega) - i \int d(x_3, x_4) \\
&\quad L_0(x_1, x_3, x_{1'}, x_3, \omega) v(x_3, x_4) L(x_4, x_2, x_4, x_{2'}, \omega) \\
&\quad - L_0(x_1, x_4, x_{1'}, x_3, \omega) W(x_3, x_4) L(x_3, x_2, x_4, x_{2'}, \omega)
\end{aligned} \tag{2.206}$$

Finally, when introducing the static-screening kernel

$$\begin{aligned}
K(x_3, x_5, x_4, x_6) &= K^x(x_3, x_5, x_4, x_6) + K^d(x_3, x_5, x_4, x_6) \\
K^x(x_3, x_5, x_4, x_6) &= -i \delta(x_3, x_4) \delta(x_5, x_6) v(x_3, x_6) \\
K^d(x_3, x_5, x_4, x_6) &= i \delta(x_3, x_6) \delta(x_4, x_5) W(x_3, x_4),
\end{aligned} \tag{2.207}$$

we get the *static BSE* (SBSE) in the frequency domain:

$$\begin{aligned}
L(x_1, x_2, x_{1'}, x_{2'}, \omega) &= L_0(x_1, x_2, x_{1'}, x_{2'}, \omega) + \int d(x_3, x_4, x_5, x_6) \\
&\quad L_0(x_1, x_4, x_{1'}, x_3, \omega) K(x_3, x_5, x_4, x_6) L(x_6, x_2, x_5, x_{2'}, \omega)
\end{aligned} \tag{2.208}$$

⁶⁸We also use the product-nature of L_0 , compare Footnote 64.

BSE in Orbital-Representation

For practical calculations, we convert the static BSE into a matrix-eigenvalue problem by expanding L , L_0 and K in Kohn-Sham (KS) orbitals and using their completeness. Details on the derivation can be found in Appendix C.1.1, where the derivation starts from the BSE in the GW- and static approximation, Eq. 2.208 and uses an expression of L_0 in terms of KS orbitals and quasiparticle (QP) energies (compare the exact Lehmann representation of L_0 , Eq. 2.196):

$$L_0(x_1, x_2, x_{1'}, x_{2'}, \omega) = i \sum_{v,c} \frac{\phi_c(x_1) \phi_v(x_2) \phi_v^*(x_{1'}) \phi_c^*(x_{2'})}{\omega - (\varepsilon_c^{QP} - \varepsilon_v^{QP}) + i\eta} - \frac{\phi_v(x_1) \phi_c(x_2) \phi_c^*(x_{1'}) \phi_v^*(x_{2'})}{\omega + (\varepsilon_c^{QP} - \varepsilon_v^{QP}) - i\eta} \quad (2.209)$$

For gas-phase calculations (isolated molecules and clusters), the full BSE then reads:

$$\begin{aligned} (\varepsilon_c^{QP} - \varepsilon_v^{QP}) X_m^{v,c} + \sum_{v',c'} [V_{c',v'}^{c,v} - W_{c',v'}^{c,v}] X_m^{v',c'} + [V_{v',c'}^{c,v} - W_{v',c'}^{c,v}] Y_m^{v',c'} &= \Omega_m X_m^{v,c} \\ (\varepsilon_c^{QP} - \varepsilon_v^{QP}) Y_m^{v,c} + \sum_{v',c'} [V_{c',v'}^{v,c} - W_{c',v'}^{v,c}] X_m^{v',c'} + [V_{v',c'}^{v,c} - W_{v',c'}^{v,c}] Y_m^{v',c'} &= -\Omega_m Y_m^{v,c}, \end{aligned} \quad (2.210)$$

where v and v' denote valence orbitals and c and c' denote conduction orbitals (see Eq. C.33 on the matrix elements of V and W). This generalized eigenvalue problem must be solved for positive energies $\Omega_m > 0$, such that we obtain L as

$$L(x_1, x_2, x_{1'}, x_{2'}, \omega) = i \sum_{m=1}^N \frac{\chi_m(x_1, x_{1'}) \chi_m^*(x_{2'}, x_2)}{\omega - \Omega_m + i\eta} - i \sum_{m=1}^N \frac{\chi_m(x_2, x_{2'}) \chi_m^*(x_{1'}, x_1)}{\omega + \Omega_m - i\eta}, \quad (2.211)$$

with⁶⁹:

$$\chi_m(x, y) = \sum_{v,c} X_m^{v,c} \phi_c(x) \phi_v^*(y) + Y_m^{v,c} \phi_v(x) \phi_c^*(y) \quad (2.212)$$

In the Tamm-Dancoff approximation (TDA; see Sec. C.1.2) the BSE simplifies to

$$(\varepsilon_c^{QP} - \varepsilon_v^{QP}) X_m^{v,c} + \sum_{v',c'} [V_{c',v'}^{c,v} - W_{c',v'}^{c,v}] X_m^{v',c'} = \Omega_m X_m^{v,c} \quad (2.213)$$

and χ_m becomes

$$\chi_m(x, y) = \sum_{v,c} X_m^{v,c} \phi_c(x) \phi_v^*(y). \quad (2.214)$$

⁶⁹Note the symbol reuse compared to Eq. 2.184 which is based on the similarity of Eq. 2.211 and the exact Lehmann representation of L , Eq. 2.192. See also Footnote 70

For periodic and gapped (the type of system we meet in our practical calculations) systems we restrict ourselves to the TDA (which we use in practice for periodic systems), such that the BSE reads:

$$(\varepsilon_{c,\mathbf{q}+\mathbf{Q}}^{QP} - \varepsilon_{v,\mathbf{q}}^{QP})X_{m,\mathbf{Q}}^{v,c,\mathbf{q}} + \sum_{v',c',\mathbf{q}'} \left[V_{c',\mathbf{Q},v',\mathbf{q}'}^{c,\mathbf{Q},v,\mathbf{q}} - W_{c',\mathbf{Q},v',\mathbf{q}'}^{c,\mathbf{Q},v,\mathbf{q}} \right] X_{m,\mathbf{Q}}^{v',c',\mathbf{q}'} = \Omega_{m,\mathbf{Q}} X_{m,\mathbf{Q}}^{v,c,\mathbf{q}} \quad (2.215)$$

Similarly to before, L reads

$$\begin{aligned} L(x_1, x_2, x_{1'}, x_{2'}, \omega) = & i \sum_{m=1}^N \sum_{\mathbf{Q}}^{\text{BZ}} \frac{\chi_{m,\mathbf{Q}}(x_1, x_{1'}) \chi_{m,\mathbf{Q}}^*(x_{2'}, x_2)}{\omega - \Omega_{m,\mathbf{Q}} + i\eta} \\ & - i \sum_{m=1}^N \sum_{\mathbf{Q}}^{\text{BZ}} \frac{\chi_{m,\mathbf{Q}}(x_2, x_{2'}) \chi_{m,\mathbf{Q}}^*(x_{1'}, x_1)}{\omega + \Omega_{m,\mathbf{Q}} - i\eta}, \end{aligned} \quad (2.216)$$

with:

$$\chi_{m,\mathbf{Q}}(x, y) = \sum_{v,c,\mathbf{q}} X_{m,\mathbf{Q}}^{v,c,\mathbf{q}} \phi_{c,\mathbf{q}+\mathbf{Q}}(x) \phi_{v,\mathbf{q}}^*(y) \quad (2.217)$$

Note the appearance of the Bloch momenta $\mathbf{q}$ and $\mathbf{q}'$ when comparing to the gas-phase equations above. Note also, that the problem splits into a separate eigenvalue equation for each $\mathbf{Q}$, which is a consequence of lattice-translation invariance.

Effective States

Note the similarities of the exact Lehmann representation of L , Eq. 2.192,

$$\begin{aligned} L(x_1, x_2, x_{1'}, x_{2'}, \omega) = & \\ = i \sum_{S=1} \frac{\chi_S(x_1, x_{1'}) \chi_S^*(x_{2'}, x_2)}{\omega - \Omega_S + i\eta} - \frac{\chi_S(x_2, x_{2'}) \chi_S^*(x_{1'}, x_1)}{\omega + \Omega_S - i\eta}, \end{aligned} \quad (2.218)$$

with the expression we have found above for L after having applied a multitude of approximations to the BSE, most notably, the QPA-like approximation of L_0 . The summation here runs over the exact excited states of the N -electron system, with Ω_S being the excitation energy of $|N, S\rangle$ and χ_S being defined as (where we expand it in KS orbitals in the second line):

$$\begin{aligned} \chi_S(x, y) &= \langle N, 0 | \hat{\Psi}^\dagger(y) \hat{\Psi}(x) | N, S \rangle \\ &= \sum_{i,j} \langle N, 0 | \hat{a}_j^\dagger \hat{a}_i | N, S \rangle \phi_i(x) \phi_j^*(y), \end{aligned} \quad (2.219)$$

where both i and j run both over all valence and conduction orbitals.

Motivated by this similarity and in analogy to what we did in the context of the QPA of G_1 , see Eq. 2.174, we introduce effective excited states of the N -electron system. Starting with gas-phase calculations, for solution m of the full BSE, the corresponding effective excited state⁷⁰ $|N, m\rangle$ must satisfy:

$$\begin{aligned} \chi_m(x, y) &= \sum_{v,c} X_m^{v,c} \phi_c(x) \phi_v^*(y) + Y_m^{v,c} \phi_v(x) \phi_c^*(y) \\ &\stackrel{!}{=} \sum_{i,j} \langle N, 0 | \hat{a}_j^\dagger \hat{a}_i | N, m \rangle \phi_i(x) \phi_j^*(y) \end{aligned} \quad (2.220)$$

⁷⁰ Note that we re-use the notation $|N, S\rangle$ of exact eigenstates. It should be clear from the context, whether we are talking about exact eigenstates or these effective (exciton) states.

Using orthogonality of the KS orbitals, this can be written as (which has to be fulfilled for all v, v', c, c'):

$$\begin{aligned}
\langle N, 0 | \hat{a}_v^\dagger \hat{a}_c | N, m \rangle &\stackrel{!}{=} X_m^{v,c} \\
\langle N, 0 | \hat{a}_c^\dagger \hat{a}_v | N, m \rangle &\stackrel{!}{=} Y_m^{v,c} \\
\langle N, 0 | \hat{a}_v^\dagger \hat{a}_{v'} | N, m \rangle &\stackrel{!}{=} 0 \\
\langle N, 0 | \hat{a}_c^\dagger \hat{a}_{c'} | N, m \rangle &\stackrel{!}{=} 0
\end{aligned} \tag{2.221}$$

Note that for a calculation beyond the TDA (so with nonzero Y), these demands can not be fulfilled if the ground state is (approximated by) a single Slater determinant of valence orbitals⁷¹! Note also, that constructing an effective state $|N, m\rangle$ satisfying Eq. 2.221 is in general not a trivial task and will not be done herein. As we will see later, in order to simulate photoemission from an excited system, we in principle do not even need to know how these effective states look like (see text around Eq. 3.50). Instead, it will turn out to be sufficient to assume that they can in principle be constructed (such that we can work with an object “ $|N, m\rangle$ ”) and that the excited system can be described by them. In the commonly used Tamm-Dancoff approximation, the conditions Eq. 2.221 become:

$$\begin{aligned}
\langle N, 0 | \hat{a}_v^\dagger \hat{a}_c | N, m \rangle &\stackrel{!}{=} X_m^{v,c} \\
\langle N, 0 | \hat{a}_c^\dagger \hat{a}_v | N, m \rangle &\stackrel{!}{=} 0 \\
\langle N, 0 | \hat{a}_v^\dagger \hat{a}_{v'} | N, m \rangle &\stackrel{!}{=} 0 \\
\langle N, 0 | \hat{a}_c^\dagger \hat{a}_{c'} | N, m \rangle &\stackrel{!}{=} 0
\end{aligned} \tag{2.222}$$

With the ansatz

$$|N, m\rangle = \sum_{v,c} \tilde{X}_m^{v,c} \hat{a}_c^\dagger \hat{a}_v |N, 0\rangle, \tag{2.223}$$

⁷¹At this point, it is important not to get confused about the relation of the ground-state DFT calculation and the BSE calculation. Kohn-Sham DFT describes the electronic ground state in terms of fictitious non-interacting electrons and gives us (in principle) the exact ground-state density, as calculated from the occupied/valence KS-orbitals. However, the single Slater determinant constructed from these valence orbitals (the “KS ground state”) is not the exact ground state (it just gives the same electron density as the exact ground state). These valence (and conduction) orbitals then enter the BSE via the KS-quasiparticle approximation we use for L_0 , see Eq. 2.209, where we replace the quasiparticle orbitals by the KS orbitals (using that they are usually very similar). Contrary to what one might expect (due to the BSE calculation being “based on” the DFT calculation) we however, for the solution of the BSE, never used the KS ground state determinant as an approximation of the exact ground state. Thus, the ground state used in the context of the BSE (which, for solving the BSE, we in fact do not need to know explicitly) still generally allows for de-excitations. Note however, that the BSE calculations (which, again, do not assume a simple KS ground state) are later used for the simulation of photoemission from excitons. And there, it will ultimately prove useful (compare text around Eq. 3.50) to approximate the exact ground state by the KS ground state, using the fact that for many systems (if the ground state is weakly correlated), the KS ground state is the dominant contribution to the exact ground state (compare Eq. 2.176).

we find:

$$\begin{aligned}
\sum_{\tilde{v}, \tilde{c}} \tilde{X}_m^{\tilde{v}, \tilde{c}} \langle N, 0 | \hat{a}_v^\dagger \hat{a}_c \hat{a}_{\tilde{c}}^\dagger \hat{a}_{\tilde{v}} | N, 0 \rangle &\stackrel{!}{=} X_m^{v, c} \\
\sum_{\tilde{v}, \tilde{c}} \tilde{X}_m^{\tilde{v}, \tilde{c}} \langle N, 0 | \hat{a}_c^\dagger \hat{a}_v \hat{a}_{\tilde{c}}^\dagger \hat{a}_{\tilde{v}} | N, 0 \rangle &\stackrel{!}{=} 0 \\
\sum_{\tilde{v}, \tilde{c}} \tilde{X}_m^{\tilde{v}, \tilde{c}} \langle N, 0 | \hat{a}_v^\dagger \hat{a}_{v'} \hat{a}_{\tilde{c}}^\dagger \hat{a}_{\tilde{v}} | N, 0 \rangle &\stackrel{!}{=} 0 \\
\sum_{\tilde{v}, \tilde{c}} \tilde{X}_m^{\tilde{v}, \tilde{c}} \langle N, 0 | \hat{a}_c^\dagger \hat{a}_{c'} \hat{a}_{\tilde{c}}^\dagger \hat{a}_{\tilde{v}} | N, 0 \rangle &\stackrel{!}{=} 0
\end{aligned} \tag{2.224}$$

If we additionally assume the ground state to be (close to) a single Slater determinant of valence orbitals, we find the conditions to be reduced to

$$\tilde{X}_m^{v, c} \stackrel{!}{=} X_m^{v, c} \tag{2.225}$$

and thus obtain the commonly used expression⁷²:

$$|N, m\rangle = \sum_{v, c} X_m^{v, c} \hat{a}_c^\dagger \hat{a}_v |N, 0\rangle \tag{2.226}$$

Thus, within the TDA and assuming the ground state to be close to a single Slater determinant, the effective excited state $|N, m\rangle$ can be written as a linear combination of *excitations* (annihilation of electron in valence orbital and creation in conduction orbital), with the linear coefficients given by the BSE eigenvector X^m . Note also that under these assumptions, $|N, m\rangle$ is normalized if the ground state is normalized and the BSE eigenvector is normalized (Eq. C.71 within TDA). Note that Eq. 2.226 is of significantly simpler form than a generic N -electron state, which, besides a ground-state contribution and *de-excitations* (annihilation of electron in conduction orbital and creation in valence orbital), can also contain valence-to-valence and conduction-to-conduction transitions as well as double-, triple, etc. transitions!

For periodic (and gapped) systems, working in the TDA, we write our effective excited state for solution $m, \mathbf{Q}$ as $|N, (m, \mathbf{Q})\rangle$ and demand analogously to before:

$$\begin{aligned}
\chi_{m, \mathbf{Q}}(x, y) &= \sum_{v, c, \mathbf{q}} X_{m, \mathbf{Q}}^{v, c, \mathbf{q}} \phi_{c, \mathbf{q} + \mathbf{Q}}(x) \phi_{v, \mathbf{q}}^*(y) \\
&\stackrel{!}{=} \sum_{i, \mathbf{q}', j, \mathbf{q}} \langle N, 0 | \hat{a}_{j, \mathbf{q}}^\dagger \hat{a}_{i, \mathbf{q}'} | N, (m, \mathbf{Q}) \rangle \phi_{i, \mathbf{q}'}(x) \phi_{j, \mathbf{q}}^*(y)
\end{aligned} \tag{2.227}$$

Using again orthogonality of the (Bloch) KS orbitals we find:

$$\begin{aligned}
\langle N, 0 | \hat{a}_{v, \mathbf{q}}^\dagger \hat{a}_{c, \mathbf{q}'} | N, (m, \mathbf{Q}) \rangle &\stackrel{!}{=} X_{m, \mathbf{Q}}^{v, c, \mathbf{q}} \delta_{\mathbf{q}', \mathbf{q} + \mathbf{Q}} \\
\langle N, 0 | \hat{a}_{c, \mathbf{q}}^\dagger \hat{a}_{v, \mathbf{q}'} | N, (m, \mathbf{Q}) \rangle &\stackrel{!}{=} 0 \\
\langle N, 0 | \hat{a}_{v, \mathbf{q}}^\dagger \hat{a}_{v', \mathbf{q}'} | N, (m, \mathbf{Q}) \rangle &\stackrel{!}{=} 0 \\
\langle N, 0 | \hat{a}_{c, \mathbf{q}}^\dagger \hat{a}_{c', \mathbf{q}'} | N, (m, \mathbf{Q}) \rangle &\stackrel{!}{=} 0
\end{aligned} \tag{2.228}$$

⁷² Compare Eq. (16) in Ref. [36]. Note that there, the creation and annihilation operator (which anticommute) are swapped, which is a result of the negative sign used in Eq. (10) of Ref. [36] as compared to our convention Eq. 2.184.

With the ansatz

$$|N, (m, \mathbf{Q})\rangle = \sum_{v, c, \mathbf{q}} \tilde{X}_{m, \mathbf{Q}}^{v, c, \mathbf{q}} \hat{a}_{c, \mathbf{q} + \mathbf{Q}}^\dagger \hat{a}_{v, \mathbf{q}} |N, 0\rangle, \quad (2.229)$$

we find:

$$\begin{aligned} \sum_{\tilde{v}, \tilde{c}, \tilde{\mathbf{q}}} \tilde{X}_{m, \mathbf{Q}}^{\tilde{v}, \tilde{c}, \tilde{\mathbf{q}}} \langle N, 0 | \hat{a}_{v, \mathbf{q}}^\dagger \hat{a}_{c, \mathbf{q}' + \mathbf{Q}} \hat{a}_{\tilde{c}, \tilde{\mathbf{q}} + \mathbf{Q}}^\dagger \hat{a}_{\tilde{v}, \tilde{\mathbf{q}}} |N, 0\rangle &\stackrel{!}{=} X_{m, \mathbf{Q}}^{v, c, \mathbf{q}} \delta_{\mathbf{q}', \mathbf{q} + \mathbf{Q}} \\ \sum_{\tilde{v}, \tilde{c}, \tilde{\mathbf{q}}} \tilde{X}_{m, \mathbf{Q}}^{\tilde{v}, \tilde{c}, \tilde{\mathbf{q}}} \langle N, 0 | \hat{a}_{c, \mathbf{q}}^\dagger \hat{a}_{v, \mathbf{q}'} \hat{a}_{\tilde{c}, \tilde{\mathbf{q}} + \mathbf{Q}}^\dagger \hat{a}_{\tilde{v}, \tilde{\mathbf{q}}} |N, 0\rangle &\stackrel{!}{=} 0 \\ \sum_{\tilde{v}, \tilde{c}, \tilde{\mathbf{q}}} \tilde{X}_{m, \mathbf{Q}}^{\tilde{v}, \tilde{c}, \tilde{\mathbf{q}}} \langle N, 0 | \hat{a}_{v, \mathbf{q}}^\dagger \hat{a}_{v', \mathbf{q}'} \hat{a}_{\tilde{c}, \tilde{\mathbf{q}} + \mathbf{Q}}^\dagger \hat{a}_{\tilde{v}, \tilde{\mathbf{q}}} |N, 0\rangle &\stackrel{!}{=} 0 \\ \sum_{\tilde{v}, \tilde{c}, \tilde{\mathbf{q}}} \tilde{X}_{m, \mathbf{Q}}^{\tilde{v}, \tilde{c}, \tilde{\mathbf{q}}} \langle N, 0 | \hat{a}_{c, \mathbf{q}}^\dagger \hat{a}_{c', \mathbf{q}'} \hat{a}_{\tilde{c}, \tilde{\mathbf{q}} + \mathbf{Q}}^\dagger \hat{a}_{\tilde{v}, \tilde{\mathbf{q}}} |N, 0\rangle &\stackrel{!}{=} 0 \end{aligned} \quad (2.230)$$

If we additionally assume that the ground state is (close to) a single Slater determinant of valence orbitals, we find these conditions to be reduced to

$$\tilde{X}_{m, \mathbf{Q}}^{v, c, \mathbf{q}} \stackrel{!}{=} X_{m, \mathbf{Q}}^{v, c, \mathbf{q}} \quad (2.231)$$

and obtain the common expression⁷³:

$$|N, (m, \mathbf{Q})\rangle = \sum_{v, c, \mathbf{q}} X_{m, \mathbf{Q}}^{v, c, \mathbf{q}} \hat{a}_{c, \mathbf{q} + \mathbf{Q}}^\dagger \hat{a}_{v, \mathbf{q}} |N, 0\rangle \quad (2.232)$$

Excitons

To conclude this section, an interpretation of what we have found is overdue. In short, we have achieved a description of the N -electron excited system in terms of an effective two-particle problem [87]. That is, the BSE can be understood as a two-particle Schrödinger equation with solutions given by the two-particle wave functions $\{\chi_m\}$ (or $\{\chi_{m, \mathbf{Q}}\}$). In particular, as a consequence of the chosen time-ordering, the wave functions are *electron-hole* wave functions, with the first argument denoting the electronic coordinate and the second one the hole-coordinate⁷⁴. That is, we describe a charge-neutral excited state by a *correlated electron-hole pair*, which we call an *exciton* and the wave function is usually called the *exciton wave function*. This becomes particularly clear from the *exciton states* (within TDA) we have constructed, see Eqs. 2.226 and 2.232, which through comparison to the quasielectron and quasihole states of Eq. 2.174 can be understood as a correlated state of a quasihole and quasielectron (we usually just call them hole and electron). In periodic calculations $\mathbf{Q}$ is called the *exciton momentum* and plays the same role as the Bloch momentum $\mathbf{q}$ in a single-particle Bloch orbital $\phi_{n, \mathbf{q}}$.

We can now also interpret the exchange K^x and direct K^d interaction kernels of the BSE, see Eq. 2.201, namely as the interaction between the electron and hole

⁷³Compare Eq. (33) in Ref. [36] and see Footnote 72.

⁷⁴This can be seen by comparing the interpretation of L (see text on the closely related G_2 given below Eq. 2.181) and the found expressions for L , as for example given in Eq. 2.211.

forming the exciton. As its name already gives away, K^x leads to an exchange interaction (in analogy to Hartree-Fock's exchange) between electron and hole, while K^d describes the attractive, screened interaction between electron and hole [36] (as expected, quasiparticles interact “weakly” through the screened Coulomb interaction [94]).

Note that we have ended up with this description of the excited system based on the form Eq. 2.209 of L_0 . This way, an effective description of the system in terms of the quasiparticle states has entered the BSE, which ultimately resulted in the appearance of excitons, which, as said above, can be thought of a correlated quasidelectron and quasihole pair, thus itself forming a quasiparticle, i.e., an effective particle-like description of the system. Thus, we can expect our approximative description of L to break down in the scenarios where the KS-quasiparticle description of L_0 breaks down (see Sec. 2.3.6), for example for excitons largely composed of electronic orbitals far from the Fermi level (typically: high-energy excitons). Note also, that the *exciton energies* $\{\Omega_m\}$ (or $\{\Omega_{m,\mathbf{Q}}\}$), which can be thought of as the energy that is needed to create the different excitons, are real-valued, meaning that the exciton states are obtained as/treated like long-lived/exact eigenstates of the N -electron system (compare text one paragraph below Eq. 2.176 and Ref. [36]). This is of course an approximation: they are not the exact eigenstates of the N -electron system, which are in general much more complicated N -electron states, with excitons being an effective quasiparticle description, just like the quasiparticle states of the ionized $N \pm 1$ -electron systems. On a technical note, the exciton energies are found to be real as a consequence of the BSE Hamiltonian being pseudo-Hermitian and an additional assumption (for details on this, see Sec. C.1.1). For the BSE Hamiltonian to be pseudo-Hermitian, the quasiparticle energies had to be assumed real. Thus, the exciton states are obtained as long-lived excitations as a consequence of assuming the quasidelectron and quasihole states to be long-lived (with negligible imaginary parts in their energies).

Note that the effective states that we obtained from the BSE above are single-exciton states. That is, we understand them as states where a single exciton has been created/added to the ground state. As is commonly done with quasiparticles (compare the treatment of phonons [113]), we could go a step further and introduce quasiparticle (here: exciton) creation and annihilation operators and use efficient second quantization language to construct additional excited states containing multiple quasiparticles, that is, in our case, N -electron excited states containing multiple (interacting) excitons⁷⁵ [114–116]. This is however beyond the scope of this text. In Sec. 3.3.10, when simulating photoemission from excited states, we will assume the exciton density to be low enough, such that exciton-exciton interaction

⁷⁵Note that this may be seen as a contradiction with L being written as a sum over all (!) excited states in the system, see Eq. 2.192. One could come to this conclusion, since from the BSE and the various approximations we used, we obtained L as a sum over the single-exciton states only, see e.g. Eq. 2.211. Assuming, however, that the amplitudes $\{\chi\}$ of the many-exciton states are negligible, this can be extended to a sum over all single- and many-exciton excited states without (significantly) changing L . At least for systems with weakly correlated ground states (which are the systems we will focus on later in Sec. 3.3.10), we can easily see that this is in fact the case: from Eq. 2.226 (or the periodic analog), we find that the n -exciton states, $n \geq 2$, are given by terms containing n valence annihilation- and n conduction creation operators, such that the overlap in the second line of Eq. 2.220 (under the assumption of a weakly correlated ground state) indeed becomes small.

becomes weak and can be neglected [114, 117] and photoemission from the system can effectively be described by one of the single-exciton states given above (or a statistical mixture of multiple (of different type/state), non-interacting excitons, see Sec. 3.3.10). It is then also common to speak of the *second exciton-state* $m = 2$ simply as the *second exciton* of the system, etc., since we never treat the case of two excitons existing at the same time.

To conclude, even though we had to employ a multitude of (commonly used) approximations to arrive at the final form of the BSE, the formalism has proven highly successful for the calculation of excited-state-, in particular optical properties [19, 118]. Notably, the BSE yields significant improvements over the *independent-(quasi)particle method*, where the excited state is described by a non-interacting quasielectron and quasihole [104]. In particular the lowest excitonic energy of the system (which is called the *optical gap* if the exciton is optically allowed, which necessitates $\mathbf{Q} = 0$ for periodic systems [36]) is smaller than the *fundamental gap* of the independent-particle method (compare L_0 in QPA), which is a result of the *exciton binding energy* [19], that is, the binding energy between electron and hole. Based on this success of the BSE in the calculation of optical properties, we will use the effective exciton states shown above for the description of photoemission from excited systems, see Sec. 3.3.10 (thus, as in Sec. 2.3.6, using these effective states beyond their immediate domain of use, which is L).

Spin-Structure of the BSE

Note that we have not explicitly treated the electronic spin in the BSE until now. As it turns out, the computational cost of solving the BSE can be dramatically reduced when we neglect spin-orbit coupling and when our system of interest has a closed-shell spin-singlet ground state, which is precisely what we will meet in our practical calculations later in this text. Without giving an explicit derivation, the simplification of the BSE can be sketched as follows:

First, note that whenever spin-orbit coupling is neglected, G_1 is given by a Kronecker delta in the spin-arguments [119]. Consequently, L_0 is given by two Kronecker deltas in its spin-arguments. As mentioned in Sec. 2.2.4, – compare also comments above Eq. (25) in Ref. [36] – (only) when neglecting spin-orbit coupling we can use spin-unpolarized Kohn-Sham DFT for our ground-state calculation and thereby obtain spin-unpolarized orbitals – that is, pure spin-up and spin-down orbitals that contain the same spatial orbitals and have the same KS energy⁷⁶. When using spin-unpolarized orbitals in Eq. 2.209 we can immediately see that L_0 is given by two Kronecker deltas in its spin-arguments. Further, using spin-

⁷⁶ Note that, while not explicitly stated in Ref. [36], their Eq. (25) assumes that the orbitals are spin-unpolarized. Note also, that in the exact-exchange-GKS formalism, orbitals are not automatically spin-unpolarized, see text below Eq. 2.101. In our practical calculations we however use restricted GKS (RGKS) to enforce spin-unpolarized orbitals. Lastly, note that for spin-unpolarized orbitals, the QP energies we obtain from Eq. 2.178 are then also equal for the two orbitals: the first part, $\varepsilon_i^{KS} - \varepsilon_i^{xc}$, is trivially the same for KS-DFT orbitals (see also Footnote 54) and also the same in RGKS when the system is (as in our practical calculations) closed-shell (where the exchange-operator becomes spin-independent, see text below Eq. 2.101). The second part is based on the self-energy and is the same for both orbitals since, when neglecting spin-orbit coupling, the self-energy acts as a Kronecker delta in its spin-arguments [119] – which can easily be seen in the GW approximation from the properties of G_1 and W mentioned throughout this paragraph.

unpolarized orbitals in Eq. 2.209, and labeling spatial orbitals by v and c and spin by s_v and s_c , the sum at the beginning can be written as $\sum_v \sum_c \sum_{s_v} \sum_{s_c}$ whenever both spin-orbitals belonging to spatial orbital v are valence spin-orbitals and the same holds for the conduction orbitals. Remembering that L_0 was constructed in a QPA-like form based on KS orbitals, this is the case if the KS ground state is closed-shell, so all valence spatial-orbitals are doubly occupied (closed-shell spin-singlet ground state, see Refs. [19, 36, 119]). Using additionally that the matrix elements of V and W in orbital-representation (see Eq. C.33) with spin-unpolarized orbitals are also given by two Kronecker deltas in the spin-indices [77] (where we use that $W(\cdot, \cdot)$ is spin-independent [81]), it can then easily be seen that the BSE falls apart into an equation for spin-singlet excitations and an equation for spin-triplet excitations [19, 36, 77, 119], with the triplet equation containing no direct interaction term V anymore and the singlet equation containing it twice, i.e. it contains $2V$, see for example Refs. [19, 36]. Importantly, the size of the BSE Hamiltonian in the respective subproblems is then only one fourth of that of the original BSE Hamiltonian [120] – thus dramatically reducing memory consumption – and is indexed purely by the spatial-orbital indices. Since we are interested in optically-allowed excitations, all our practical calculations shown later employ the spin-singlet equation [77, 119] (although a decay to spin-triplet excitations cannot be ruled out and may be of interest in studies beyond this text). As an example, the gas-phase exciton wave function of Eq. 2.214 can then be written as (with v and c indexing spatial orbitals):

$$\chi_m((\mathbf{r}_e, s_e), (\mathbf{r}_h, s_h)) = \left[\sum_{v,c} X_m^{v,c} \varphi_c(\mathbf{r}_e) \varphi_v^*(\mathbf{r}_h) \right] \left[\frac{1}{\sqrt{2}} (\delta_{\uparrow, s_e} \delta_{\uparrow, s_h} - \delta_{\downarrow, s_e} \delta_{\downarrow, s_h}) \right], \quad (2.233)$$

where we started with

$$\begin{aligned} \chi_m((\mathbf{r}_e, s_e), (\mathbf{r}_h, s_h)) &= \sum_{v,c} \sum_{s_v, s_c} X_m^{v, s_v, c, s_c} \phi_{c, s_c}(\mathbf{r}_e, s_e) \phi_{v, s_v}^*(\mathbf{r}_h, s_h) \\ &= \sum_{v,c} \sum_{s_v, s_c} X_m^{v, s_v, c, s_c} \varphi_c(\mathbf{r}_e) \delta_{s_c, s_e} \varphi_v^*(\mathbf{r}_h) \delta_{s_v, s_h} \end{aligned} \quad (2.234)$$

and used:

$$\begin{aligned} \frac{1}{\sqrt{2}} X_m^{v,c} &\equiv X_m^{v, \uparrow, c, \uparrow} = -X_m^{v, \downarrow, c, \downarrow} \\ X_m^{v, \downarrow, c, \uparrow} &= X_m^{v, \uparrow, c, \downarrow} = 0 \end{aligned} \quad (2.235)$$

Note that s_h here denotes the spin of the initially occupied orbital, so the inverse of what is commonly understood as the “hole’s spin” [36]. Our effective states, see Eqs. 2.226 and 2.232, then also take a corresponding form. A detailed discussion of the spin-structure in the BSE can also be found in Ref. [120].

2.4.5 BSE in Practice

We now conclude this section by again focusing on the parts we need in practice for our photoemission simulations – in this case photoemission from an exciton.

As can be seen in Sec. 3.3.10 we need in practice the exciton energies $\{\Omega_{m(\mathbf{Q})}\}$ and the excitations $\{X_{m(\mathbf{Q})}\}$, which we obtain by solving the Bethe-Salpeter equation (in the gas-phase variant Eq. 2.210 or in the periodic variant Eq. 2.215).

Note that in order to construct the BSE Hamiltonian we first need to perform DFT and GW calculations. In particular, we need Kohn-Sham wave functions (see Sec. 2.2.6) for the calculation of the matrix elements of V and W . In addition, for the latter we also need the static screened Coulomb interaction or, equivalently (see Eq. C.137), the static (inverse) dielectric function (see Sec. 2.3.7). Lastly, we need quasiparticle GW energies corresponding to the used KS orbitals (see Sec. 2.3.7). With all these quantities at hand, the BSE Hamiltonian can then be constructed and diagonalized such that the needed quantities are obtained. Here, we can distinguish between iterative diagonalization techniques that give us only the energetically-low-lying excitons (which are the ones we are generally interested in here) or full diagonalization that gives us all excitons. Further details on how the BSE is solved in practice can for example be found in Ref. [104].

With the so-obtained BSE eigenvectors⁷⁷ $\{X_{m(\mathbf{Q})}\}$ and eigenvalues $\{\Omega_{m(\mathbf{Q})}\}$ we can then use the exPOT formalism, see for example Eq. 3.62. Two final comments are important here: first, note that the exPOT formalism uses GW quasiparticle energies and KS wave functions in addition to the mentioned BSE-quantities, see for example Eq. 3.54. It is crucial that we use the exact-same KS wave functions that were used in the construction of the BSE, since the (in principle arbitrary, see text below Eq. 2.100) phases of KS orbitals are relevant in the coherent sum over conduction orbitals (compare similar comments in Ref. [36]). While we for consistency should (and typically do) use the same GW quasiparticle energies that were also used in the construction of the BSE, using different energies poses no direct problem, as long as the assignment to valence-KS orbitals is clear – see also the text above Eq. 3.51. Secondly, note that for periodic systems, the Brillouin zone sampling used in the BSE (see Appendix C.1.4) determines the resolution of momentum maps and band-structure plots that we can create with the obtained BSE eigenvectors. This is a consequence of in-plane crystal-momentum conservation, see Appendix D.2.1. Thus, the BZ sampling in the BSE must be converged not only from a physics-related standpoint, but also with regard to the desired resolution of the momentum distributions we want to calculate and plot.

⁷⁷Of course, the full eigenvectors also contain de-excitations, provided the BSE has been solved beyond the TDA. Since the exPOT formalism only uses the excitation-part (see text around Eq. 3.50), we will routinely speak of the excitations alone simply as the *BSE eigenvector* for simplicity.

3 Theoretical Description of Photoemission

In this chapter we focus on photoemission simulations. We start with a small introduction to angle-resolved photoemission spectroscopy (ARPES) and then focus for the remaining chapter on our theoretical approach for simulating ARPES experiments. The derivation is kept general for as long as possible, until a separation into ground-state and exciton photoemission as well as into gas-phase- and periodic systems becomes necessary. While the previous Chapter recapitulates well-known theory and serves as a basis for the upcoming photoemission formalism, this chapter contains new results developed by the author and co-workers during his PhD. Besides the unifying treatment of ground-state and exciton photoemission in a single consistent manner, the main result constitutes the extension of the exciton photoemission formalism to periodic systems, which was first published by the author and co-workers in Ref. [121]. Additionally, details for an efficient implementation of the ground-state and exciton formalism are given, which have been developed by the author and were used for the practical calculations presented in Chapters 4 and 5.

3.1 Introduction

The fundamental observation underlying all experimental techniques given below is, that the interaction of light and matter can best be understood when describing light as consisting of elementary particles, called *photons*. While the quantum-theory of light is far beyond the scope of this work, it is for our purposes sufficient to know that the energy of the photons is determined by the frequency ω of the light (electromagnetic radiation) and that a photon can be *absorbed* by an atomic system (matter), whereby the photon ceases to exist and its energy is absorbed by the system. This absorption process is governed by the following energy-conservation law:

$$E_i + \omega = E_f, \tag{3.1}$$

where E_i is the (initial) energy of the atomic system before absorption, E_f is its (final) energy after absorption and ω is the photon energy in atomic units ($\hbar = 1$). A complete picture of such absorption processes needs to account for virtual states [122], energy broadening effects, changes in the full nuclear-electronic state of the system (compare Sec. 2.1.3), etc. and is, again, beyond the scope of this work. Further details can for example be found in Ref. [123].

We are herein interested in situations where the Born-Oppenheimer approximation (see Sec. 2.1.3) can be used and additionally assume the nuclei to be completely frozen⁷⁸, such that the state of the atomic system is completely described by an N -electron state. Additionally, we assume that before and after absorption the system resides in a pure eigenstate of the N -electron Hamiltonian. For the energy-conservation we then find

$$E(N, i) + \omega = E(N, f), \quad (3.2)$$

where $E(N, i)$ and $E(N, f)$ are respectively the energy of the initial and the final state (using the notation of Eq. 2.126).

A special case of this absorption process is the excitation from the electronic ground state to a bound⁷⁹ excited state of the system, for which we find the energy-conservation

$$\omega = E(N, S) - E(N, 0) = \Omega_S, \quad (3.3)$$

where $E(N, 0)$ and $E(N, S)$ are respectively the energy of the ground state and the excited state and Ω_S is the excitation energy. We will revisit this process in pump-probe photoemission below.

The second case of interest to us is the excitation from a bound state of the system to a *scattering state*, that is, a state that has a non-vanishing electron-density asymptotically far away from the nuclei (and is thus non-normalizable and part of the Hamiltonian's continuous spectrum, see again Appendix A.1.1). In the *sudden approximation*, we then assume that the N -electron scattering state can be expressed sufficiently well as the antisymmetrized product of a state describing a bound part of the system and a state describing the scattering part of the system. We will restrict ourselves to the special case where the bound part is an $N - 1$ -electron state and the scattering state is a one-electron state. The photon-absorption-induced transition to such a state is known as *photoemission* (also: *photoelectric effect*) and the one-electron scattering state is known as the *photoelectron state*. Note that this antisymmetrized product state is strictly speaking in general not an eigenstate of the N -electron Hamiltonian⁸⁰ and does therefore strictly speaking not have a distinct energy! We will get back to this at the end of Sec. 3.3.1. Assuming then additionally that the $N - 1$ -electron state is an eigenstate of the $N - 1$ -electron Hamiltonian with energy $E(N - 1, f)$ and denoting the photoelectron (kinetic) energy as E_{kin} , we approximate the product state's energy (distribution) by the single value $E(N, f) \approx E(N - 1, f) + E_{\text{kin}}$ and get for the energy conservation:

$$E(N, i) + \omega = E(N - 1, f) + E_{\text{kin}} \quad (3.4)$$

⁷⁸We keep the nuclei frozen for simplicity and for computational reasons. However, the N -electron exciton state used in Sec. 3.3.10, as well as the $N - 1$ -electron post-photoemission states could in principle also be calculated for changed (relaxed) geometries. Note also, that in the context of (exciton-) photoemission from periodic system, a coupling to phonons (see also $\mathbf{Q} \neq 0$ in Sec. 3.3.10) may become important for some systems (and temperatures) but is beyond the scope of this work.

⁷⁹An electronic state is called *bound* if the electron density of the state falls off quickly when moving away from the nuclei. See Appendix A.1.1 for details.

⁸⁰When writing its energy as $E(N, f)$ we thus slightly abuse the notation Eq. 2.126.

Note that we did not further specify the initial state beside the condition that it is a pure N -electron energy eigenstate. The most common initial state is simply the N -electron ground state, from which photoemission will be called *ground-state photoemission*. We can however take an excited state as our initial state and thus look at *excited-state photoemission*. In a pump-probe photoemission experiment (see below), we then use a first light source to bring the system to an excited state (specifically excitons, see Sec. 3.3.10) and then a second light source that leads to photoemission from the excited state.

3.2 Angle-Resolved Photoemission Spectroscopy

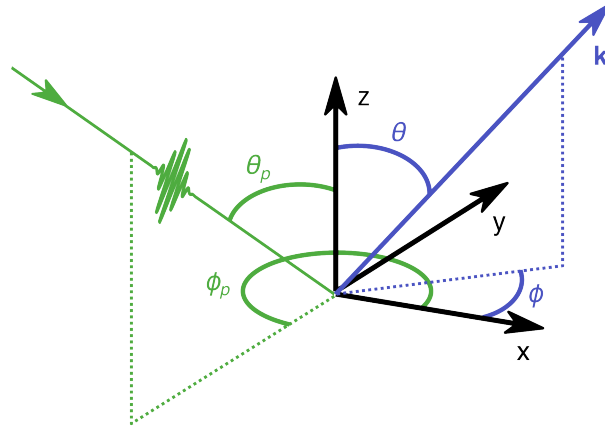


Figure 3.1: Definition of angles in ARPES. An incoming light pulse with polar angle θ_p and azimuthal angle ϕ_p is indicated in green. An outgoing photoelectron of photoelectron momentum $\mathbf{k}$ with polar angle θ and azimuthal angle ϕ is indicated in blue. In ground-state ARPES, there is one incoming pulse – the probe pulse – while in pump-probe ARPES there are two incoming pulses – the pump- and the probe pulse – at generally different angles. The atomic system is located at the origin.

Using the concepts introduced above, it is now straightforward to give the generic setup of an angle-resolved photoemission spectroscopy (ARPES) experiment. In brief, in an ARPES experiment we irradiate an atomic system with a light-source and count the number of emitted photoelectrons as a function of their kinetic energy E_{kin} and the angles θ, ϕ (see below) at which they are emitted. The number of emitted electrons at a given energy E_{kin} and angles θ, ϕ is called the *photoemission intensity* $I(E_{\text{kin}}, \theta, \phi)$ and I itself is called the *photoemission distribution*. Comparison of experimentally obtained photoemission intensities with simulated ones then allow us to extract system properties – see for example Ref. [16] – from the experimental data. Before going into more details, let us introduce the main building blocks of such an experiment.

Sample

The atomic system from which photoelectrons shall be emitted is usually called *the sample*. The goal of an ARPES experiment then is to obtain information about

the sample by measuring the photoemission distribution I and using theory (see below) to derive system properties from it. Therefore, if the properties of a specific system shall be determined it is of utmost importance that the sample has been prepared in the desired state before photoemission.

We focus herein on photoemission from surfaces of crystalline solids, with a particular focus on surfaces (then called *substrate*) with adsorbed molecular layers/films or 2D semiconductors – the *adsorbate*. For such system it is then crucial that the crystal’s surface has been cleaned of contaminations and is as close to a perfect (microscopically planar) crystal surface as possible.

In our computational simulations we assume that the adsorbate forms large-scale well-ordered domains (experimentally usually self-assembled) on the substrate, where each such domain can be described by a periodically-repeated *supercell*. For the case of adsorbed molecules, the supercell may then contain only a single molecule meaning that all molecules in the domain are rotated equally (usually as a result of geometrical/spatial constraints or inter-molecular interaction), or it may also contain multiple molecules. Trivially, the smaller the supercells are, the better, since the computational cost in performing the involved calculations (DFT and possibly GW and BSE, see below) grows rapidly with the system size (see Sec. 2.1.4).

The adsorbate is typically rotated differently (or mirrored) in the different domains, hence why they are often also termed *rotational* (or mirror-) domains. Meaningful application of ARPES demands that there are not too many different rotational orientations of the adsorbate, since the presence of too many rotational orientations can result in the dependence of the photoemission intensity on possibly both, the azimuthal ϕ and polar θ , angle becoming less structured (*smearred out*), making its analysis less fruitful (see also Sec. 3.3.11 on symmetrization of k-maps over domains).

Besides, this discussion presupposes that the additional structure (for example molecules) *stick* at all to the substrate, i.e. that it can be bound by the crystal surface (at the used temperature), and that we know how long we need to deposit it onto the substrate to get sufficient coverage (or possibly a distinct number of layers). The latter point is important not only so we know which structure we are working with, but also because sufficient coverage is often needed to suppress photoemission from the crystalline substrate (when we are more interested in the adsorbed structure), see also Ref. [35].

It should therefore at this point have become clear that sample preparation is a difficult task on its own, and that the sample is usually kept (starting in preparation and throughout the ARPES experiment) in vacuum-chambers, often at low temperatures. Fortunately, additional techniques like scanning tunnelling microscopy (STM) or low-energy electron-diffraction (LEED) can be used to assess translational order and to identify different domains as well as estimate coverages.

Probe Light-Source

The next building block of any ARPES experiment is the *probe* light source, whose job it is to stimulate photoemission from the atomic system. As a first demand, the light source has to be monochromatic, that is, deliver photons with a sufficiently sharp photon energy ω . Note that this assumption can become problematic in ultrafast trARPES (see below) experiments, where probe pulses can become very

short (down to the attosecond-scale [124]). In these cases, the delta-functions enforcing energy conservations given below (e.g. in Eq. 3.62) must be replaced by an appropriately broadened (typically Gaussian) peak, see also Appendix D.3. Additionally, the energy of the photons must be large enough such that photoelectrons can be emitted from the system, that is, it must be large enough such that E_{kin} in the energy conservation law of ARPES Eq. 3.4 can become positive. Typical values for POT and exPOT (see below) are in the extreme ultraviolet, specifically from 15 eV to 50 eV (going to too high energies beyond this range will lead to the breakdown of the dipole approximation, see Sec. 3.3.2). We assume a directed light-beam which can be characterized by its angles-of-incidence θ_{probe} and ϕ_{probe} , which is then directed at the atomic system, the *sample*, as illustrated in Fig. 3.1. Additionally, while this is not strictly necessary, we restrict ourselves herein to polarized light-sources with the unit-vector ε denoting the polarization direction (which is defined relative to the light's direction, as determined by the angles-of-incidence).

As a last important demand, the intensity A_0 of the light-beam must be high enough such that within reasonable time-scales a large-enough amount of electrons is emitted leading to a statistically-significant photoemission distribution I (such that the true distribution can be read from it, see below). However, it must also be weak enough, such that we stay in the *linear regime* (as explicitly used in Eq. 3.8). We can then neglect interactions between photoholes (which encompasses the case where an already ionized area photoemits again, before the photohole can be filled by charge transfer, typically from the substrate) – compare Sec. 2.3.6 – as well as two-photon processes and theoretically describe the whole photoemission process, based on a single photoemission event. Within the used approximations – the so-obtained calculated photoemission distributions is then the true quantum-mechanical probability distribution of the photoemitted electrons, which the experimentally measured intensity distribution approaches asymptotically with increasing measurement time, that is, increasing number of collected/detected photoelectrons,

Note that we usually use light-sources that emit Gaussian pulses, that is, the light's intensity over time follows a (repeated) Gaussian envelope. We will thus also often talk about the *probe-pulse*, when referring to the probe-light

Detector

Finally, the photoelectrons emitted from the sample hit a *detector*, which has to be able to measure/count the number of emitted electrons as a function of their kinetic energy and their emission angles θ and ϕ , see, again, Fig. 3.1. Alternatively, so-called *momentum microscopes* directly measure the in-plane momenta k_x and k_y instead of the emission angles, see also Eq. 3.5.

Ground-state ARPES

In a *ground-state ARPES* experiment, the sample is then directly irradiated (sometimes at low temperature) by the probe light for a fixed amount of time and the detector counts the emitted photoelectrons. Once finished, the obtained photoemission distribution I can be analyzed by comparison to theory.

There are various ways in which the data cube I can be sliced as a function of the variables E_{kin} , θ and ϕ . A very common way is to look at so-called *momentum-maps* or *k-maps*, where we fix the kinetic energy E_{kin} and plot the remaining angular photoemission distribution as a heatmap. For such k-maps, the angles are usually converted to *in-plane* (meaning: parallel to the crystal surface, see text on sample above) momentum components k_x and k_y of the photoelectron momentum $\mathbf{k}$ (see Sec. 3.3.4) via

$$\begin{aligned} E_{\text{kin}} &= \frac{k^2}{2} \\ k &= \sqrt{k_x^2 + k_y^2 + k_z^2} \\ k_x &= k \sin(\theta) \cos(\phi) \\ k_y &= k \sin(\theta) \sin(\phi) \\ k_z &= k \cos(\theta) \end{aligned} \tag{3.5}$$

and the intensity is then plotted as a function of k_x and k_y . See also Appendix D.3 for details on how the photoemission intensity is plotted in momentum maps (and photoemission band-structure plots). Examples can be found throughout the remaining text, see for example Fig. 5.2b. To obtain statistically more significant k-maps from experimental data, we often *integrate* over a given energy window, that is, look at the k_x and k_y distribution of all photoelectrons within said energy window. See also Appendix. D.3.3 for details.

Pump-Probe ARPES

In *pump-probe ARPES* or *excited-state ARPES*, we use an additional light-source, the *pump-light*, or *pump-pulse*, to bring the system (which is, again, often cooled) to a (bound) excited state, and then use the probe light to emit photoelectrons from the excited system.

We focus, as for the probe-light, on the case of a monochromatic light-source (thus assuming a long-enough pump-pulse duration), and on the special case of a *resonant* excitation, that is, the photon energy coincides (reasonably-well) with some (charge-neutral) excitation energy of our sample, see Eq. 3.3 (compare also Sec. 3.3.10). Additionally, as for the probe-pulse, we demand the pump-pulse to be polarized (see also Sec. 4.4), which can be used to maximize the probability of exciting the system by aligning the polarization with the transition dipole from the ground state to the excited state [36]. The pump-pulse must again form a directed beam and is characterized by its angles-of-incidence θ_{pump} and ϕ_{pump} , see Fig. 3.1. Regarding its intensity, for our description of the excited system in terms of isolated excitons (see Sec. 2.4.4), we again need it to be weak enough to stay in the *low exciton-density regime* (well below the exciton Mott transition threshold, such that excitons can be viewed as isolated), but strong enough to sufficiently excite the system (create a sufficient amount of excitons). That is, we again stay in the linear regime (see e.g. Ref. [125]). Take the pump-probe experiments of Chapter 5 as an example, where we can see in Fig. 5.2a that the pump-related photoemission signal is approximately $\frac{1}{1000}$ of the ground-state-related signal (see below).

As mentioned above, after exciting the sample with the pump-pulse, the probe pulse is then used to stimulate photoemission and the photoelectrons hit the detector. This process of *pump* $\rightarrow$ *delay* $\rightarrow$ *probe* $\rightarrow$ *detect* is then repeated many times, such that the photoemission distribution I becomes statistically-significant. Now, since we think of the excited system in terms of particle-like excitations, excitons (see Sec. 2.4.4), we can still talk about a *ground-state signal*, which then describes photoemission of an electron that was *not* part of an exciton (correlated electron-hole pair). Trivially, the repeated process mentioned before thus gives us a photoemission distribution which is a mixture of a ground-state photoemission signal and an excited-state photoemission signal. It is then the task of theory to disentangle these signals (see comments below Eq. 3.65).

Lastly, in a variation of pump-probe ARPES known as *time-resolved ARPES* (trARPES), the above-given process is repeated multiple times, but with varying time-delays between the pump- and the probe-pulse. The photoemission intensity data cube then gets an additional dimension, the *time-delay* t between the pump-and the probe-pulse. By comparing the intensity distribution across different time-delays, the temporal evolution (formation, decay) of the created excitation can be analyzed (see also the comments on the pump-probe time-delay given in Sec. 3.3.10).

3.3 Photoemission Orbital Tomography

To analyze the photoemission distribution obtained from ARPES experiments we perform *ab initio* simulations of photoemission on the basis of Fermi's golden Rule. The comparison and analysis of experimentally obtained ARPES intensities with theoretical simulations based on the formalism⁸¹ shown below is termed *photoemission orbital tomography* (POT) and comes in various flavors and levels of sophistication.

3.3.1 Fermi's Golden Rule for Photoemission

The starting point for our photoemission simulations is Fermi's golden Rule, a result of first-order time-dependent perturbation theory, giving us a simple expression for the transition rate (transition probability per unit time) from an initial state to a final state of an N -electron quantum-system, where both states must be eigenstates of the N -electron Hamiltonian Eq. 2.42.

The perturbing Hamiltonian $\hat{H}'$ represents the action of the probe pulse on the system, whose intensity must be small enough (see above) to justify the use of first-order perturbation theory. Assuming a monochromatic probe pulse of frequency ω and using the Coulomb gauge, the electromagnetic field is determined by the electromagnetic vector potential [39, 126]:

$$\tilde{\mathbf{A}}(\mathbf{r}, t) = \mathbf{A}(\mathbf{r})e^{-i\omega t} + \mathbf{A}^*(\mathbf{r})e^{i\omega t} \quad (3.6)$$

The perturbation is then given by the light-matter interaction Hamiltonian (some-

⁸¹Occasionally, we also refer to the theoretical formalism itself as *POT*.

times called the *minimal coupling* Hamiltonian) [38, 126]:

$$\hat{H}'(t) = \sum_{i=1}^N \frac{1}{2} \left(-\tilde{\mathbf{A}}(\hat{\mathbf{r}}_i, t) \cdot \hat{\mathbf{p}}_i - \hat{\mathbf{p}}_i \cdot \tilde{\mathbf{A}}(\hat{\mathbf{r}}_i, t) + \tilde{\mathbf{A}}(\hat{\mathbf{r}}_i, t) \cdot \tilde{\mathbf{A}}(\hat{\mathbf{r}}_i, t) \right) \quad (3.7)$$

Assuming a weak probe pulse, the quadratic term can be neglected (linear regime) and we get

$$\hat{H}'(t) \approx \sum_{i=1}^N \frac{1}{2} \left(-\tilde{\mathbf{A}}(\hat{\mathbf{r}}_i, t) \cdot \hat{\mathbf{p}}_i - \hat{\mathbf{p}}_i \cdot \tilde{\mathbf{A}}(\hat{\mathbf{r}}_i, t) \right) = -\hat{H}_{\text{int}} e^{-i\omega t} - \hat{H}_{\text{int}}^\dagger e^{i\omega t}, \quad (3.8)$$

with the time-independent operator

$$\hat{H}_{\text{int}} \equiv \sum_{i=1}^N \frac{1}{2} (\mathbf{A}(\hat{\mathbf{r}}_i) \cdot \hat{\mathbf{p}}_i + \hat{\mathbf{p}}_i \cdot \mathbf{A}(\hat{\mathbf{r}}_i)), \quad (3.9)$$

which will for simplicity be called the light-matter interaction Hamiltonian from now on (remembering that strictly speaking, the light-matter interaction is given by the time-dependent operator given in Eq. 3.7). Note that $\hat{H}_{\text{int}}$ is not Hermitian if $\mathbf{A}$ is complex (circular polarization)! We have thus found, that the perturbation $\hat{H}'$ is harmonic in time! The first term corresponds to photon absorption, the second one to stimulated emission of a photon. We can then use Fermi's golden rule for a harmonic potential and find for the photon absorption part⁸² the *transition rate* from the initial state to a single final state [39, 126]:

$$W_{i \rightarrow f} = 2\pi \left| \langle N, f | \hat{H}_{\text{int}} | N, i \rangle \right|^2 \delta(\omega + E(N, i) - E(N, f)), \quad (3.10)$$

where $|N, i\rangle$, $E(N, i)$ and $|N, f\rangle$, $E(N, f)$ are respectively the initial state and its energy and final state and its energy. Note that the delta-function enforces the energy conservation already mentioned in Eq. 3.1. While the above form of Fermi's golden rule is commonly met in photoemission theory [92], the appearance of an isolated Dirac-delta (not inside an integral) may appear mathematically questionable. In a more rigorous treatment, we calculate the rate of transition from an initial state to a *group of final states*, where the above expression represents a transition rate *density* and is integrated over [39, 126]. Details can be found in Appendix D.3, where we also mention details of the presumed normalization of the initial and final state.

On a final, technical note, as mentioned above, the initial- and final state used in Fermi's golden rule must in principle be exact (properly normalized) eigenstates

⁸²Stimulated emission is only possible when starting from an excited state and is therefore irrelevant for ground-state ARPES. In excited-state ARPES, we can justify neglecting it (i) by the fact that we generally have a very low excitation density (see text above about the pump-pulse) and (ii) more generally by the fact, that it does not contribute to the photoelectron distribution and is therefore not of interest to us (Strictly speaking, stimulated emission reduces the number of excitations and therefore the relative strength of the excited-state signal relative to the ground-state signal. However, it does not change the “internal” energy- and angle-distribution of each of these two signals! Based on point (i) before and since we never try to predict absolute intensities, or the relative strength of the ground- vs excited-state signal anyway, the influence of stimulated emission can be neglected.). See also Ref. [126] on the smallness of the stimulated emission matrix element relative to the absorption matrix element.

of the N -electron Hamiltonian, which is why we use the notation Eq. 2.126. Already in Sec. 3.3.3, we will break this demand by approximating the final state by an antisymmetrized product state, which is in general not an exact N -electron eigenstate. Similarly, in the context of excited-state photoemission, we will use an approximate excited state of the N -electron system, an *exciton*, as the initial state. Assuming in both cases, that the used states are to good approximation (although not exactly) eigenstates of the N -electron Hamiltonian, we are justified in still using Fermi's golden rule and (ab)using the notation Eq. 2.126.

3.3.2 Dipole Approximation

We continue by applying the commonly used *dipole approximation* [92], where the spatial dependence of the probe pulse is neglected, that is $\mathbf{A}(\mathbf{r}) \approx \mathbf{A} = A_0 \boldsymbol{\varepsilon}$, where $\boldsymbol{\varepsilon}$ is the polarization vector. Note that, while we use $\mathbf{A}$ in the upcoming equations, we ultimately will only calculate relative photoemission intensities such that the value of A_0 drops out of the calculation. This approximation is justified whenever $\mathbf{A}(\mathbf{r})$ varies only weakly on atomic length scales⁸³ [92]. This is usually well-justified for the probe-energies of 15–50 eV typically used in POT, which correspond to wavelengths of ≈ 820 –250 Å, such that even in the “worst-case” scenario of grazing-incidence, the dipole approximation remains justified. The light-matter interaction Hamiltonian then becomes:

$$\hat{H}_{\text{int}} \approx \sum_{i=1}^N \mathbf{A} \cdot \hat{\mathbf{p}}_i = \mathbf{A} \cdot \hat{\mathbf{P}}, \quad (3.11)$$

with the N -electron momentum operator:

$$\hat{\mathbf{P}} = \sum_{i=1}^N \hat{\mathbf{p}}_i \quad (3.12)$$

Inserting this into Eq. 3.10 we get the starting point for all upcoming variants of POT:

$$W_{i \rightarrow f} = 2\pi \left| \langle N, f | \mathbf{A} \cdot \hat{\mathbf{P}} | N, i \rangle \right|^2 \delta(\omega + E(N, i) - E(N, f)) \quad (3.13)$$

3.3.3 Sudden Approximation

The next approximation which we use is the *sudden approximation*, which was already introduced above Eq. 3.4. As detailed there, we approximate the N -electron eigenstate by the antisymmetrized product of an $N - 1$ -electron (bound) eigenstate $|N - 1, f\rangle$ (energy $E(N - 1, f)$) and a one-electron (scattering) photoelectron state $|\gamma\rangle$ (energy E_{kin}):

$$\begin{aligned} |N, (f, \gamma)\rangle &\approx \frac{1}{\sqrt{N!}} \hat{\mathcal{A}}(|\gamma\rangle \otimes |N - 1, f\rangle) \\ E(N, (f, \gamma)) &\approx E(N - 1, f) + E_{\text{kin}}, \end{aligned} \quad (3.14)$$

⁸³From a more technical point of view, the region where $\mathbf{A}(\mathbf{r})$ must remain approximately constant is given by the region where the Dyson orbital and the photoelectron state both have relevant amounts of density, see Eq. 3.24.

where the prefactor ensures proper normalization (see Appendix D.3 and Eq. A.23 for details). In such a product state, all correlation between the photoelectron and the remaining $N - 1$ -electron system is neglected (besides the always-necessary antisymmetrization). As can be guessed from its name, this approximation is valid under the assumption that the photoelectron is *instantaneously* removed from the remaining system [92]. Loosely speaking, there is then no time for the N -electron state of the system to adapt/change into a correlated N -electron state including correlations between a remaining system and a scattered electron. Instead, the two systems are fully separated/decoupled, except for the antisymmetrization. The sudden approximation is therefore particularly justified whenever a photoelectron *does not need to pass through a lot of the remaining system before escaping*, which is for example the case for the emission from planar molecules adsorbed on a substrate. Additionally, higher probe energies increase the photoelectron kinetic energy such that it leaves the system quicker. In POT, we generally use 15–50 eV for the probe-energy and consequently generally expect the sudden approximation to be justified – at least for electrons coming from high-lying orbitals (like a molecular HOMO).

The transition rate to this product final state then reads:

$$W_{i \rightarrow (f, \gamma)} = 2\pi \left| \langle N, (f, \gamma) | \mathbf{A} \cdot \hat{\mathbf{P}} | N, i \rangle \right|^2 \delta(\omega + E(N, i) - E(N - 1, f) - E_{\text{kin}}) \quad (3.15)$$

3.3.4 Photoelectron States

Before continuing the derivation, let us briefly look into the photoelectron states $\{|\gamma\rangle\}$ in a bit more detail. These states describe the possible states of the photoemitted electrons and must therefore be non-normalizable, since the photoelectrons are not bound anymore, that is, their wave functions generally do not vanish at infinity (compare Appendix A.1.1).

Instead of simply describing them as free particles via plane-wave states (see Sec. 3.3.7), more sophisticated approaches account for the influence of the remaining system on the photoelectron state. Common to these approaches is the use of *scattering boundary conditions*, where we demand the photoelectron states far from the atomic system to be composed of an outgoing plane wave and an ingoing wave [127–129]⁸⁴. These boundary conditions are also known as *time-reversed LEED* boundary conditions, since they describe the inverse of a LEED (low-energy electron diffraction) experiment, where we have an ingoing plane-wave and outgoing (scattering) wave. Note that, due to the use of these boundary conditions, we will occasionally also simply refer to the photoelectron states as *scattering states*.

A common approach to including the influence of the surface and incorporate these boundary conditions is to obtain the photoelectron states via solution of the *Lippmann-Schwinger equation* [127, 130]. Equivalently, they can also be obtained as solutions of the Kohn-Sham equation (using a converged ground-state density) by employing scattering boundary conditions [128]. Note that for systems modelled

⁸⁴Note that the apparent difference in the boundary conditions presented in Ref. [129] (for example in Chapter 10) and in Refs. [127, 128] is geometric, since the latter focus on periodic 2D systems while the former focuses on finitely-sized systems.

as periodic surfaces, the photoelectron states are then Bloch functions in the in-plane directions [128, 130].

Calculated in such a way, note that the scattering states are orthogonal to the bound Kohn-Sham (KS) orbitals and that scattering states and bound states together span the entire single-particle Hilbert space [129] (in case of spin-unpolarized KS-DFT, all these states are pure spin-up/down states, see text around Eq. 2.101). More importantly for us, every scattering state is uniquely indexed by its *photoelectron momentum* $\mathbf{k}$ (and, in principle, its spin, compare Sec. 3.3.7) and has energy $E_{\text{kin}} = \frac{k^2}{2}$ – compare Ref. [130] and Chapter 10 in Ref. [129]. Here, $\mathbf{k}$ denotes the momentum of the outgoing plane wave in the scattering boundary condition far from the atomic system and is thus the momentum measured at the detector in an ARPES experiment.

Note also that since they are non-normalizable to 1 we instead resort to Dirac delta normalization. That is, for two photoelectron states $\gamma_{\mathbf{k}}$ and $\gamma_{\mathbf{k}'}$ we have⁸⁵:

$$\langle \gamma_{\mathbf{k}} | \gamma_{\mathbf{k}'} \rangle = \delta(\mathbf{k} - \mathbf{k}') \quad (3.16)$$

Compare Ref. [129] as well as Appendix A.1.1. This is also the normalization needed in Fermi's golden rule, see Appendix D.3 for details.

Lastly, note that a middle ground between the simple plane-wave approximation and the approaches described above is for example given by the *damped plane-wave* photoelectron state of Ref. [35], where the photoelectron state is modelled by a plane wave that vanishes exponentially in the atomic surface. This exponential decay serves as a first step towards a proper description of the photoelectron state, which becomes apparent when, again, thinking of it as originating from the inverse of a LEED experiment, where the effect of an ingoing electron on a surface can intuitively be understood to exponentially decay inside the atomic region.

The explicit treatment of such scattering states is however beyond the scope of this text and we will in fact later resort to the simple plane-wave approximation, see Sec. 3.3.7. Further details on scattering states can also be found in Refs [84, 126] and the spin-dependence of scattering states is discussed in Ref. [131]. See also the comments in Chapter 10-c, notably, below Eq. (10.21) in Ref. [129] for a general discussion of scattering states and scattering boundary conditions.

3.3.5 Dropping Indirect Terms

We continue by making use of the second-quantization formalism (see also Appendix A.1). We denote the complete set of orthonormal one-electron orbitals by $\{\phi_i\}$ (creation operators $\{\hat{a}_i^\dagger\}$ and annihilation operators $\{\hat{a}_i\}$). These should be obtained via some effective one-electron theory, in practice we will always use Kohn-Sham density functional theory (KS-DFT) to get these orbitals. Note that for completeness, $\{\phi_i\}$ must in principle also contain scattering states, see Appendix A.1.1. The initial state $|N, i\rangle$ can then exactly be expressed as a linear combination of Slater determinants build from these orbitals (compare Appendix A.1.2). Later, we will choose the initial state to be either the (an) N -electron ground state, or a (bound) N -electron excited state. If we restrict ourselves to not-too-high-lying excited states (which is precisely the domain we work in, compare Sec. 2.4.4) and

⁸⁵We omitted spin here for simplicity. For photoelectron states that are spin-position product states, we additionally get an overlap of the spin-functions, see Sec. 3.3.7.

if we have used a sophisticated one-electron theory, the initial state is then usually composed of Slater determinants built from the energetically more low-lying bound orbitals.

Next, we focus on the photoelectron state, which we denote as usual as $|\gamma\rangle$ and normalize via Eq. 3.16. We can then define a corresponding creation operator $\hat{a}_\gamma^\dagger$ and annihilation operator $\hat{a}_\gamma$ and write the final state as (compare Eq. A.32):

$$\frac{1}{\sqrt{N!}} \hat{\mathcal{A}}(|\gamma\rangle \otimes |N-1, f\rangle) = \hat{a}_\gamma^\dagger |N-1, f\rangle \quad (3.17)$$

When using photoelectron states obtained as scattering solutions of the Kohn-Sham equation (see Sec. 3.3.4), these scattering states (and creation/annihilation operators) are simply the scattering states (and corresponding operators) mentioned in the beginning of this section. Conversely, in the plane-wave approximation of Sec. 3.3.7, they are plane waves with corresponding operators. To incorporate the various approaches, we write the photoelectron state $|\gamma\rangle$ in a general form by expressing it as linear combination of the one-electron orbitals $\{\phi_i\}$:

$$\begin{aligned} |\gamma\rangle &= \sum_j c_j |\phi_j\rangle \\ \hat{a}_\gamma^\dagger &= \sum_j c_j \hat{a}_j^\dagger \\ \hat{a}_\gamma &= \sum_j c_j^* \hat{a}_j \end{aligned} \quad (3.18)$$

Finally, following Refs. [84, 87], we express the light-matter interaction $\mathbf{A} \cdot \hat{\mathbf{P}}$ in terms of creation and annihilation operators:

$$\begin{aligned} \hat{H}_{\text{int}} &= \sum_{l,m} h_{l,m}^{(\text{int})} \hat{a}_l^\dagger \hat{a}_m \\ h_{l,m}^{(\text{int})} &= \langle \phi_l | \mathbf{A} \cdot \hat{\mathbf{p}} | \phi_m \rangle \end{aligned} \quad (3.19)$$

Plugging everything into Fermi's golden rule Eq. 3.15, we get:

$$\begin{aligned} W_{i \rightarrow (f, \gamma)} &= 2\pi \left| \sum_j \sum_{l,m} c_j^* h_{l,m}^{(\text{int})} \langle N-1, f | \hat{a}_j \hat{a}_l^\dagger \hat{a}_m | N, i \rangle \right|^2 \\ &\quad \delta(\omega + E(N, i) - E(N-1, f) - E_{\text{kin}}) \end{aligned} \quad (3.20)$$

We now continue by neglecting terms $j \neq l$ (compare Ref. [84]). First, remember that we generally assume that the initial state consists mostly of low-lying bound orbitals. When using Kohn-Sham scattering orbitals as our photoelectron states, orthogonality of bound- and scattering states (see Sec. 3.3.4 and Appendix A.1.1) then tells us that action of $\hat{a}_j$ will annihilate the whole state it acts on, unless $l = j$. Conversely, in the plane-wave approximation, the linear combination in Eq. 3.18 will generally also contain bound-state contributions (simply calculate the overlap of a plane wave and a bound orbital to see this) and it is thus not immediately clear how we can justify neglecting terms $j \neq l$ in that case.

To better understand this approximation, note that comparison⁸⁶ with Ref. [132] shows that neglecting terms $j \neq l$ corresponds to singling out the contribution of direct photoemission to the transition rate and neglecting indirect contributions like the Auger effect. Thus, while the indirect terms $j \neq l$ do not vanish in the plane-wave approximation, we can justify neglecting them by the fact that we want to single out and focus on the contribution of direct photoemission to the photoemission signal.

Neglecting now these indirect terms the transition rate becomes:

$$W_{i \rightarrow (f, \gamma)} = 2\pi \left| \sum_j \sum_m c_j^* h_{j,m}^{(\text{int})} \langle N-1, f | \hat{a}_m | N, i \rangle \right|^2 \delta(\omega + E(N, i) - E(N-1, f) - E_{\text{kin}}) \quad (3.21)$$

Using Eqs. 3.18 and 3.19 we can then more compactly write:

$$W_{i \rightarrow (f, \gamma)} = 2\pi \left| \sum_m h_{\gamma,m}^{(\text{int})} \langle N-1, f | \hat{a}_m | N, i \rangle \right|^2 \delta(\omega + E(N, i) - E(N-1, f) - E_{\text{kin}}) \quad (3.22)$$

3.3.6 Dyson Orbital

We can write the transition rate Eq. 3.22 even more compactly when introducing the *Dyson orbital* $d_{i,f}(x)$:

$$\begin{aligned} h_{\gamma,d_{i,f}}^{(\text{int})} &= \sum_m h_{\gamma,m}^{(\text{int})} \langle N-1, f | \hat{a}_m | N, i \rangle \\ |d_{i,f}\rangle &= \sum_m |\phi_m\rangle \langle N-1, f | \hat{a}_m | N, i \rangle \\ d_{i,f}(x) &= \langle x | d_{i,f} \rangle = \langle N-1, f | \hat{\Psi}(x) | N, i \rangle, \end{aligned} \quad (3.23)$$

where we used the quantum field operator of Eq. 2.119 in the last line. Note that the given definition coincides with the definition of the Dyson orbital given e.g. in Ref. [132] (Eq. (8) there) which can for example be seen by expanding both quantities in our one-electron ONB $\{\phi_i\}$ and observing that they have the same expansion coefficients and are therefore equal (see Appendix D.1).

The transition rate then becomes:

$$W_{i \rightarrow (f, \gamma)} = 2\pi \left| h_{\gamma,d_{i,f}}^{(\text{int})} \right|^2 \delta(\omega + E(N, i) - E(N-1, f) - E_{\text{kin}}) \quad (3.24)$$

3.3.7 Plane-Wave Approximation

As mentioned in Sec. 3.3.4, we resort in our practical calculations shown below, to the simple (spin-) *plane-wave approximation* (PWA) for the photoelectron states,

⁸⁶Compare the “third approximation” in Ref. [132] which there leads from Eq. (4) to Eq. (9). Similarly, neglecting terms $j \neq l$ here leads from the same starting point to the same form of the matrix element, see Eq. 3.24.

which are then called *plane-wave final states* (PWFS) and read:

$$\begin{aligned}\gamma_{\mathbf{k}}(\mathbf{r}, s) &= \langle \mathbf{r}, s | \gamma_{\mathbf{k}, \sigma} \rangle = (2\pi)^{-3/2} e^{i\mathbf{k} \cdot \mathbf{r}} \sigma(s) \\ E_{\text{kin}} &= \frac{k^2}{2} \\ \sum_{s=\uparrow, \downarrow} |\sigma(s)|^2 &= 1,\end{aligned}\tag{3.25}$$

where the chosen normalization ensures (using Eq. A.51):

$$\begin{aligned}\langle \gamma_{\mathbf{k}, \sigma} | \gamma_{\mathbf{k}', \sigma'} \rangle &= \int_{\mathbb{R}^3} \sum_{s=\uparrow, \downarrow} (2\pi)^{-3} e^{-i\mathbf{k} \cdot \mathbf{r}} e^{i\mathbf{k}' \cdot \mathbf{r}} \sigma^*(s) \sigma'(s) \\ &= \delta(\mathbf{k} - \mathbf{k}') \sum_{s=\uparrow, \downarrow} \sigma^*(s) \sigma'(s)\end{aligned}\tag{3.26}$$

In the PWA, we describe the photoelectron as a completely free particle in empty space (compare Appendix A.4) and thereby neglects the influence of the remaining system on the photoelectron state, compare Sec. 3.3.4. For a pure spin-up (by convention in z direction) plane wave we use $\sigma(s) = \delta_{s, \uparrow}$ and equivalently $\sigma(s) = \delta_{s, \downarrow}$ for a spin-down plane-wave.

Clearly, the PWFS approximation works better at higher kinetic energies (i.e. at higher probe energies), since the potential of the remaining system then becomes a smaller term relative to the kinetic-energy part of the Hamiltonian, such that the Hamiltonian is effectively closer to that of a free particle. Similarly, it should work better for photoemission *of electrons that are already at the interface of the system to the vacuum*, since electrons emitted from there would then be less affected by a potential of the nuclei or other electrons (compare Sec. 3.3.4). Examples for this are electrons emitted from π orbitals of planar, flat-lying molecules adsorbed on some substrate [33]. More generally, however, the PWA has been proven successful (for probe-energies in the 15–50 eV probe-energy range) in ground-state POT of organic molecular layers [133–135], as well as 2D materials [136, 137]. Similarly, its usability for exciton POT has been shown in Ref. [16].

Continuing in the PWFS, the matrix element in the transition rate Eq. 3.24 then becomes

$$\begin{aligned}h_{\gamma_{\mathbf{k}, \sigma}, d_{i, f}}^{(\text{int})} &= \langle \gamma_{\mathbf{k}, \sigma} | \mathbf{A} \cdot \hat{\mathbf{p}} | d_{i, f} \rangle \\ &= -i \sum_{s=\uparrow, \downarrow} (2\pi)^{-3/2} \int_{\mathbb{R}^3} d^3r e^{-i\mathbf{k} \cdot \mathbf{r}} \sigma^*(s) \mathbf{A} \cdot \nabla d_{i, f}(\mathbf{r}, s) \\ &= -\mathbf{A} \cdot \mathbf{k} \sum_{s=\uparrow, \downarrow} (2\pi)^{-3/2} \int_{\mathbb{R}^3} d^3r e^{-i\mathbf{k} \cdot \mathbf{r}} \sigma^*(s) d_{i, f}(\mathbf{r}, s),\end{aligned}\tag{3.27}$$

where we used partial integration and dropped surface terms to get to the last line⁸⁷. We can identify the integral in the last line as the Fourier transform Eq. A.52

⁸⁷For gas-phase systems as well as finitely-sized periodic systems (from where we can then perform the thermodynamic limit), the Dyson orbital (built from a bound N and $N - 1$ -electron state) can be expected to vanish at infinity, which becomes particularly clear in the variant of the Dyson orbital given in Ref. [132].

and thus find:

$$\begin{aligned} h_{\gamma\mathbf{k},\sigma,d_{i,f}}^{(\text{int})} &= -\mathbf{A} \cdot \mathbf{k} \mathcal{F} \left[d_{i,f}^{(\sigma)} \right] (\mathbf{k}) \\ d_{i,f}^{(\sigma)}(\mathbf{r}) &= \sum_{s=\uparrow,\downarrow} \sigma^*(s) d_{i,f}(\mathbf{r}, s), \end{aligned} \quad (3.28)$$

where $d_{i,f}^{(\sigma)}$ denotes the spin-projected Dyson orbital. The transition rate then becomes:

$$W_{i \rightarrow (f, (\mathbf{k}, \sigma))} = 2\pi |\mathbf{A} \cdot \mathbf{k}|^2 \left| \mathcal{F} \left[d_{i,f}^{(\sigma)} \right] (\mathbf{k}) \right|^2 \delta(\omega + E(N, i) - E(N - 1, f) - E_{\text{kin}}) \quad (3.29)$$

Note that the prefactor $|\mathbf{A} \cdot \mathbf{k}|^2$ is a distinct result of the PWA and will appear many times below. It controls the influence of the probe-polarization on the PWA photoemission distribution $I(\mathbf{k}, \sigma)$ (see e.g. Eq. 3.39) and will due to its simple and always-same appearance not be explicitly mentioned in the discussion of the various PWA photoemission expressions given below.

3.3.8 Photoemission Intensity

Until now, we have focused on the transition rate $W_{i \rightarrow (f, \gamma)}$ from some initial state to a specific final state, given by the antisymmetrized product of some photoelectron state $|\gamma\rangle$ and a specific eigenstate $|N - 1, f\rangle$ of the remaining $N - 1$ -electron system. In a photoemission experiment, the photoelectron then hits the detector, while the remaining system remains “untouched”, that is, the experiment does not measure in which state the system remains after photoemission. Therefore, to calculate the photoemission intensity for some specific photoelectron state and initial state, we have to sum up the transition rates, Eq. 3.24, over all eigenstates of the $N - 1$ -electron system⁸⁸:

$$I_{i \rightarrow \gamma} = C \sum_f \left| h_{\gamma, d_{i,f}}^{(\text{int})} \right|^2 \delta(\omega + E(N, i) - E(N - 1, f) - E_{\text{kin}}) \quad (3.30)$$

Note that we have included an overall constant C (which is independent of $|\gamma\rangle$ but may depend – via the absorption rates – on the initial state) that accounts for influences like the (pump- and) probe pulse intensity and -absorption rate as well as the duration of the experiment. In the calculation of relative photoemission intensities for different photoelectron states $\{\gamma\}$ this constant can be dropped such that we obtain:

$$I_{i \rightarrow \gamma} \propto \sum_f \left| h_{\gamma, d_{i,f}}^{(\text{int})} \right|^2 \delta(\omega + E(N, i) - E(N - 1, f) - E_{\text{kin}}) \quad (3.31)$$

Finally, when identifying one photoelectron state $\gamma_{\mathbf{k},s}$ with each photoelectron momentum $\mathbf{k}$ and spin $s = \uparrow / \downarrow$ (see Sec. 3.3.4; in the PWA, Sec. 3.3.7, we can

⁸⁸These eigenstates form an orthonormal basis of the $N - 1$ -electron system. From the probability-based derivation of Fermi’s golden rule (Ref. [126]) and its use with N -electron final states in the sudden approximation (Appendix D.3) it then becomes clear that summing over the $N - 1$ -electron eigenstates gives us the transition probability – and further the transition rate – to a specific photoelectron state.

trivially choose them to be pure spin-up/down), we then get the relative intensity of different photoelectron momenta and spins via:

$$I_i(\mathbf{k}, s) \propto \sum_f \left| h_{\gamma, \mathbf{k}, s, d_{i,f}}^{(\text{int})} \right|^2 \delta(\omega + E(N, i) - E(N - 1, f) - E_{\text{kin}}) \quad (3.32)$$

Note that, in analogy to the comments given below Eq. 3.10, the expression Eq. 3.32 should formally be understood as a photoemission intensity *density*, which then allows us to calculate the photoemission intensity for a group of final states. Details can again be found in Appendix D.3, see for example Eq. D.53.

On a final, technical point, note that in the case of degenerate $N - 1$ -electron final states, the choice of the subspace basis does not influence the resulting photoemission intensity! Suppose we have a subspace of g degenerate $N - 1$ -electron final states. Focusing on the matrix-element-part (since the delta function is the same for all the degenerate states in the subspace) we find:

$$\begin{aligned} |N - 1, j\rangle &\equiv \sum_{l=1}^g U_{j,l} |N - 1, \tilde{l}\rangle \\ \sum_{j=1}^g \left| h_{\gamma, d_{i,j}}^{(\text{int})} \right|^2 &= \sum_{j=1}^g \left| \sum_m h_{\gamma, m}^{(\text{int})} \langle N - 1, j | \hat{a}_m | N, i \rangle \right|^2 \\ &= \sum_{j=1}^g \left| \sum_{l=1}^g U_{j,l}^* \sum_m h_{\gamma, m}^{(\text{int})} \langle N - 1, \tilde{l} | \hat{a}_m | N, i \rangle \right|^2 \\ &= \sum_{j=1}^g \left| \sum_{l=1}^g U_{j,l}^* h_{\gamma, d_{i,\tilde{l}}}^{(\text{int})} \right|^2 \\ &= \sum_{j=1}^g \sum_{l=1}^g U_{j,l}^* h_{\gamma, d_{i,\tilde{l}}}^{(\text{int})} \sum_{n=1}^g U_{j,n} h_{\gamma, d_{i,\tilde{n}}}^{(\text{int})*} \\ &= \sum_{l=1}^g h_{\gamma, d_{i,\tilde{l}}}^{(\text{int})} \sum_{n=1}^g h_{\gamma, d_{i,\tilde{n}}}^{(\text{int})*} \sum_{j=1}^g U_{j,l}^* U_{j,n} \\ &= \sum_{l=1}^g h_{\gamma, d_{i,\tilde{l}}}^{(\text{int})} \sum_{n=1}^g h_{\gamma, d_{i,\tilde{n}}}^{(\text{int})*} \sum_{j=1}^g U_{l,j}^{-1} U_{j,n} \\ &= \sum_{l=1}^g \left| h_{\gamma, d_{i,\tilde{l}}}^{(\text{int})} \right|^2, \end{aligned} \quad (3.33)$$

where we used Eq. 3.23.

3.3.9 Ground-state POT

We are now finally at the point where we can give practical expressions to calculate the photoemission intensity distribution I . We start with photoemission from the ground state, that is:

$$|N, i\rangle = |N, 0\rangle \quad (3.34)$$

Let us start with the general expression Eq. 3.32 for the photoemission intensity, so with an arbitrary photoelectron state of momentum $\mathbf{k}$ and spin s :

$$I_0(\mathbf{k}, s) \propto \sum_f \left| h_{\gamma\mathbf{k},s,d_{0,f}}^{(\text{int})} \right|^2 \delta(\omega + E(N, 0) - E(N - 1, f) - E_{\text{kin}}) \quad (3.35)$$

Note that the Dyson orbital here takes the form (see Eq. 3.23):

$$d_{0,f}(x) = \langle x | d_{0,f} \rangle = \langle N - 1, f | \hat{\Psi}(x) | N, 0 \rangle \quad (3.36)$$

Comparing with Eq. 2.132, we can identify this with the electron-removal Lehmann amplitude $f_f^-(x)$. Similarly, using Eq. 2.133 we can identify the electron-removal energy $\varepsilon_f^- = E(N, 0) - E(N - 1, f)$ in the delta function. This strong relation of the photoelectron intensity to the one-particle Green's function and the spectral function has already been illuminated in Sec. 2.3.3.

In the quasiparticle approximation (see Sec. 2.3.6), which is in fact motivated by observations made in photoemission experiments, we then replace the sum over exact eigenstates $\{|N - 1, f\rangle\}$ by a sum over quasiparticle states⁸⁹, with quasiparticle orbitals replacing the Dyson orbitals (see Eq. 2.172). In practice, the quasiparticle orbitals are usually not explicitly calculated, but we instead simply use the one-electron orbitals already mentioned in Sec. 3.3.5, which will typically be (occupied) Kohn-Sham orbitals. Concomitantly, the exact electron-removal energies $\{\varepsilon_f^-\}$ are replaced by the quasiparticle energies (where typically only the real part of the complex quasiparticle energy is used), such that we have $E_{\text{kin}} = \omega + \varepsilon_v$, where ε_v is the energy of the “removed quasielectron”, that is, the v -th quasiparticle energy. These are in practice either calculated on a GW level, or replaced by Kohn-Sham energies, where we are often limited to the use of Kohn-Sham energies for computational reasons. As mentioned in Sec. 2.3.7, KS energies are often sufficient for the study of photoemission spectra, can, however, not be trusted blindly [103]. Lastly, while details on the validity of the quasiparticle approximation can be found in Sec. 2.3.6, the presented approach has proven highly successful, compare for example the references given in Sec. 3.3.7.

Gas-Phase Calculations

For *gas-phase* calculations, we then sum over the discrete occupied/valence orbitals $\{\phi_v\}$ with energies ε_v and get for the photoemission intensity (starting from Eq. 3.35):

$$I_0(\mathbf{k}, s) \propto \sum_v \left| h_{\gamma\mathbf{k},s,\phi_v}^{(\text{int})} \right|^2 \delta(\omega + \varepsilon_v - E_{\text{kin}}) \quad (3.37)$$

In the PWA this becomes (compare Eq. 3.29):

$$I_0(\mathbf{k}, s) \propto |\mathbf{A} \cdot \mathbf{k}|^2 \sum_v \left| \mathcal{F}[\phi_v^{(s)}](\mathbf{k}) \right|^2 \delta(\omega + \varepsilon_v - E_{\text{kin}}), \quad (3.38)$$

⁸⁹Note that we do not need to explicitly derive the form of these quasiparticle states. It is sufficient to assume their existence and that they satisfy Eq. 2.172. Thus, it is here not necessary to use the states given in Eq. 2.174 and thus, which was an assumption of Eq. 2.174, we do not need to restrict ourselves to a weakly correlated ground state. Details on the normalization of these states can be found in Appendix D.3.

where the spin-dependence enters via the photoelectron state, see Eq. 3.28. Further, if our KS orbitals are spin-unpolarized and spin-paired (see text around Eq. 2.101 and Footnote 76) then we find $I_0(\mathbf{k}, \uparrow) = I_0(\mathbf{k}, \downarrow) \equiv I_0(\mathbf{k})$. It is then sufficient to use spatial orbitals $\{\varphi\}$ to obtain (v here indexes the spatial orbitals instead of spin-orbitals):

$$I_0(\mathbf{k}) \propto |\mathbf{A} \cdot \mathbf{k}|^2 \sum_v |\mathcal{F}[\varphi_v](\mathbf{k})|^2 \delta(\omega + \varepsilon_v - E_{\text{kin}}) \quad (3.39)$$

Out of all the variants, Eq. 3.39 is what we will use later for practical calculations. As we can see, the photoemission intensity based on this formulation has a very simple structure: for a fixed probe energy ω , each orbital can contribute at some specific kinetic energy given by $E_{\text{kin}} = \omega + \varepsilon_v$. The momenta $\mathbf{k}$ at which photoemission from this orbital occurs are then points on a hemisphere (with $k_z > 0$, since we want to simulate photoemission from surfaces, see below) with radius $k = \sqrt{2E_{\text{kin}}}$. The resulting k-map can thus be thought of as a hemispherical cut through the Fourier-transformed orbital, justifying the methods name *photoemission orbital tomography*. See Appendix D.3 for further details. Thus, for a given ω , we get one k-map per orbital, located at $E_{\text{kin}} = \omega + \varepsilon_v$.

Note that we can also use Eq. 3.39 to simulate photoemission from the system’s (low-lying, see Sec. 2.3.6) unoccupied/conduction orbitals, starting from the LUMO (lowest unoccupied molecular orbital). Formally, the usage of Eq. 3.39 is then justified by assuming that the orbitals are filled in the ground state, making them effectively valence orbitals and thereby including them in the set of valence orbitals used in the derivation given above (In principle, we can even assume that e.g. the LUMO+1 is filled, while the LUMO is not, which may happen if (gas-phase-)DFT orders the orbitals incorrectly.). Physically, this is justified by the fact that we use gas-phase calculations to simulate photoemission from molecules adsorbed onto a substrate (see below), and electronic charge-transfer from the substrate (often metallic) – which is missing in the gas-phase calculation – to the molecules may fill up initially (meaning: in the case of an isolated molecule) unoccupied molecular orbitals (typically in energetic order obtained from gas-phase Kohn-Sham DFT), making them “visible” in ARPES experiments. The same holds for ground-state POT of periodic systems (see below) and can for example be seen in Figs. 5.2 and 4.5.

Finally, note that it is also common [121] to express the energy conservation not in terms of quasiparticle energies, but in terms of the related *ionization energies*, such that then energy-conservation instead reads as $\delta(\omega - \varepsilon_v - E_{\text{kin}})$. The sign-change is explained below Eq. 2.134.

Periodic Calculations

While gas-phase calculations can serve as a first step to simulate the photoemission from molecules adsorbed on some substrate (by rotating the molecule to the same orientation it would have on the substrate, see also Sec. 3.3.11), they neglect interactions of the molecule with the substrate (on the electronic and often also geometric level). Additionally, if only a single molecule (or a too small cluster) is used, possibly important inter-molecular interactions are not (sufficiently) accounted for. For more sophisticated photoemission simulations of molecular films, as well as for 2D semiconductors, *periodic* calculations can then be used.

We start by modelling our system as a macroscopic but finite (thin) surface, such that the bound KS orbitals can to good approximation be described via Bloch orbitals on a discrete Bloch momentum grid (see Appendix A.1.1 for details). Replacing the discrete orbitals used above by the so-obtained valence-band Bloch orbitals $\{\phi_{v,\mathbf{q}}\}$ with energies $\{\varepsilon_{v,\mathbf{q}}\}$, we get for the photoemission intensity for generic photoelectron states:

$$I_0(\mathbf{k}, s) \propto \sum_{\mathbf{q}} \sum_v^{\text{BZ}} \left| h_{\gamma\mathbf{k},s,\phi_{v,\mathbf{q}}}^{(\text{int})} \right|^2 \delta(\omega + \varepsilon_{v,\mathbf{q}} - E_{\text{kin}}) \quad (3.40)$$

Note that we here assume the system to be gapped, such that we have only fully filled bands – the valence bands – and fully empty bands – the conduction bands. These are the systems we will meet in practice later. In the PWA we further get:

$$I_0(\mathbf{k}, s) \propto |\mathbf{A} \cdot \mathbf{k}|^2 \sum_{\mathbf{q}} \sum_v^{\text{BZ}} |\mathcal{F}[\phi_{v,\mathbf{q}}^s](\mathbf{k})|^2 \delta(\omega + \varepsilon_{v,\mathbf{q}} - E_{\text{kin}}) \quad (3.41)$$

For spin-unpolarized and spin-paired systems we then find (compare Eq. (4) in Ref. [35]):

$$I_0(\mathbf{k}) \propto |\mathbf{A} \cdot \mathbf{k}|^2 \sum_{\mathbf{q}} \sum_v^{\text{BZ}} |\mathcal{F}[\varphi_{v,\mathbf{q}}](\mathbf{k})|^2 \delta(\omega + \varepsilon_{v,\mathbf{q}} - E_{\text{kin}}) \quad (3.42)$$

This is the variant we will use later.

We can further simplify Eq. 3.42 by using crystal-momentum conservation: To see this we follow Appendix D.2 and initially restrict ourselves to photoelectron states that are periodic at the ends of the macroscopic finite surface, such that their in-plane Bloch momenta $\mathbf{q}_\gamma$ are restricted to the same grid as those of the bound KS states used above. That is, the allowed photoelectron momenta take the form

$$\mathbf{k} = \mathbf{q}_\gamma + \mathbf{G}_{\gamma,\parallel} + \mathbf{e}_z k_z, \quad (3.43)$$

where $\mathbf{G}_{\gamma,\parallel}$ is an in-plane reciprocal lattice vector. Comparison with Appendix D.2 and in particular Eq. D.42 then gives us

$$I_0(\mathbf{k}) \propto |\mathbf{A} \cdot \mathbf{k}|^2 \sum_v \left| \sum_{\mathbf{G}} c_{v,\mathbf{q}_\gamma}(\mathbf{G}) \int_{A_c} d^2 r_{\parallel} \int_0^L dz e^{i\mathbf{G} \cdot \mathbf{r}} e^{-i\mathbf{G}_{\gamma,\parallel} \cdot \mathbf{r}_{\parallel}} e^{-ik_z z} \right|^2 \delta(\omega + \varepsilon_{v,\mathbf{q}_\gamma} - E_{\text{kin}}), \quad (3.44)$$

which can be further evaluated to:

$$I_0(\mathbf{k}) \propto |\mathbf{A} \cdot \mathbf{k}|^2 \sum_v \left| \sum_{G_z} c_{v,\mathbf{q}_\gamma}(\mathbf{G}_{\gamma,\parallel} + \mathbf{e}_z G_z) \int_0^L dz e^{i(G_z - k_z)z} \right|^2 \delta(\omega + \varepsilon_{v,\mathbf{q}_\gamma} - E_{\text{kin}}) \quad (3.45)$$

Finally, as detailed in Appendix D.2.2 this expression stays well-defined when approaching an infinite surface again, such that the restriction on the photoelectron

momenta is lifted and they become effectively continuous again. Compared to Eq. 3.42 we have thus eliminated the sum over the Brillouin zone which will significantly improve computational efficiency when implementing the formalism, see Sec. 3.3.11.

Note also that in the above equations, $c_{v,\mathbf{q}_\gamma}(\mathbf{G})$ denotes the plane-wave expansion coefficients of $u_{v,\mathbf{q}_\gamma}$ (actually, $\tilde{u}_{v,\mathbf{q}_\gamma}$, see Appendix D.2.2 for the difference in normalization). While such an expansion can generally be performed, it is already clear from the appearance of the coefficients that plane-wave code packages in combination with a repeated-slab approach form the optimal basis for our formalism, since we directly obtain these coefficients in such an approach!

We will return to Eq. 3.45 later to show how it is used in practice. For now, let us briefly analyze what we have found. First, remember that $I_0(\mathbf{k})$ is (proportional to) the number of photoelectrons with momentum $\mathbf{k}$ that are emitted from the ground state. For a given photoelectron momentum $\mathbf{k}$, the photoemission intensity is intrinsically connected to the valence orbitals at the Bloch momentum $\mathbf{q}_\gamma$. That is, only the Bloch orbitals $\{\varphi_{v,\mathbf{q}_\gamma}\}_v$ can contribute to the photoemission intensity at $\mathbf{k}$. Additionally, photoemission is then only possible if $E_{\text{kin}} = \frac{k^2}{2} = \omega + \varepsilon_{v,\mathbf{q}_\gamma}$ for any of the valence bands v . Further, we can also look at Eq. 3.45 from the point of view of the system's valence bands: for valence band v , photoemission at the in-plane photoelectron momenta k_x and k_y is connected to the single Bloch orbital $\varphi_{v,\mathbf{q}_\gamma}$ with $k_{x/y} = \mathbf{q}_{\gamma,x/y} + \mathbf{G}_{\gamma,x/y}$ and can only appear at $E_{\text{kin}} = \frac{k^2}{2} = \omega + \varepsilon_{v,\mathbf{q}_\gamma}$ ($k_z = \sqrt{2(\omega + \varepsilon_{v,\mathbf{q}_\gamma}) - k_x^2 - k_y^2}$). When thinking of molecular systems, where the highest valence band can often be identified with the gas-phase HOMO of a single isolated molecule, the photoemission signal from this band then usually appears as the gas-phase HOMO k-map, with different parts of the k-map appearing at different kinetic energies, in accordance with the HOMO's band structure. Compare also Appendix D.3.3 which explains how the momentum map may be pieced together again, if desired.

Note also, that from the above conditions it may first appear that a momentum map at a given kinetic energy should be rather empty, after all $E_{\text{kin}} = \frac{k^2}{2} = \omega + \varepsilon_{v,\mathbf{q}_\gamma}$ is likely only (exactly) satisfied for few to no photoelectron momenta on the hemisphere defined by E_{kin} . At this point it is thus important to remember again that $I_0(\mathbf{k})$ as presented here is strictly speaking an intensity *density*. Real momentum maps instead show the intensity for photoelectrons on a finite kinetic-energy interval δE_{kin} and are in practice calculated by replacing the Dirac delta with a Gaussian $\exp\left(-\frac{[E_{\text{kin}} - (\omega + \varepsilon_{v,\mathbf{q}_\gamma})]^2}{2\sigma_E^2}\right)$, compare Appendix D.3. Note also, that this Gaussian broadening of the delta function can also be used in the gas-phase (ground-state POT and exPOT) calculations in order to mimic experimental conditions. As long as valence-orbitals are energetically separated such that only a single valence orbital contributes significantly (considerable Gaussian weight) at a given kinetic energy it is however not necessary from a computational viewpoint, since the k-maps are not “split up” by a band dispersion, that is, each valence orbital there leads to a complete k-map at a given kinetic energy and in principle zero photoemission anywhere else (when neglecting broadening).

3.3.10 Exciton POT

The second type of initial state we are interested in are *excitons*, a specific type of N -electron excited states which can be characterized by a correlated electron-hole pair (see Sec. 2.4.4 for details) which is used as an approximate eigenstate in Fermi's golden rule (in practice: long-lived, such that finite-lifetime-effects like energy-broadening or its decay can be neglected). The resulting formalism is termed *exciton POT*, or *exPOT* and was first published in Ref. [34], where it was formulated for gas-phase calculations as detailed in the following.

Gas-Phase Calculations

We start again with gas-phase calculations, where the exciton initial state is given as a sum over valence and conduction orbitals:

$$|N, i\rangle = |N, m\rangle = \sum_v \sum_c X_{v,c}^m \hat{a}_c^\dagger \hat{a}_v |N, 0\rangle \quad (3.46)$$

Note that we assume here that the initial state is the m -th exciton state of the system, following the notation⁹⁰ of Ref. [34]. Also note that the exciton state is written in the *Tamm-Dancoff approximation* (TDA) (thereby neglecting de-excitations) and under the assumption of a weakly correlated ground state (compare Eq. 2.226). We will get back to this later.

The Dyson orbital Eq. 3.23 for final state $|N - 1, f\rangle$ then becomes

$$d_{m,f}(x) = \sum_j \sum_v \sum_c X_{v,c}^m \phi_j(x) \langle N - 1, f | \hat{a}_j \hat{a}_c^\dagger \hat{a}_v | N, 0 \rangle, \quad (3.47)$$

where j runs over all orbitals, valence and conduction (omitting, as usual, scattering states, compare Appendix C.1.1). We now apply two approximations: (1) we assume that the final state can be expressed as $\hat{a}_f |N, 0\rangle$, i.e. as the annihilation operator for orbital f acting on the ground state (compare Eq. 2.174) and (2) we assume that the ground state is (close to) a single Slater determinant built from the valence orbitals⁹¹. We then get (using the orthonormality of the orbitals):

$$\langle N - 1, f | \hat{a}_j \hat{a}_c^\dagger \hat{a}_v | N, 0 \rangle = \langle N, 0 | \hat{a}_f^\dagger \hat{a}_j \hat{a}_c^\dagger \hat{a}_v | N, 0 \rangle = \delta_{v,f} \delta_{j,c} \quad (3.48)$$

Thus, f must refer to a valence orbital! Indexing the final state by the valence orbital v it annihilates from the ground state, the Dyson orbital becomes:

$$d_{m,v}(x) = \sum_c X_{v,c}^m \phi_c(x) \quad (3.49)$$

⁹⁰Note that in Sec. 2.4 we followed the matrix-notation used in Appendix C, where excitations were written as $X_m^{v,c}$ and $X_{m,\mathbf{Q}}^{v,c,\mathbf{q}}$. From hereon, we follow the notation of Refs. [34] and [121], thus writing them as $X_{v,c}^m$ for gas-phase systems and $X_{v,c,\mathbf{q}}^m$ for periodic systems.

⁹¹As mentioned below, this approximation is also implicitly used in other places throughout this derivation. Even though it therefore poses a slight inconsistency with other expressions used (e.g. with Eq. 3.46), we may go beyond a single Slater determinant ground state (as suggested in Ref. [34]) and write it instead as a sum of Slater determinants (compare Eq. 2.176). Using a final state $\hat{a}_{v'} |N, 0\rangle$ and an initial state Eq. 3.46, the matrix element $\langle N, 0 | \hat{a}_{v'}^\dagger \hat{a}_j \hat{a}_c^\dagger \hat{a}_v | N, 0 \rangle$ must then be expanded and becomes a double-sum over Slater determinants and the whole formalism becomes more cumbersome. While this may be beneficial for systems with moderately-correlated ground states (at highly-correlated ground states, the other expressions used here may become problematic), we keep the following derivation simple and consistent, thus restricting ourselves to a single Slater determinant ground state built from occupied KS orbitals.

For completeness, note that we in principle do not need to use the form Eq. 3.46 to arrive at the Dyson orbital Eq. 3.49. As outlined in Sec. 2.4.4, we do not necessarily need to know the exact form of the exciton states, but merely need to assume they can in principle be constructed and that they satisfy Eq. 2.221. Using, as before, a final state $\hat{a}_f |N, 0\rangle$ and denoting the effective exciton state as $|N, m\rangle$, the Dyson orbital becomes

$$\begin{aligned} d_{m,f}(x) &= \sum_j \phi_j(x) \langle N, 0 | \hat{a}_f^\dagger \hat{a}_j | N, m \rangle \\ &= \begin{cases} \sum_c X_{v,c}^m \phi_c(x) & \text{if } f = v \\ \sum_v Y_{v,c}^m \phi_v(x) & \text{if } f = c, \end{cases} \end{aligned} \quad (3.50)$$

where we used Eq. 2.221. This way, de-excitations can in principle be incorporated into the formalism. Note that, following the energy conservation outlined below, the de-excitation-based signal is expected to occur at kinetic energies determined by the conduction orbitals, and thus be separated energetically from the excitation-based signal discussed below (with the de-excitation-based signal occurring at higher kinetic energies). This justifies the computational approach we will occasionally take later, where Bethe-Salpeter equation (BSE) calculations are performed beyond the TDA, we however only take excitations into account when simulating exciton photoemission⁹² (see Chapter 6). Note also, that this way we can drop the assumption of a weakly correlated ground state when introducing the effective exciton state (which was needed for the derivation of Eq. 2.226). For the case $f = v$ of Eq. 3.50, so the excitation-based signal, approximating the ground state as a single Slater determinant is, however, still intrinsic to the form of the (quasiparticle) final state $\hat{a}_v |N, 0\rangle$, as outlined around Eq. 2.174. Thus (remembering additionally that under the assumption of a single Slater determinant ground state we cannot have de-excitations, see text below Eq. 2.221), the exciton states Eq. 3.46 may be seen as a more consistent description relative to the used (“valence-hole”) final states. For the case $f = c$, so the de-excitation-based signal, it should be noted that the final states $\{\hat{a}_c |N, 0\rangle\}$ were not included in the KS-quasiparticle expansions of G_1 (compare Eq. 2.174) and L_0 (compare Eq. 2.209). Just like the de-excitations, such states are only allowed if the ground state is correlated, that is, it contains also excited determinants (compare Eq. 2.176). We will not dive any deeper into the validity of these “conduction-hole” final states and the de-excitation-based signal, but acknowledge, that closer examination thereof poses an interesting path for future work! For the systems studied later, de-excitations only form a minor contribution to the BSE eigenvector (compare Eq. 5.3) and we thus focus from hereon again on the excitation-based signal, thus continuing the derivation from Eq. 3.49.

Following Eq. 2.183, we write the initial state energy as $E(N, i) = E(N, 0) + \Omega_m$ with Ω_m denoting the excitation energy of the m -th exciton. In analogy to the quasiparticle approximation used in ground-state POT, the energy of the final state $|N - 1, f\rangle = |N - 1, v\rangle = \hat{a}_v |N, 0\rangle$ is expressed in terms of the quasiparticle energy of orbital v , such that $E(N - 1, f) = E(N, 0) - \varepsilon_v$ and the transition rate Eq. 3.24 to this specific final state and an arbitrary photoelectron state $|\gamma\rangle$

⁹²The fact that X_m is then not normalized to 1, see Eq. C.71, is of no harm, since exPOT only gives relative photoemission intensities anyway, see e.g. Eq. 3.54.

becomes:

$$W_{i=m \rightarrow (v,\gamma)} = 2\pi \left| h_{\gamma,d_{m,v}}^{(\text{int})} \right|^2 \delta(\omega + \Omega_m + \varepsilon_v - E_{\text{kin}}) \quad (3.51)$$

To get the photoelectron intensity according to Eq. 3.32 we sum over all final states, that is, over all valence orbitals, and get for a photoelectron state of momentum $\mathbf{k}$ and spin s :

$$I_{i=m}(\mathbf{k}, s) \propto \sum_v \left| h_{\gamma\mathbf{k},d_{m,v}}^{(\text{int})} \right|^2 \delta(\omega + \Omega_m + \varepsilon_v - E_{\text{kin}}) \quad (3.52)$$

In the PWA, this becomes (using the linearity of the Fourier transform):

$$I_{i=m}(\mathbf{k}, s) \propto |\mathbf{A} \cdot \mathbf{k}|^2 \sum_v \left| \sum_c X_{v,c}^m \mathcal{F}[\phi_c^{(s)}](\mathbf{k}) \right|^2 \delta(\omega + \Omega_m + \varepsilon_v - E_{\text{kin}}) \quad (3.53)$$

Further, if our KS orbitals are spin-unpolarized and spin-paired (see text around Eq. 2.101 and Footnote 76) and our exciton is a spin-singlet exciton whose BSE eigenvector then satisfies Eq. 2.235, we find $I_{i=m}(\mathbf{k}, \uparrow) = I_{i=m}(\mathbf{k}, \downarrow) \equiv I_{i=m}(\mathbf{k})$. The same holds for the spin-triplet ($v \uparrow c \uparrow + v \downarrow c \downarrow$) while for ($v \uparrow c \downarrow$) we find $I_{i=m}(\mathbf{k}, \downarrow) \equiv I_{i=m}(\mathbf{k})$ and $I_{i=m}(\mathbf{k}, \uparrow) = 0$ and for ($v \downarrow c \uparrow$) we find $I_{i=m}(\mathbf{k}, \uparrow) \equiv I_{i=m}(\mathbf{k})$ and $I_{i=m}(\mathbf{k}, \downarrow) = 0$ (compare Refs. [36, 120]). With $I_{i=m}(\mathbf{k})$ as defined now for the different situations – in practice we focus herein on singlet excitons – it is then again sufficient to use spatial orbitals $\{\varphi\}$ to obtain (v and c here index the spatial orbitals instead of spin-orbitals) and we find:

$$I_{i=m}(\mathbf{k}) \propto |\mathbf{A} \cdot \mathbf{k}|^2 \sum_v \left| \sum_c X_{v,c}^m \mathcal{F}[\varphi_c](\mathbf{k}) \right|^2 \delta(\omega + \Omega_m + \varepsilon_v - E_{\text{kin}}) \quad (3.54)$$

This final variant is what we will use later for practical calculations. In terms of this formulation, photoemission from an exciton can then be understood as follows: For a given probe energy ω and starting from exciton m , photoemission can occur at kinetic energies $\{E_{\text{kin}} = \omega + \Omega_m + \varepsilon_v\}_v$, each corresponding to one of the *valence* orbitals which contribute to the exciton and where the photohole can thus reside after photoemission. Conversely, the k-map at each of these energies is given by a linear combination of Fourier-transformed *conduction* orbitals, which can be thought of as the orbitals from which the (photo)electron was taken (in contrast to ground-state POT, where the photoelectron can be thought of as having been taken from a valence orbital). The correlated nature of the exciton initial state is encapsulated in this linear combination via the BSE eigenvector X^m and leads to the coherent superposition of conduction orbitals, such that resulting k-maps can in principle significantly differ from those of the individual contributing conduction orbitals. As in ground-state POT, the one-electron orbitals are usually (and in the upcoming applications: always) Kohn-Sham DFT orbitals, namely the orbitals based on which the BSE is solved and the BSE eigenvectors and exciton energies are obtained. For the orbital energies, we usually (in applications below, again, always) take GW-level quasiparticle energies. See Sec. 3.3.11 for details.

Periodic Calculations

As in ground-state POT, the exPOT formalism can readily be extended to periodic calculations. The following derivation is based on Ref. [121], where exPOT was first extended to periodic calculations by the author of this thesis and Christian S. Kern, with auxiliary input from the remaining co-authors of that manuscript. Throughout the derivation we assume our system to be gapped, that is, we assume its KS ground state to be given by fully filled *valence* bands and fully empty *conduction* bands. Additionally, we again start with a macroscopic but finite (thin) surface, such that the bound states are Bloch(-like) orbitals on a discrete grid of Bloch momenta.

Compared to Eq. 3.46 for non-periodic systems, the expression for the initial state $|N, i\rangle$ now involves an additional sum over the crystal momentum $\mathbf{q}$ (compare Eq. 2.232),

$$|N, i\rangle = |N, (m, \mathbf{Q})\rangle = \sum_{\mathbf{q}} \sum_v \sum_c^{\text{BZ}} X_{v,c,\mathbf{q}}^{(m,\mathbf{Q})} \hat{a}_{c,\mathbf{q}+\mathbf{Q}}^\dagger \hat{a}_{v,\mathbf{q}} |N, 0\rangle, \quad (3.55)$$

and represents the m -th exciton with center-of-mass momentum $\mathbf{Q}$. Note that we again restrict ourselves to the TDA, which is commonly used for periodic systems [118] (compare also the discussion around Eq. 3.50). The Dyson orbital Eq. 3.23 for a generic final state $|N-1, f\rangle$ becomes (expressing the quantum field operator in Bloch orbitals $\{\phi_{j,\mathbf{q}'}\}$, where j runs over all valence and conduction bands):

$$d_{(m,\mathbf{Q}),f}(x) = \sum_{\mathbf{q}'} \sum_j \sum_{\mathbf{q}} \sum_v \sum_c^{\text{BZ}} X_{v,c,\mathbf{q}}^{(m,\mathbf{Q})} \phi_{j,\mathbf{q}'}(x) \langle N-1, f | \hat{a}_{j,\mathbf{q}'} \hat{a}_{c,\mathbf{q}+\mathbf{Q}}^\dagger \hat{a}_{v,\mathbf{q}} | N, 0 \rangle \quad (3.56)$$

We apply the same approximations as before, writing the final state as $|N-1, f\rangle = \hat{a}_{f,\mathbf{q}''} |N, 0\rangle$ and assuming a single Slater determinant ground state built from valence-band orbitals⁹³. The matrix element then becomes (using orthonormality of the Bloch orbitals)

$$\begin{aligned} \langle N-1, f | \hat{a}_{j,\mathbf{q}'} \hat{a}_{c,\mathbf{q}+\mathbf{Q}}^\dagger \hat{a}_{v,\mathbf{q}} | N, 0 \rangle &= \langle N, 0 | \hat{a}_{f,\mathbf{q}''}^\dagger \hat{a}_{j,\mathbf{q}'} \hat{a}_{c,\mathbf{q}+\mathbf{Q}}^\dagger \hat{a}_{v,\mathbf{q}} | N, 0 \rangle \\ &= \delta_{f,v} \delta_{\mathbf{q}'',\mathbf{q}} \delta_{j,c} \delta_{\mathbf{q}',\mathbf{q}+\mathbf{Q}} \end{aligned} \quad (3.57)$$

and the Dyson orbital reads

$$d_{(m,\mathbf{Q}),f}(x) = \sum_c X_{f,c,\mathbf{q}''}^{(m,\mathbf{Q})} \phi_{c,\mathbf{q}''+\mathbf{Q}}(x), \quad (3.58)$$

where f denotes a valence band. For a final state $|N-1, f\rangle = |N-1, (v, \mathbf{q})\rangle = \hat{a}_{v,\mathbf{q}} |N, 0\rangle$ and an arbitrary photoelectron state, the transition rate then becomes:

$$W_{i=(m,\mathbf{Q}) \rightarrow ((v,\mathbf{q}),\gamma)} = 2\pi \left| h_{\gamma,d_{(m,\mathbf{Q}),v,\mathbf{q}}}^{(\text{int})} \right|^2 \delta(\omega + \Omega^{(m,\mathbf{Q})} + \varepsilon_{v,\mathbf{q}} - E_{\text{kin}}), \quad (3.59)$$

where, in complete analogy to the gas-phase case, $\Omega^{(m,\mathbf{Q})}$ denotes the excitation energy of the exciton and $\varepsilon_{v,\mathbf{q}}$ is the quasiparticle orbital energy determining the final-state energy $E(N-1, (v, \mathbf{q})) = E(N, 0) - \varepsilon_{v,\mathbf{q}}$.

⁹³See also Footnote 91 and the discussion around Eq. 3.50.

The photoemission intensity for a photoelectron states of momentum $\mathbf{k}$ and spin s is then obtained by summing over all final states, that is, over the valence bands and the Brillouin zone:

$$I_{i=(m,\mathbf{Q})}(\mathbf{k}, s) \propto \sum_{\mathbf{q}} \sum_v^{\text{BZ}} \left| h_{\gamma_{\mathbf{k},s},d(m,\mathbf{Q}),(\mathbf{v},\mathbf{q})}^{(\text{int})} \right|^2 \delta(\omega + \Omega^{(m,\mathbf{Q})} + \varepsilon_{v,\mathbf{q}} - E_{\text{kin}}) \quad (3.60)$$

In the PWA, this becomes:

$$I_{i=(m,\mathbf{Q})}(\mathbf{k}, s) \propto |\mathbf{A} \cdot \mathbf{k}|^2 \sum_v \sum_{\mathbf{q}}^{\text{BZ}} \left| \sum_c X_{v,c,\mathbf{q}}^{(m,\mathbf{Q})} \mathcal{F}[\phi_{c,\mathbf{q}+\mathbf{Q}}^{(s)}](\mathbf{k}) \right|^2 \delta(\omega + \Omega^{(m,\mathbf{Q})} + \varepsilon_{v,\mathbf{q}} - E_{\text{kin}}) \quad (3.61)$$

And finally, analogously to Eq. 3.54, we find for a spin singlet/triplet exciton based on spin-unpolarized and spin-paired (in the ground state) KS orbitals that the PWA intensity becomes (with v and c denoting spatial bands):

$$I_{i=(m,\mathbf{Q})}(\mathbf{k}) \propto |\mathbf{A} \cdot \mathbf{k}|^2 \sum_v \sum_{\mathbf{q}}^{\text{BZ}} \left| \sum_c X_{v,c,\mathbf{q}}^{(m,\mathbf{Q})} \mathcal{F}[\varphi_{c,\mathbf{q}+\mathbf{Q}}](\mathbf{k}) \right|^2 \delta(\omega + \Omega^{(m,\mathbf{Q})} + \varepsilon_{v,\mathbf{q}} - E_{\text{kin}}) \quad (3.62)$$

As above, this spin-less and PWFS-approximated variant is what we will use in practice below. Note that Eq. 3.62 forms the *key result of this text* and was first presented by the author of this text and co-workers as Eq. (16) in Ref. [121].

We now use crystal-momentum conservation to further simplify Eq. 3.62 Following along the same steps that lead us to Eq. 3.45, we again initially restrict ourselves to photoelectron states that are periodic at the ends of the macroscopic finite surface, such that their in-plane Bloch momenta $\mathbf{q}_\gamma$ ($\in \text{BZ}$) are restricted to the same grid as those of the bound KS states used above. That is, the allowed photoelectron momenta again take the form

$$\mathbf{k} = \mathbf{q}_\gamma + \mathbf{G}_{\gamma,\parallel} + \mathbf{e}_z k_z, \quad (3.63)$$

where $\mathbf{G}_{\gamma,\parallel}$ is an in-plane reciprocal lattice vector. Comparison with Appendix D.2 and in particular Eq. D.42 then gives us

$$I_{i=(m,\mathbf{Q})}(\mathbf{k}) \propto |\mathbf{A} \cdot \mathbf{k}|^2 \sum_v \left| \sum_{\mathbf{G}} \sum_c X_{v,c,\mathbf{q}_\gamma-\mathbf{Q} \bmod \mathbf{G}}^{(m,\mathbf{Q})} \mathcal{G}_{c,\mathbf{q}_\gamma}(\mathbf{G}) \int_{A_c} d^2 r_{\parallel} \int_0^L dz e^{i\mathbf{G} \cdot \mathbf{r}} e^{-i\mathbf{G}_{\gamma,\parallel} \cdot \mathbf{r}_{\parallel}} e^{-ik_z z} \right|^2 \delta(\omega + \Omega^{(m,\mathbf{Q})} + \varepsilon_{v,\mathbf{q}_\gamma-\mathbf{Q} \bmod \mathbf{G}} - E_{\text{kin}}), \quad (3.64)$$

which can be further evaluated to:

$$I_{i=(m,\mathbf{Q})}(\mathbf{k}) \propto |\mathbf{A} \cdot \mathbf{k}|^2 \sum_v \left| \sum_c X_{v,c,\mathbf{q}_\gamma-\mathbf{Q} \bmod \mathbf{G}}^{(m,\mathbf{Q})} \sum_{G_z} c_{c,\mathbf{q}_\gamma}(\mathbf{G}_{\gamma,\parallel} + \mathbf{e}_z G_z) \int_0^L dz e^{i(G_z - k_z)z} \right|^2 \delta(\omega + \Omega^{(m,\mathbf{Q})} + \varepsilon_{v,\mathbf{q}_\gamma-\mathbf{Q} \bmod \mathbf{G}} - E_{\text{kin}}) \quad (3.65)$$

Finally, as detailed in Appendix D.2.2 this expression stays well-defined when approaching an infinite surface again, such that the restriction on the photoelectron momenta is lifted and they become effectively continuous again. Compared to Eq. 3.65 we have thus again eliminated the sum over the Brillouin zone. Before continuing, a few comments are noteworthy:

First, note that Eq. 3.65 can be understood analogously to Eqs. 3.54 and 3.45: $I_{i=(m,\mathbf{Q})}(\mathbf{k})$ is the number of photoelectrons with momentum $\mathbf{k}$ that are emitted from the initial state, which is the m -th exciton with center-of-mass momentum $\mathbf{Q}$ (more on $\mathbf{Q}$ below). For a given photoelectron momentum $\mathbf{k}$, the photoemission intensity is intrinsically connected to the valence orbitals at the Bloch momentum $\mathbf{q}_\gamma - \mathbf{Q} \bmod \mathbf{G}$ and the conduction orbitals with Bloch momentum $\mathbf{q}_\gamma$. First, the kinetic energies at which photoelectrons are emitted are determined (for a given probe-energy ω and exciton energy $\Omega^{(m,\mathbf{Q})}$) by the (quasiparticle) valence band structure. In particular, photoemission at k_x and k_y (with $k_{x/y} = \mathbf{q}_{\gamma,x/y} + \mathbf{G}_{\gamma,x/y}$) is then only possible at E_{kin} that satisfy $E_{\text{kin}} = \frac{k^2}{2} = \omega + \Omega^{(m,\mathbf{Q})} + \varepsilon_{v,\mathbf{q}_\gamma - \mathbf{Q} \bmod \mathbf{G}}$ for any of the valence bands v . As before, this can be understood as the photohole determining the energy available to the photoelectron. The photoemission intensity contribution for each valence band that satisfies the energy condition is then obtained by summing over all conduction bands and is determined by the plane-wave coefficients of the conduction orbitals at Bloch momentum $\mathbf{q}_\gamma$, with linear coefficients given by the BSE eigenvector (at $\mathbf{q}_\gamma - \mathbf{Q} \bmod \mathbf{G}$), thereby including the electron-hole correlation of the excitonic state. Again, as in the gas-phase case, this can be understood as photoelectrons having been emitted from the conduction bands.

Second, in analogy to Eq. 3.45, we should understand Eq. 3.65 as an intensity *density*. As detailed there, real momentum maps are calculated using finite kinetic-energy interval δE_{kin} and a Gaussian in place of the Dirac delta. Details can be found in Appendix D.3 (where we also discuss the normalization of initial and final states).

Third, remember that the exPOT formalism derived here does not take into account how the excitonic state has been created, it simply starts from it as the initial state. Therefore, even though $\mathbf{Q} \neq 0$ excitons cannot be directly created by an optical pump-pulse and are therefore called *optically-dark* or *momentum-forbidden*, the exPOT formalism can still be used to simulate photoemission from such exciton states and is therefore also suitable for systems where exciton-phonon coupling becomes important. The same goes for the optically dark spin-triplet states discussed above Eq. 3.54

Fourth, note that the excitation energy $\Omega^{(m,\mathbf{Q})}$ leads to an energetic separation between the exciton-photoemission signal, which occurs at $E_{\text{kin}} = \omega + \Omega^{(m,\mathbf{Q})} + \varepsilon_{v,\mathbf{q}}$ and the ground-state photoemission signal of Eq. 3.45, which occurs at $E_{\text{kin}} = \omega + \varepsilon_{v,\mathbf{q}}$, for a given valence band v and Bloch momentum $\mathbf{q}$. This is an important result, because it allows us to disentangle the exciton signal from the much stronger ground-state signal (see Sec. 3.2), at least within this energy-window $[0, \Omega^{(m,\mathbf{Q})}]$ above the signal from the Fermi-level. This of course also holds equivalently for the gas-phase formulations of ground-state POT and exPOT.

Exciton Photoemission From Mixed States

The derivation of both, the gas-phase and periodic exPOT photoemission intensities given above is based on a single exciton state (m for gas-phase, $(m, \mathbf{Q})$ for periodic systems) as the initial state. This is of course a simplification, since due to energy broadening (in combination with off-resonant pumping) the state created by the pump pulse can in principle be a superposition of many different exciton states. Such a superposition state is out of reach for the exPOT formalism derived here (Fermi's golden rule itself, which stands at the very beginning of POT, assumes a pure eigenstate as the initial state, see Sec. 3.3.1). At finite temperature, exciton-phonon coupling may additionally become relevant for periodic systems, making the situation even more complicated.

Not all is lost, however, since such complicated superposition states tend to very quickly dephase into statistical mixtures of pure states, see for example Ref. [138]. Such statistical mixtures are then again accessible to exPOT by decomposing/deconvoluting an experimentally obtained momentum map into a linear combination of momentum maps from pure excitons, with the linear coefficients representing the weights ($\in \mathbb{R}^+$, including 0) of each contributing pure state. For periodic exPOT, the photoemission intensity then reads (for the gas-phase, just remove $\mathbf{Q}$ and the corresponding sum):

$$I(\mathbf{k}) = \sum_m \sum_{\mathbf{Q}} v_{m,\mathbf{Q}} I_{i=(m,\mathbf{Q})}(\mathbf{k}) \quad (3.66)$$

If such a deconvolution can be performed for given experimental data, the contributing exciton states and their weights are then obtained from it. When looking at exPOT's energy conservation, as expressed by the delta function, it becomes for example clear, that in the case of large-enough energetic separation of excitons (i.e. their excitation energies) as well as low valence-band dispersion, deconvoluting exciton signals becomes a less demanding task due to the smaller energetic overlap of the signals. Similarly, differing valence-band contributions may lead to exciton signals at differing kinetic energies, while differing conduction-band contributions may lead to photoemission in different angular directions (different parts of the momentum maps). In the case of overlapping signals, deconvolution techniques like least-squares fitting can be used.

Thus, exPOT is applicable for situations where dephasing has already occurred and the system is in a *mixed state* with incoherent population of different excitonic states [139, 140]. For pump-probe ARPES and in particular trARPES, we thus focus on pump-probe delays that are longer than the dephasing time of the system. In the case of smaller delays, the exPOT formalism may still be used for comparison with experimental data – for example by comparing to calculated momentum maps of single excitons – should however be treated with caution. For pump-probe delays below the exciton lifetime(s), the time-dependent exciton photoemission signal can then be calculated (or deconvoluted, if many excitons are present) using the exPOT formalism. To conclude, note that in Chapter 5 good agreement with experimental data was achieved using only a single exciton.

3.3.11 Implementation – POT in Practice

Having the ground-state POT and exPOT theory at hand, we still need to implement it to perform photoemission simulations. The aim of this section is not to give all details of the implementation based on which the upcoming calculations were performed, but rather an overview. We focus in the following on the case of using both the PWA and the spinless versions of our formalism, since all upcoming calculations have been done under these approximations. Note however, that dropping these restrictions is not a major problem, and in our PYTHON [141] implementation for periodic systems we have in fact also included a damped plane-wave photoelectron state [35] and a spinor (PWA) photoelectron state. Note that the $\mathbf{A} \cdot \mathbf{k}$ polarization factor is trivial to implement and is therefore not mentioned below.

Gas-Phase Systems: Ground-state POT

For the ground-state photoemission from gas-phase calculations, Eq. 3.39, the implementation is straightforward [142]: we first need a parser for the wave functions obtained from DFT (usually available on a real-space grid as *cube*-files). Additionally, we need a parser for KS (here: ORCA [143, 144]) or GW (here: FIESTA [145]) energies of the orbitals, in practice we usually use KS energies in ground-state POT. To get the photoemission signal from a given (valence) orbital, it is then Fourier-transformed and values at a k_x and k_y grid on a hemispherical cut of the appropriate radius (determined by ω and the orbital energy) are extracted, with subsequent calculation of the absolute square (not mentioned from now on) giving us the k-map. As detailed in Appendix D.3, we additionally multiply the so-obtained k-map by a Gaussian weight and sum over orbitals, whenever multiple occupied orbitals are energetically close at the desired kinetic energy. Finally, a k_x - and k_y -dependent geometric factor may be included, see Appendix D.3 for details.

Gas-Phase Systems: exPOT

For the exciton photoemission from gas-phase calculations, Eq. 3.54, the implementation is similarly straightforward: in addition to the wave function parser and the orbital-energy parser we need a parser for the BSE eigenvector (here: FIESTA). For a given exciton m there are then multiple photoemission signals, with (kinetic) energetic locations determined by the valence orbital energies. The k-map at each of these energies is then obtained by Fourier transforming the conduction orbitals, taking a hemispherical cut of each (Fourier-transformed) orbital at the radius determined by kinetic energy (as determined by the valence-orbital energy) and calculating the linear combination at a grid of k_x and k_y values while using the BSE eigenvector's entries (at the given valence-orbital index) as coefficients. From there we may additionally sum over valence band and use the geometric factor as detailed before. Note that it is important to use precisely the KS orbitals which were used in the BSE, due to the in-principle arbitrary phases (here: signs) of the KS orbitals, see Sec. 2.4.5. Note also that, since we already have them available from solution of the BSE, we typically use GW orbital-energies in the exPOT formalism.

Periodic Systems: Ground-state POT

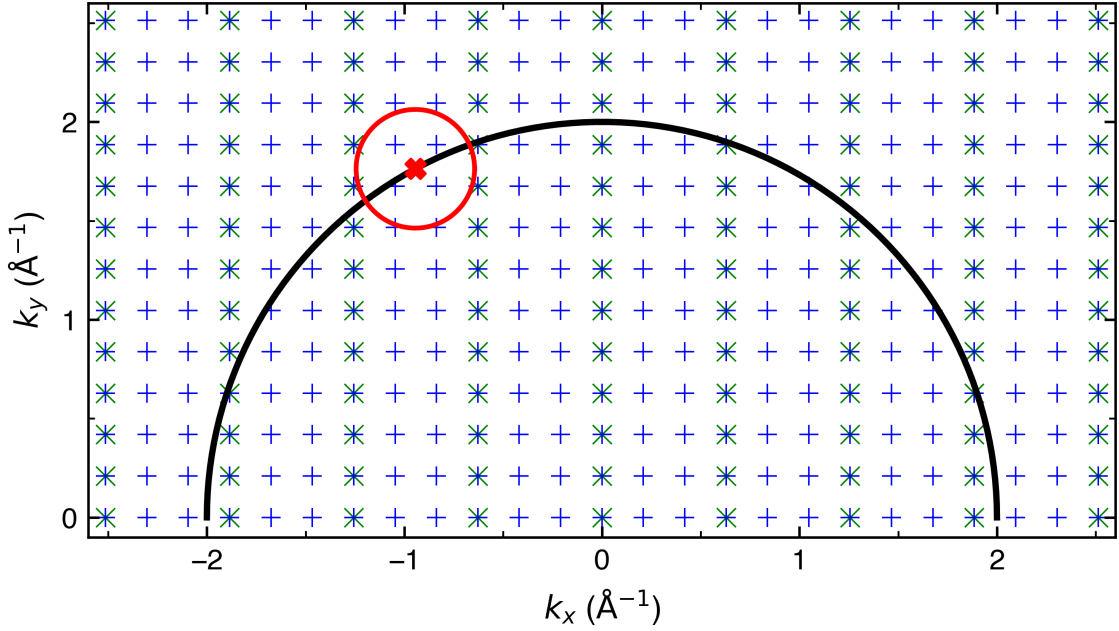


Figure 3.2: Interpolation scheme for momentum maps used in the implementation of POT for periodic systems. Momentum space is shown from the side for a fixed value of k_y and the black half circle is a cross-section (at k_y) of a (half-spherical) surface defined by E_{kin} . Green crosses indicate the grid of reciprocal lattice vectors $\{\mathbf{G}\}$ and blue +-markers indicate the internal set $\{\mathbf{G} + \mathbf{q}\}$. Photoemission intensities are precalculated on $\{\mathbf{G} + \mathbf{q}\}$ and then interpolated to points on the sphere (red cross) by taking neighbors (red circle) into account.

To see how we use Eq. 3.45 in practice, let us evaluate the remaining integral:

$$\int_0^L dz e^{i(G_z - k_z)z} \quad (3.67)$$

For $k_z \notin \{G_z\}$ we find:

$$\int_0^L dz e^{i(G_z - k_z)z} = \frac{e^{i(G_z - k_z)L} - 1}{i(G_z - k_z)}, \quad k_z \notin \{G_z\} \quad (3.68)$$

Conversely, for $k_z \in \{G_z\}$ we write $G_{z,\gamma} \equiv k_z$ and find

$$\int_0^L dz e^{i(G_z - k_z)G_{z,\gamma}} = L\delta_{G_z, G_{z,\gamma}} \quad (3.69)$$

In the latter case we thus find for the photoemission intensity:

$$I_0(\mathbf{k}) \propto |\mathbf{A} \cdot \mathbf{k}|^2 \sum_v \left| c_{v, \mathbf{q}_\gamma}(\mathbf{G}_\gamma) \right|^2 \delta(\omega + \varepsilon_{v, \mathbf{q}_\gamma} - E_{\text{kin}}), \quad (3.70)$$

where we defined $\mathbf{G}_\gamma \equiv \mathbf{G}_{\gamma, \parallel} + \mathbf{e}_z G_{z,\gamma}$. This expression is very appealing due to its computational simplicity: to calculate the photoemission intensity at $\mathbf{k} = \mathbf{q}_\gamma + \mathbf{G}_\gamma$ all we need are the plane-wave coefficients $\{c_{v, \mathbf{q}_\gamma}(\mathbf{G}_\gamma)\}_v$ and the corresponding

orbital energies $\{\varepsilon_{v,\mathbf{q}_v}\}_v$, both of which are directly available – the prior of course only if wave functions are calculated using plane-wave basis sets. For this reason, our implementation is based on this equation and is directly compatible with plane-wave codes like VASP [146–149] and QUANTUM ESPRESSO [150–152]. While a connection to codes that do not use plane-wave basis sets is possible, an additional computational step where these coefficients are calculated would be necessary. Note that based on Eq. 3.70 we can only calculate photoemission at the discrete surface-normal momenta $k_z \in \{G_z\}$. If we used a sufficiently large vacuum in our slab unit cell (resulting in a slab height of $\approx 20\text{--}50\text{\AA}$), these values will lie close enough to each other such that we can then use interpolation techniques to obtain photoemissions at values $k_z \notin \{G_z\}$ (see also below). On the other hand, if the used vacuum was on the shorter end (but still large enough to allow the bound states to decay in it, see Appendix A.1.1 for details, e.g. paragraph around Eq. A.9), then this can – depending on the used interpolation technique – lead to artifacts in the calculated momentum maps, most notably ring-like structures. For such cases it may then make sense to additionally implement photoemission based on Eq. 3.68 via inclusion of the sum over G_z . This can in fact also be done in a highly efficient way, for example by using vectorized operations based on the grid of $\{G_z\}$ values and a desired, finer grid of $\{k_z\}$ values (the damped photoelectron state of Ref. [35] has been implemented in a similar way) and then interpolating to arbitrary values of k_z based on the obtained data on the finer grid. This simple task is however left for future work.

Let us now briefly focus on how *momentum maps* are then calculated in our implementation of Eq. 3.70: the first input to our code are pre-calculated KS orbitals on a set of Bloch momenta $\{\mathbf{q}\}$ determined by the used sampling of the surface Brillouin zone (compare Secs. 2.2.6 and B.3). Typically – for momentum maps – we use a regular sampling of the Brillouin zone. The used repeated-slab unit-cell determines the grid of lattice vectors $\{\mathbf{G}\}$. Combining these, we get a set $\{\mathbf{G} + \mathbf{q}\}$ of photoelectron momenta, below called the *internal set*, for which the photoemission intensity can be directly obtained from the plane-wave coefficients $\{c_{v,\mathbf{q}}(\mathbf{G})\}$ by using Eq. 3.70 and the corresponding pre-calculated orbital-energies $\{\varepsilon_{v,\mathbf{q}}\}$, which form the second input to our code. That is, we first pre-calculate $I_0(\mathbf{k})$ on the internal set of photoelectron momenta which gives us a dataset of photoemission intensities. To get a k-map at a given kinetic energy E_{kin} , we can then determine a set of photoelectron momenta $\{\mathbf{k}\}$ on the hemisphere determined by E_{kin} and interpolate the photoemission intensities from the known dataset to the new photoelectron momenta (not in the internal set). While the effect of this interpolation in the k_z direction has already been discussed above, note that we can also use this step to decrease the in-plane spacing of the photoelectron momenta compared to the Brillouin-zone spacing (assuming regular sampling) of the KS orbitals which determined the spacing of the photoelectron momenta in the internal dataset. Of course, the spacing of the internal set determines the achievable resolution in the so-obtained momentum maps. Note that this interpolation of course assumes that E_{kin} is smaller than the plane-wave cutoff of the plane-wave wave-function coefficients, which is typically well-satisfied for converged DFT calculations and our probe-energy range of 15–50 eV (see Sec. 3.3.2). Note also, that in practice, as in the gas-phase case before, we replace the Dirac delta by a Gaussian centered around $E_{\text{kin}} = \frac{k^2}{2}$ and may use the geometric factor shown in Appendix D.3.

The interpolation scheme is shown schematically in Fig. 3.2 for a quadratic unit-cell of side length $a = 10 \text{ \AA}$ and height $L = 30 \text{ \AA}$ in combination with a 3×3 Γ -centered regular BZ sampling (which is rather rough, compare the 10×40 sampling used for exciton momentum maps in Chapter 5, see Sec. 5.6.2). These value determine the internal set $\{\mathbf{G} + \mathbf{q}\}$, which is depicted in Fig. 3.2 for a fixed k_y from the set (say $k_y = 0$). Photoemission intensities are precalculated on this set and are in a second step interpolated to points on a hemisphere determined by E_{kin} in order to give us the desired momentum map. For the cut at the chosen k_y , the hemisphere appears as a half circle in Fig. 3.2. For any desirable point $\mathbf{k}$ on that circle (hemisphere) the photoemission intensity is then obtained via interpolation based on the photoemission intensities at the neighboring points from the internal set. This neighborhood is indicated in Fig. 3.2 by a circle, but is in reality of course spherically symmetric around the desired momentum $\mathbf{k}$ (red cross). While regular sampling of the BZ results in the internal set being a regular grid and would therefore allow for the usage of corresponding specialized interpolators, we generally use a *radial basis function interpolator* instead (SciPy's *RBFInterpolator* [153]), which allows interpolation agnostic of the used BZ sampling (and is thus automatically compatible with the way photoemission band-structures are calculated, see below).

While we have now focused on momentum maps, note that our implementation is also able to calculate *photoemission band-structure* plots. Though such calculations could in principle be performed analogously to above by first calculating intensities on an internal regular grid and then interpolating to the desired k_x - k_y -path and kinetic energies, we in practice instead use Kohn-Sham orbitals and orbital energies that have already been calculated for Bloch momenta on the desired path. Based on this non-regular Brillouin-zone sampling we then proceed as before and achieve this way high-resolution band-structure plots with low computational cost. The interpolation can then be performed as described above, with the only practical difference being that viewed from a desired point $\mathbf{k}$ on the path, the internal set $\{\mathbf{G} + \mathbf{q}\}$ will generally be more dense in the directions along the path than perpendicular to it, such that photoelectron momenta (from the internal set) along the path will be dominant reference points in the interpolation (since they are generally nearer to $\mathbf{k}$).

Note that to simplify the implementation and since we are usually interested in calculating k-maps, we can also calculate the dataset mentioned above for a pre-determined kinetic energy. That is, instead of using $E_{\text{kin}} = \frac{(\mathbf{q} + \mathbf{G})^2}{2}$, we can already use the specific kinetic energy-value in which we are interested and insert it into the delta function (or, in practice, the Gaussian). This was done in the actual implementation used later. For band-structure plots, we then need to repeat this process for each kinetic energy in the plot, hinting at the general approach given above being worth an implementation in future work.

Without going into details, note that the implementation has additionally been sped up by dropping plane-wave coefficients for large reciprocal lattice vectors beyond common kinetic energies, caching of plane-wave coefficients and other calculation results in calculation-specific databases and the overall usage of vectorization wherever adequate.

Lastly, note that the above approach necessitates the implementation of wave-function and orbital-energy parsers. Wave functions and KS energies can in the

current implementation be parsed from QUANTUM ESPRESSO, VASP and YAMBO [154, 155] while GW energies can currently be parsed from BERKELEYGW [36, 95, 104] and YAMBO.

Periodic Systems: exPOT

The exPOT formalism is implemented analogously to the ground-state formalism: for $k_z \in \{G_z\}$ we again write $G_{z,\gamma} \equiv k_z$ and $\mathbf{G}_\gamma \equiv \mathbf{G}_{\gamma,\parallel} + \mathbf{e}_z G_{z,\gamma}$ and find from Eq. 3.65:

$$I_{i=(m,\mathbf{Q})}(\mathbf{k}) \propto |\mathbf{A} \cdot \mathbf{k}|^2 \sum_v \left| \sum_c X_{v,c,\mathbf{q}_\gamma-\mathbf{Q} \bmod \mathbf{G}}^{(m,\mathbf{Q})} \mathbf{G}^{c,\mathbf{q}_\gamma}(\mathbf{G}_\gamma) \right|^2 \delta(\omega + \Omega^{(m,\mathbf{Q})} + \varepsilon_{v,\mathbf{q}_\gamma-\mathbf{Q} \bmod \mathbf{G}} - E_{\text{kin}}) \quad (3.71)$$

In practice we then typically solve the Bethe-Salpeter equation using a regular sampling of the surface Brillouin zone (see Sec. 2.4.5). With an additional parser for the BSE eigenvectors (and eigenvalues) the code is then handed the BSE eigenvector and the corresponding Kohn-Sham orbitals (which must be the same used for the solution of the BSE, see Sec. 2.4.5), that is, their plane-wave coefficients. Using additionally the GW energies used in the BSE we then again calculate photoemission intensities on the *internal set* $\{\mathbf{G} + \mathbf{q}\}$ of photoelectron momenta. Note that for $\mathbf{Q} \neq 0$ excitons, the Bloch momentum of the BSE eigenvector and the orbital energies must be shifted accordingly.

From the so-obtain dataset of photoemission intensities we can then again calculate momentum maps and photoemission band-structure plots as detailed above. Note, however, that for the latter, a specific Brillouin-sampling along the desired path is non-trivial, since the internal set $\{\mathbf{G} + \mathbf{q}\}$ is determined by the sampling used in the BSE, which is typically – in our case, always – regular.

Note also that Eq. 3.71 can be seen to coincide with Eq. (B5) in Ref. [121] when remembering the identity $c_{n,\mathbf{q}}(\mathbf{G}) = c_{n,\mathbf{q}+\mathbf{G}'}(\mathbf{G} - \mathbf{G}')$.

The implementation was done in one package together with the ground-state implementation for periodic systems described above and shares the efficiencies mentioned there. The two methods share wide areas of the code, with the only major difference being the linear combination of plane-wave coefficients in the exPOT case. At the current time, exPOT maps can be created based on QUANTUM ESPRESSO wave functions in combination with BERKELEYGW GW energies and BSE eigenvectors. Additionally, a BSE and GW parser has been implemented for YAMBO which can be used in combination with QUANTUM ESPRESSO wave functions or YAMBO's own wave-function format.

Symmetrization of Momentum Maps

When simulating photoemission from adsorbates (molecules or 2D semiconductors, see Sec. 3.2), we have to take into account all domains which are found on the surface. These domains can either be the result of the substrate's or the adsorbate's symmetry, or we can in principle also have symmetry-inequivalent, but degenerate or (quasi-stable) nondegenerate structures/domains.

Assuming for simplicity that all different domains are symmetry-equivalent and given by in-plane symmetry operations and restricting ourselves for simplicity to

the PWA (as in the practical calculations given below), we can then simply pick one of them and perform the photoemission simulation for that one specific domain. In particular, this simulation is performed without the $|\mathbf{A} \cdot \mathbf{k}|^2$ prefactor, since this factor depends on the orientation of the surface relative to the probe laser. We then obtain the k-map (without polarization prefactor) for one specific domain. The k-maps for the other domains are then obtained by applying the symmetry operation, that connects each domain to the one used for the calculation, onto the k-map. Assuming for simplicity that the probe-pulse illuminates a large area, the k-maps belong to the different domains can then simply be summed up with equal weights. For smaller probe-pulse areas, different domains may dominate and we may need to fit their weights to the experimental k-map. Finally, the $|\mathbf{A} \cdot \mathbf{k}|^2$ prefactor is multiplied onto the result of said summation/combination. Note that this procedure neglects effects of domain-boundaries and is therefore best-suited for systems with large domains and for large probe-pulse areas, such that boundaries are negligible. Note also, that in the scenarios like the one shown in Sec. 4.4 where the exciton initial state depends on the orientation of the atomic system relative to the pump polarization, it may be necessary to perform multiple calculations for otherwise symmetry-equivalent domains. For the case of hBN this was not necessary, since there is only a single rotational domain (when assuming a perfect monolayer).

For gas-phase calculations, we neglect the substrate and only include the adsorbed molecules, thus neglecting inter-supercell inter-molecular interactions. Using only one domain then means that we take the molecules from the corresponding supercell, without repeating the cell. If the molecule was not commensurate with the substrate, or if inter-molecular interactions are sizable this cell might contain multiple molecules. In both cases, assuming that the molecules are (relative to each other) not heavily deformed, we may additionally (or: partially) neglect the inter-molecular intra-supercell interaction by using only a single molecule (or: a smaller cluster from which the supercell can be constructed approximately via different orientations) and symmetrize over its momentum maps, in addition to the symmetrization over the domains.

For periodic simulations, we simply take one of the symmetry-equivalent supercells and simulate photoemission from the system, as if the whole surface was given by this single domain (assumption of large domains). Symmetrization of the so-obtained photoemission intensity over all supercell orientation then gives the experimentally-expected photoemission signal.

4 Hexagonal Boron Nitride

This chapter is based on results which have first been published in Ref. [121] and the text and figures in this chapter have widely been adopted from there and subsequently restructured. The formalism of exPOT for periodic systems was co-derived and the original text was co-written by the author of this thesis and Christian S. Kern, with auxiliary input from the remaining co-authors of that manuscript. Similarly, the *ab initio* calculations were performed and analyzed by the author of this thesis and Christian S. Kern, with auxiliary input from the remaining co-authors of that manuscript. Photoemission simulations were carried out by the author of this thesis.

4.1 Introduction

The aim of this chapter is to exemplify the exPOT formalism for periodic systems by the simulation of excitonic photoemission in monolayer hexagonal boron nitride (hBN) – a prototypical 2D system.

We begin this chapter with a brief overview of hBN’s quasiparticle and optical properties, where we will in particular focus on the two low-lying absorption peaks S_1 and S_2 , each of which is related to a (two-fold) degenerate excitonic subspace. We continue by illustrating the consequences of our theory for exciton photoemission, where the peculiar structure of the S_1 and S_2 excitons ultimately allows us to directly dissect photoemission intensity distributions in terms of individual contributing factors. Finally, we show how the degenerate nature of S_1 and S_2 leads to a direct dependence of photoemission intensity distributions on the pump-polarization.

4.2 Calculation of hBN Quasiparticle and Optical Properties

As a starting point, we obtain wave functions and energy levels from density functional theory (DFT) calculations with QUANTUM ESPRESSO [150–152], using the PBE-GGA exchange-correlation functional [66] and a lattice constant of 2.507 Å, see Fig. 4.1 (a). To compensate for the systematic underestimation of the band gap within semi-local DFT, we apply the G_0W_0 method to correct the energy levels. Utilizing the BERKELEYGW code [36, 95, 104], we obtain a direct (indirect) band gap of 7.6 eV (7.4 eV), which is comparable to literature values from similar methods, see e.g. Ref. [157] for a comparison. We show the G_0W_0 band structure in Fig. 4.1 (b).

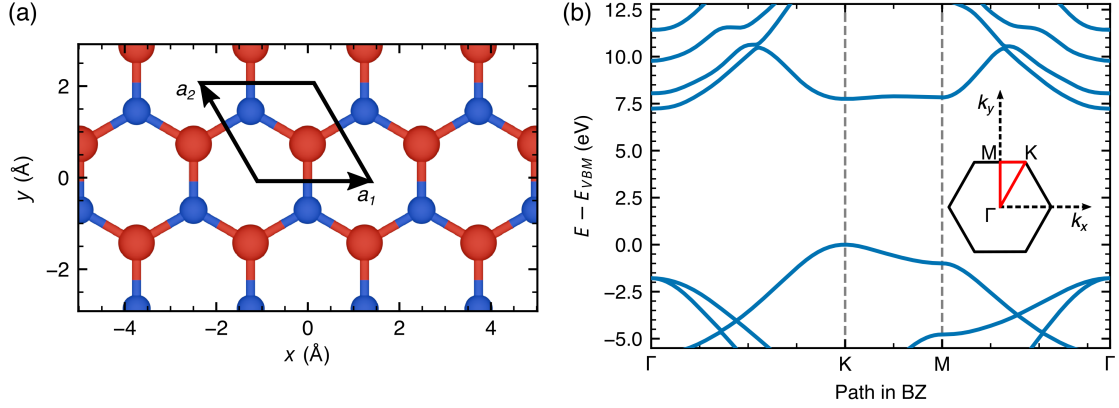


Figure 4.1: (a) Atomic structure of hBN. Boron and nitrogen atoms are depicted in red and blue, respectively. The vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ span the primitive unit cell, which contains one atom of each kind. (b) G_0W_0 band structure of hBN. Quasiparticle energies are shown along the $\Gamma - K - M - \Gamma$ high symmetry path. The calculated band structure exhibits an indirect band-gap, with the valence-band maximum and conduction-band minimum being located at K (and K') and Γ , respectively. Panel (a) was created with BLENTOm [156].

Subsequently, we use the DFT wave functions and G_0W_0 energy levels, and solve the Bethe-Salpeter equation (BSE) within the Tamm-Dancoff approximation (TDA) and for $\mathbf{Q} = 0$. This yields the excitation energies Ω_m and the BSE eigenvectors $|N, (m, \mathbf{Q} = \mathbf{0})\rangle =: |N, m\rangle$, which we will use to simulate photoemission spectra via Eq. 3.62. As shown in Fig. 4.2, the BSE optical absorption spectrum (see Eq. (26) in Ref. [36]) features a range of excitonic peaks below the band gap. These are often interpreted as hydrogen-like solutions of the Wannier equation [158], though they have also been found to deviate from that simple model [159]. For comparison, we include the optical spectrum computed within the independent-particle approximation (compare Eq. 2.196), shown as a dashed blue curve in Fig. 4.2. In the following, we focus on the two lowest excitons, located at 5.3 eV (S_1) and 6.2 eV (S_2).

Both, S_1 and S_2 are composed of two degenerate eigenstates of the BSE Hamiltonian. This results in an additional dependence on the pump polarization, as discussed in Sec. 4.4. For S_1 at 5.3 eV, the two degenerate valence-conduction transitions occur at K and K' , respectively, with their momentum-dependent transition weights indicated in Fig. 4.3 (a). The situation is similar for S_2 at 6.2 eV, albeit with transition weights being more spread out along the Brillouin-zone boundary, as can be seen in Fig. 4.3 (b).

Additional details on the computational methods described here can be found in Sec. 4.6.

4.3 Exciton Photoemission in hBN

With the quasiparticle and optical properties at hand, we now illustrate consequences of our theory for exciton photoemission from monolayer hBN. In the following, we use a 26.5 eV probe energy with a Gaussian energy broadening of 0.1 eV

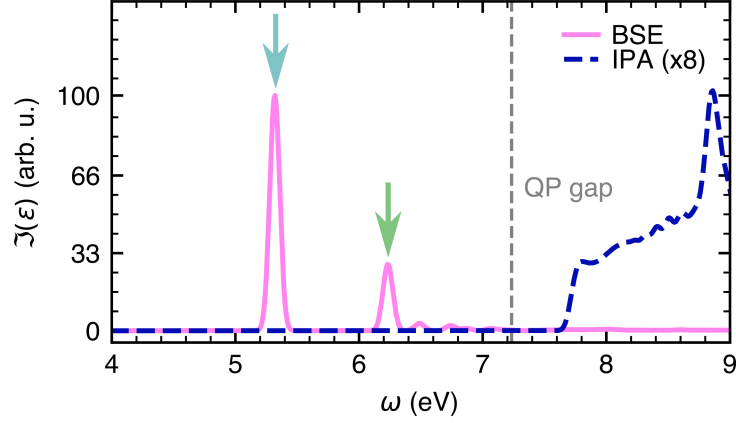


Figure 4.2: Optical absorption spectrum of monolayer hBN. Independent-particle spectrum, based on a G_0W_0 calculation in dark blue and the BSE spectrum in pink. In the latter, S_1 and S_2 energies are marked by arrows.

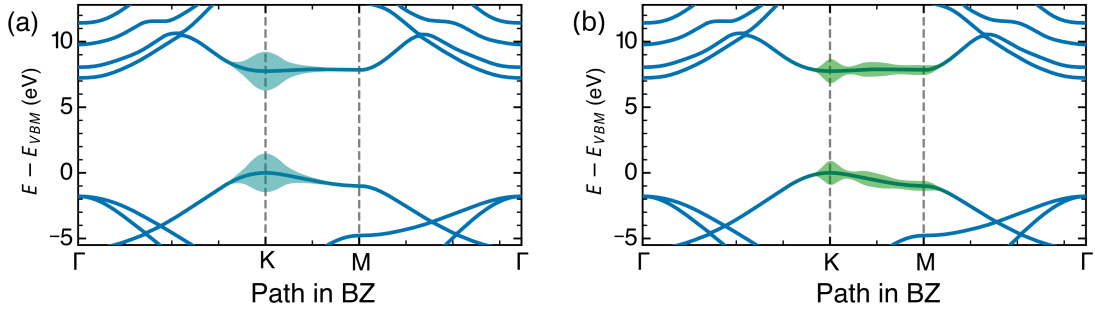


Figure 4.3: Low-energy excitons of monolayer hBN. Panels (a) and (b) show the G_0W_0 band structure with overlays indicating the BSE eigenvector composition of the S_1 (blue) and S_2 (green) excitations of the system, respectively.

(see Appendix D.3). For a better insight into the pump-induced effects on the momentum maps, we ignore the trivial effect of probe polarization, which gives rise to the $|\mathbf{A} \cdot \mathbf{k}|^2$ prefactor in Eq. 3.62, throughout this chapter. Note that our formulation only considers excitonic photoemission, thereby neglecting photoemission from the initially populated electronic structure and associated effects like its depopulation due to exciton creation, which is justified by the energy conservation in excitonic photoemission Eq. 3.62: as explained below Eq. 3.65, the exciton energy $\Omega^{(m,\mathbf{Q})}$ is transferred to the photoelectron, yielding higher kinetic energies than those obtained from ground-state photoemission directly from the valence bands (see Fig. 4.4), thus allowing us to focus solely on the exciton photoemission signal.

In Fig. 4.4 we show the simulated bandmap for photoemission from the S_1 exciton together with the G_0W_0 band structure (full blue lines) along the $\Gamma - K' - M_2$ path (corresponding to the k_x direction, see inset). According to Eq. 3.62, the energy dispersion of exciton photoemission is determined by the hole component of the exciton. Consequently, the exciton's trARPES signature appears at the photoelectron kinetic energy corresponding to the valence band energy plus the pump energy Ω (blue dashed line). This finding, which is well-established in the

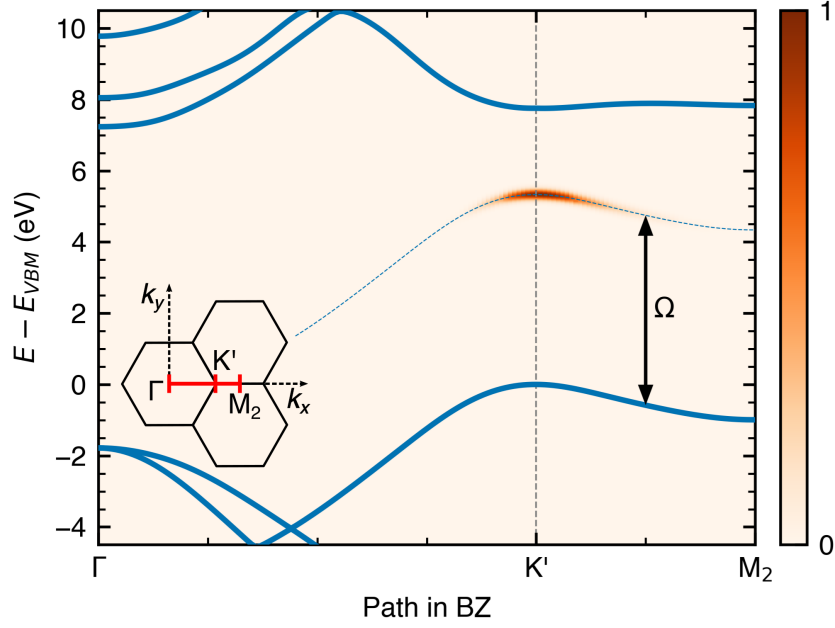


Figure 4.4: ARPES bandmap for the S_1 exciton in k_x direction (cut of the BZ along $\Gamma - K' - M_2$, see inset with three neighboring BZs). The G_0W_0 band structure is overlaid in full blue lines, with a duplicate of the valence band, shifted by Ω , as a blue dashed line.

literature [23, 160], enables the estimation of the exciton’s spatial extent from photoemission data under the assumption of an s -like envelope function [7, 8, 161].

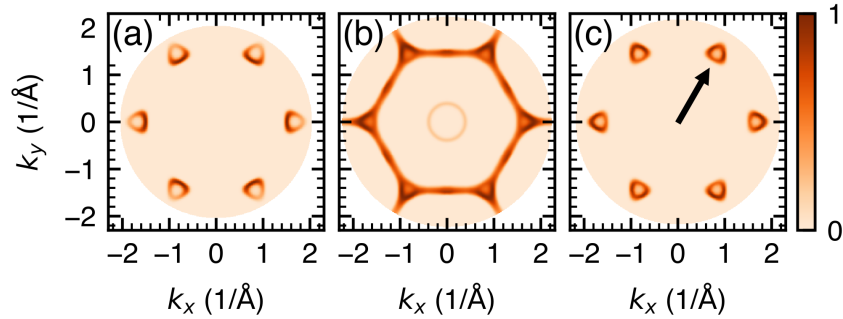


Figure 4.5: Momentum maps for three different cases: (a) valence band at $E_b = E_{\text{VBM}} - 0.2$ eV ($E_{\text{kin}} = 18.6$ eV), (b) conduction band at $E_b = E_{\text{CBM}} + 0.6$ eV ($E_{\text{kin}} = 26.6$ eV), and (c) S_1 exciton at $E_b = E_{\text{VBM}} + \Omega - 0.2$ eV ($E_{\text{kin}} = 23.9$ eV).

Next, it is expedient to compare momentum maps of exciton photoemission with those for photoemission from the ground state, which we obtain by the standard way of simulating POT [35] (see Eq. 3.42). In Fig. 4.5 (a), we present such a map for a kinetic energy slightly below the valence band maximum (VBM) ($E - E_{\text{VBM}} = -0.2$ eV). It is composed of six triangular features, each around the K/K' points. This pattern is analogous to the case of graphene, where the triangular features are also broken in the outgoing direction of the Brillouin-zone, leading to croissant- or horseshoe-like shapes. This “dark corridor” is due to matrix element effects in the photoemission process and has already been described in great detail for the case of graphene [162–164]. When assuming a static population of

the conduction band, it would also be accessible to photoemission from the ground state, which we simulate in panel (b) of Fig. 4.5, using a kinetic energy of 26.6 eV, which is above the conduction band minimum (CBM) ($E - E_{\text{CBM}} = +0.6$ eV). Note that this is a *hypothetical* example for illustration purposes; in an actual experiment, this would correspond to the situation where a formerly unoccupied state gets populated by e.g. a charge-transfer process across an interface. In contrast to the valence-band case depicted in panel (a), the features around the Dirac point are now elongated in the directions going to the M/M' points, which is reasonable when looking at the band structure (see e.g. Fig. 4.1 and compare text below Eq. 3.45 for the connection between the band structure and photoemission). Remarkably, the dark corridor from the matrix element effect is now pointing to the *inside* of the BZ. Returning now to the simulation of exciton photoemission, we show a momentum map of the S_1 exciton in Fig. 4.5 (c), using a kinetic energy of 23.9 eV and a pump polarization as indicated by a black arrow. As already discussed in the preceding paragraph, the exciton inherits the energy dispersion of the *hole* (here: the highest valence band), but, in light of Eq. 3.62, follows the momentum distribution given by the Fourier-transformed *electron* part of the exciton wave function (here: the lowest conduction band). As a direct imprint of the latter, the dark corridor is also pointing to the inside of the BZ, which we can see clearly in Fig. 4.5 (c). Having established the unoccupied part of the electronic structure as another direct marker of exciton photoemission, we will now examine the different contributions to the momentum maps in more detail.

Using Eq. 3.62, we dissect the photoemission maps for both excitons, S_1 and S_2 , in order to understand the influence of each contributing factor. Since – in this case to a very good approximation – both excitons only involve transitions from the highest valence to the lowest conduction band (denoted as ξ from hereon), the sums over v and c in Eq. 3.62 collapse. Consequently – remembering crystal-momentum conservation (see for example Eq. 3.65) – we are left with a single product of $|\mathcal{F}[\xi]|^2$, δ_E and $|X|^2$, involving only wave functions from the lowest conduction band, energies of the highest valence band and BSE transition coefficients from the highest valence band to the lowest conduction band. Fig. 4.6 shows these three factors, as well as the full photoemission maps, for the two excitons in rows (a) (S_1) and (b) (S_2), respectively. The direction of the pump polarization is indicated in the rightmost column. For both excitons S_1 and S_2 , the triangular patterns are generated by the δ_E factor (broadened Gaussian, see Appendix D.3), with $|\mathcal{F}[\xi]|^2$ only leading to slight modifications. The maps in the first two columns, $|\mathcal{F}[\xi]|^2$ and δ_E , are very similar between the two excitons S_1 and S_2 , with minor differences arising due to the unequal photoelectron kinetic energies (23.9 eV for S_1 and 24.8 eV for S_2). Since all other areas already have vanishing intensity, the additional multiplication with the BSE eigenvector can at most lead to intensity differences within the area of the horseshoes. As can be seen from the third column, the BSE eigenvectors of the two excitons differ significantly in this area, and are ultimately responsible for the distinct appearance of the respective photoemission maps (rightmost column of Fig. 4.6). In the following, those differences are inspected more closely.

For S_1 , the BSE eigenvector (third column in Fig. 4.6 (a)) mostly exhibits a six-fold symmetry. It is centered around the K and K' points and varies weakly along the contours of the horseshoes, thus leading only to small intensity variations

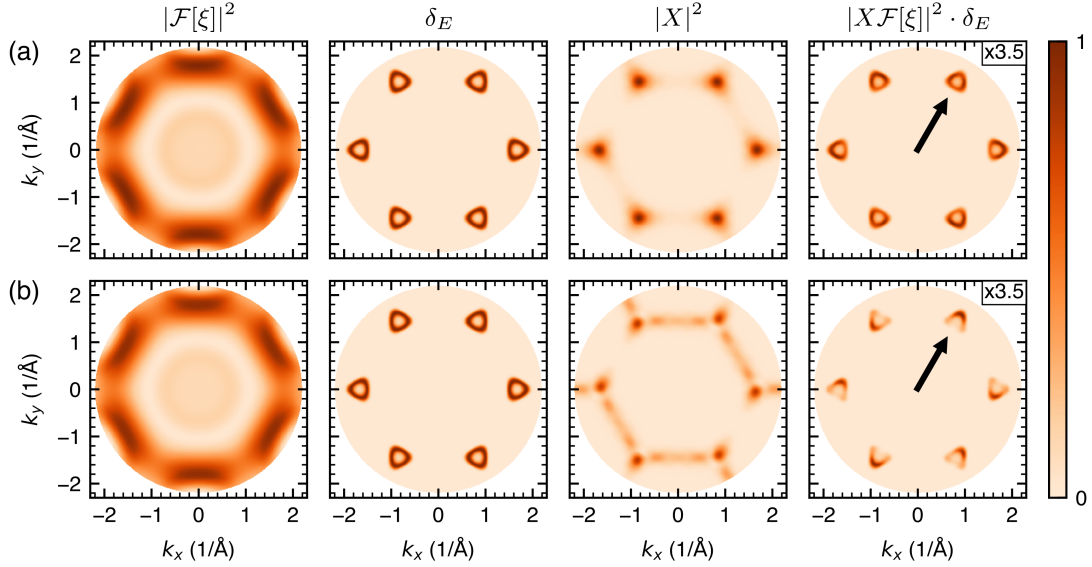


Figure 4.6: Decomposition of exciton ARPES maps for S_1 in row (a) and S_2 in row (b), with black arrows indicating the polarization of the pump laser. First column: Fourier-transformed conduction-band wave functions. Second column: energy-conservation function. Third column: BSE eigenvectors. Fourth column: resulting exciton ARPES maps as products of first to third columns. Each map in the first three columns is individually normalized to one. For S_1 in row (a), the horseshoes point away from Γ , with minor modulations along their contours. For S_2 in row (b), four of the six horseshoes are rotated, when compared to the first exciton. This is a direct result of the differences in the momentum-space distribution of their BSE eigenvectors.

(fourth column in Fig. 4.6 (a)) along them. Contrary, in the case of S_2 in row (b), the BSE eigenvector exhibits a nodal line perpendicular to the pump polarization – which has broken the six-fold symmetry – while being non-zero along the remaining four sides of the hexagonal BZ. Since the pump polarization was chosen along a high-symmetry direction (indicated by black arrows in the rightmost column), it acts as a symmetry axis for the BSE eigenvector and, consequently, for the resulting photoemission map. In contrast to the BSE eigenvector of S_1 , the regions around K and K' show much more details for S_2 , particularly featuring small nodal lines, which, upon multiplication of the BSE eigenvector with the horseshoe pattern produced by $|\mathcal{F}[\xi]|^2$ and δ_E , suppress photoemission intensity. Moreover, the local maxima are shifted off K and K' . As can be seen in the last column of Fig. 4.6, the combination of all three factors effectively leads to a redistribution of spectral intensity within the horseshoes. By selectively accessing the different factors in Eq. 3.62, we are thus able to deconvolute different contributions to the momentum maps. In the general case of multiple transitions within an exciton, however, the sums over different valence and conduction bands remain and, as a result, the above analysis would become less straightforward, especially due to the coherent summation of the electron part. Since in the present case of the hBN example we found the most asymmetry to arise due to the BSE eigenvectors in conjunction with the pump polarization, we will discuss this effect in more detail in the following.

4.4 Pump Polarization Effects in 2D hBN

4.4.1 Theory

In the derivation of the exPOT formalism for periodic systems shown in Sec. 3.3.10, we assumed the system to be in an *eigenstate* of the BSE Hamiltonian, $|N, (m, \mathbf{Q})\rangle$. As we have seen now for hBN, exciton S_1 and S_2 in fact belong each to a two-dimensional degenerate subspace. The two excitons in each subspace obtained from diagonalizing the BSE Hamiltonian then serve as a basis for their respective subspace. Any linear combination of the two “basis-” excitons from such a subspace is again a BSE eigenstate and therefore a usable initial state for exPOT. The question then arises, which linear combination should be used as the initial state in exPOT. Naturally, if we want to simulate pump-probe ARPES experiments, we should use the linear combination that we expect to appear in experiments. Assuming a resonant (to S_1 or S_2) pump-pulse and negligible pump broadening as well as all other effects that may create a more diverse population of excitonic states (compare the section on mixed states in Sec. 3.3.10), we can expect the pump-pulse to create a linear combination $|N, S_l\rangle$ (dropping $\mathbf{Q} = 0$ for simplicity) of the two basis-excitons with the expansion coefficients c_m^l , dependent on the polarization $\mathbf{E}$ of the pump pulse, given by the optical transition matrix elements (from first-order time-dependent perturbation theory [126]):

$$\begin{aligned} |N, S_l\rangle &= \sum_m c_m^l |N, m\rangle \\ c_m^l &\propto \langle N, m | \mathbf{E} \cdot \hat{\mathbf{P}} | N, 0 \rangle \end{aligned} \quad (4.1)$$

Here $|N, 0\rangle$ denotes the ground state and $\hat{\mathbf{P}}$ the N -electron momentum operator (compare Sec. 3.3.2). Note that m here indexes the eigenvectors as obtained from diagonalizing the BSE Hamiltonian, so $m = 1, 2$ for S_1 and $m = 3, 4$ for S_2 . Note also, that the transition matrix elements may alternatively be calculated based on the *velocity operator* for a more sophisticated treatment of the electron-photon interaction [36, 165]. These velocity-based transition matrix elements are directly available in the BERKELEYGW code and were used to form the superposition states throughout this chapter.

The transition density matrix elements (BSE eigenvector elements) of the superposition (eigen)state $|N, S_l\rangle$ can then also be written as a linear combination $\sum_m c_m^l X_{v,c,\mathbf{q}}^{(m)}$ of the elements of the basis-vectors. Explicitly writing this linear combination, Eq. 3.62 reads ($\mathbf{Q} = 0$):

$$\begin{aligned} I_{i=S_l}(\mathbf{k}) &\propto |\mathbf{A} \cdot \mathbf{k}|^2 \sum_v \sum_{\mathbf{q}}^{\text{BZ}} \left| \sum_c \sum_m c_m^l X_{v,c,\mathbf{q}}^{(m)} \mathcal{F}[\varphi_{c,\mathbf{q}}](\mathbf{k}) \right|^2 \\ &\quad \cdot \delta(\omega + \Omega_l + \varepsilon_{v,\mathbf{q}} - E_{\text{kin}}) \end{aligned} \quad (4.2)$$

To summarize, the procedure presented in this section can be understood as a simple basis change within the subspace of degenerate eigenstates, or, in other words, as a change from the basis obtained through solution of the BSE to a basis determined by the pump polarization.

In 2D systems excitons typically occur as degenerate pairs, and only their superposition should be considered as the physical exciton, which then, for instance,

also respects the symmetries of the system [159, 166]. In contrast to those eigenstates, the pump pulse in general breaks the system's symmetry and may create superimposed exciton states that depend on the pump polarization. Until now, we have used the pump-polarization depicted in Fig. 4.6. Now, we will also try out other pump polarizations and will see that the pump polarization can have a considerable imprint on exciton photoemission.

4.4.2 Results

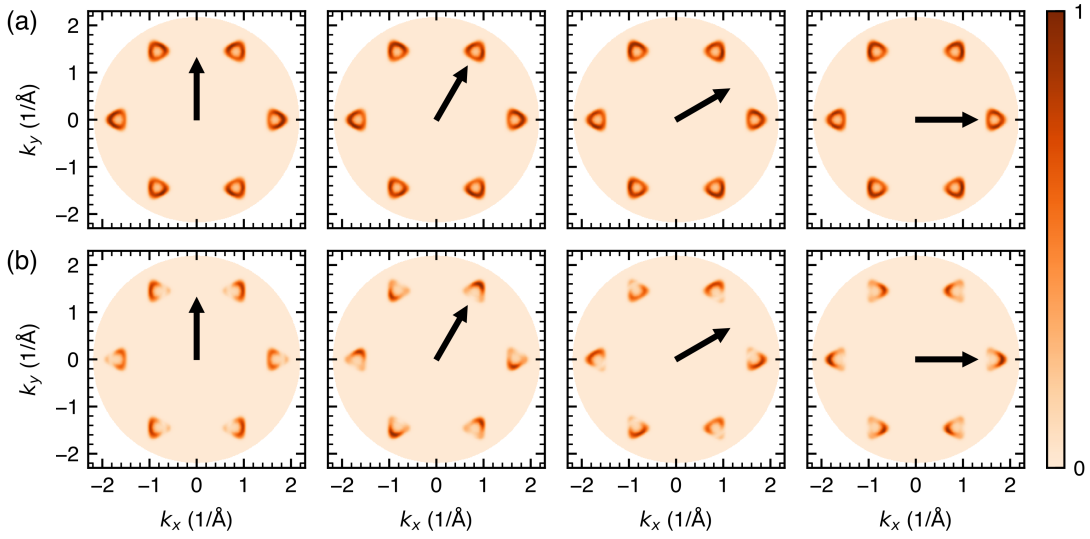


Figure 4.7: Influence of pump laser's polarization on exciton photoemission. The four columns show ARPES photoemission maps for different polarizations of the pump laser (black arrows). (a) shows photoemission from the lowest-energy exciton while (b) shows the second exciton. In the case of the first exciton, only small differences in the intensity distribution along the horseshoes are visible, while for the second exciton, there is a strong dependence on the pump polarization, with different polarizations leading to different rotations of the horseshoes. In the case of both excitons, the photoemission maps are mirror symmetric across the (high-symmetry) polarization directions.

As outlined above, the summation of energy-degenerate BSE eigenvectors, in order to form a superimposed exciton, involves coefficients that depend on the polarization of the pump pulse. The influence of pump polarization is illustrated in detail in Fig. 4.7. Panels (a) and (b) depict the photoemission from the S_1 exciton (5.3 eV) at a kinetic energy of 23.9 eV and the S_2 exciton (6.2 eV) at 24.8 eV, respectively. The black arrows indicate the polarization direction of the pump pulse. Photoemission from the first exciton is only weakly dependent on the pump pulse's polarization and retains the horseshoe intensity pattern. Varying the polarization reveals minor variations in the intensity distributions along the horseshoes. For the second exciton, however, there is a strong dependence of the photoemission intensity distribution on the pump pulse, where different polarization directions lead to different redistributions of spectral weight within the horseshoes. Although the probe pulse polarization may introduce an overall attenuation in an trARPES ex-

periment, pump-induced effects on exciton photoemission are therefore expected to be observable, provided that sufficient energy and momentum resolution are achieved.

4.5 Summary

As a proof of concept, we have applied the exPOT formalism for periodic systems to the prototypical case of monolayer hexagonal boron nitride. The resulting exPOT maps exhibit distinct patterns for different excitonic states. These patterns are characterized by an energy dispersion that follows the hole states, while the electron part of the exciton wave function is reflected in the photoemission matrix element. The photoemission intensity is further modified by the BSE eigenvectors, which introduces an additional dependence on the pump polarization, resulting in the suppression of spectral weight in the momentum maps as a direct consequence of the excitonic character.

4.6 Computational Details

For the example of monolayer hBN, we calculate Kohn-Sham DFT wave functions and energies in QUANTUM ESPRESSO (PWSCF v.7.2 and v.7.3.1) [150–152] using the Perdew-Burke-Ernzerhof exchange-correlation functional [66], ONCV pseudopotentials, a 12x12x1 BZ mesh and a cutoff energy of 50 Ry and 200 Ry for the wave functions and the representation of the density, respectively. The lattice constant was set to 2.507 Å (bulk experimental value: 2.506 Å [167]) and we use a vacuum layer of 20 Å, as well as a truncation of the Coulomb interaction in z direction [168], in order to avoid spurious interaction between repeated slabs from the periodic boundary condition. Based on these ground-state properties, we perform a G_0W_0 calculation using BERKELEYGW 4.0 [36, 95, 104] (as is commonly done, we only correct the energies, but leave the Kohn-Sham wave functions unchanged). For the G_0W_0 calculation as well as for all other BERKELEYGW calculations, we use the slab truncation scheme [104]. In particular, we use the *NNS* subsampling technique, which, for systems with reduced dimensionality, accelerates convergence with respect to the Brillouin-zone sampling [169]. Additionally, for faster convergence with respect to the number of empty bands, we used the static remainder approach of Ref. [170] (“exact_static_ch” flag set to 1). For the calculation of the static inverse dielectric function we use a 12x12x1 sampling of the Brillouin-zone, a cutoff energy of 30 Ry for reciprocal lattice vectors and sum over 200 bands. Based on this, we use the generalized plasmon pole model [95] to calculate (summing again over 200 bands) the G_0W_0 energies for 4 valence and 44 conduction bands, using the same BZ mesh and reciprocal lattice cutoff as for the inverse dielectric function. Finally, using again BERKELEYGW 4.0, we construct the (static) BSE Hamiltonian within TDA (Eq. 2.215) and for $\mathbf{Q} = 0$ using 4 valence and 9 conduction bands on a 12x12x1 BZ mesh, interpolate it to a 96x96x1 BZ mesh (4 valence, 4 conduction bands) and diagonalize it.

5 Sexithiophene - 6T

This chapter contains results of a combined experimental and theoretical study which has been published in Ref. [16]. The text and figures in this chapter have widely been adopted from there and subsequently restructured. The author of this thesis contributed to the main text given there, and wrote Appendices B and C, with significant input from Peter Puschnig and auxiliary input from the remaining co-authors of that manuscript. The *ab initio* calculations and photoemission simulations were performed and analyzed by the author of this thesis, with auxiliary input from the remaining co-authors of that manuscript.

5.1 Introduction

As a second application of exPOT for periodic systems we use α -sexithiophene (6T) thin films. 6T is a prototypical organic semiconductor, which is relevant for optoelectronic applications such as solar cells [3], and its photophysics has been extensively studied in the past, both, experimentally [171–174] and theoretically [175–177]. As substrate, we select oxygen-passivated Cu(110) which leads to the growth of uniaxially aligned molecules in a herringbone structure [178–180]. This ensures intermolecular overlap of the molecules’ π electron systems, enabling exciton delocalization across multiple molecules, which is an essential condition to explore the crossover from localized Frenkel excitons to delocalized Frenkel-Wannier excitons [181, 182] and thereby necessitates the use of molecular clusters or periodic systems in exPOT simulations (see below). This contrasts with earlier trPOT work on weakly coupled molecules [10], in which flat-lying molecules with negligible intermolecular coupling have been investigated, where excitations were essentially confined to single-molecule Frenkel excitons.

In the following, we first focus on the experimentally-obtained excited-state photoemission signal and show that a simple independent-particle photoemission calculation fails to reproduce the observed intensity distribution. This motivates the use of more sophisticated photoemission simulations based on our exPOT formalism. To perform these simulations, we first introduce model systems of varying sizes, ranging from a single molecule to a full, free-standing layer of 6T molecules and discuss their differences. Finally, we compare the photoemission signal based on low-lying excitons of these systems to the experimental data, show that the experimental intensity distribution is well-reproduced by our simulations and discuss the remaining discrepancies.

5.2 Pump-Probe ARPES of a 6T Film

In contrast to the example of hBN given in Chapter 4, experimental momentum maps have been obtained for this system via trARPES experiments. While time-dependent changes in the excited-state momentum signatures are discussed in Ref. [16], these effects are rather small⁹⁴ and we herein restrict ourselves to the k-map obtained at a time-delay of 0 fs between the pump- and the probe pulses (and at energies integrated from 0.6 and 1.4 eV above E_F , see below). In this section, experimental details and an initial comparison to theory are given. More details on the sample preparation and time-resolved ARPES experiments as well as information on the post-processing of the experimental data can be found in Appendix A of Ref. [16].

The ultrafast trPOT measurements on aligned α -sexithiophene (6T) films were performed using femtosecond high-harmonic probe pulses, to record the momentum-space distribution and time evolution of the exciton. As illustrated in Fig. 5.1a, the experiments used a sample consisting of an oriented thin film of the rod-like organic semiconducting molecule 6T, whose chemical structure is depicted in Fig. 5.1b, adsorbed on an oxygen-passivated Cu(110) surface. This substrate serves two important purposes. Firstly, it electronically decouples the molecules from the metallic substrate [10], thereby preventing a rapid quenching of the exciton. Secondly, the (2×1) missing-row O-reconstruction aligns the 6T molecules with their long axes along the $y = [001]$ direction of the Cu substrate since the molecules get trapped in the troughs between two adjacent Cu-O rows. Importantly, the molecules do not adsorb flat, but with their molecular planes tilted by $\sim 32^\circ$ about their long axis [180], as indicated in Fig. 5.1a, thereby facilitating an effective overlap of the π electron systems between neighboring molecules. For these experiments, a four-monolayer film was chosen, in which the molecules adopt a herringbone-like arrangement with alternating tilt angles, similarly to the stacking in the bulk crystal structure of 6T [183].

In order to select the photon energy and polarization direction of the pump laser pulse, we computed the optical properties of 6T. In a first step, we performed GW/BSE (Bethe-Salpeter equation) calculations for an *isolated* 6T molecule. The resulting quasiparticle energies of the frontier molecular orbitals, obtained within the GW approximation, are depicted in Fig. 5.1c and show a gap of 5.3 eV between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO). The solution of the BSE then reveals the energetically lowest exciton S_1 to exhibit a transition dipole moment parallel to the long axis of 6T at a transition energy of 2.8 eV. Thus, for an isolated 6T molecule a substantial exciton binding energy of 2.5 eV is to be expected. Note that the calculations also show that, in addition to the major HOMO to LUMO contribution, there is

⁹⁴Remember that the exPOT formalism becomes inapplicable if the system is in a superposition state of nondegenerate excitons, which is why for such cases we restrict its applicability to time-delays larger than the dephasing time, see Sec. 3.3.10. Using the k-map at a time-delay of 0 fs (remember also that both pulses are Gaussian pulses and we here mean that their intensity peaks hit the system at the same time) is here justified by the fact, that we do not observe much time-dependence in the experimental data (within the selected window of kinetic energies), such that it does not make a significant difference which time-delay is used for comparison with theory. This little time-dependence at early times may also hint that it is unlikely that such a superposition state has been created by the pump pulse.

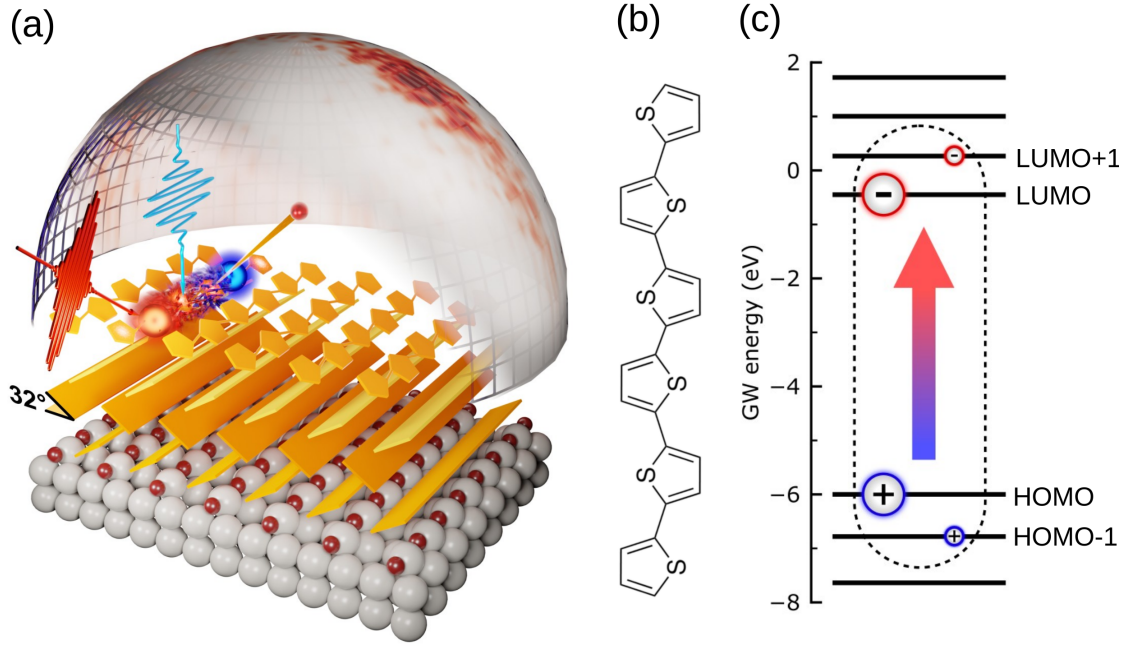


Figure 5.1: (a) Structural model of four monolayers of 6T (yellow) on the Cu(110)-(2 × 1)O substrate in which molecular planes are tilted by $\pm 32^\circ$ with respect to the sample surface (gray: copper atoms, red: oxygen atoms). The normal incidence pump (blue) and p-polarized probe at 55° incidence (red) pulses as well as the angular distribution of the emitted electrons are illustrated. (b) Chemical structure of 6T. (c) Illustration of the lowest optically allowed exciton state S_1 with the primary HOMO to LUMO and the secondary HOMO-1 to LUMO+1 contributions.

a secondary 8%-share of a HOMO-1 to LUMO+1 transition in the S_1 state. As shown in Refs. [14, 34], such an entangled excited state is predicted to exhibit a clear energy and momentum space signature.

Based on this analysis and on experimental optical reflection data [178], a normal-incidence pump pulse linearly polarized parallel to the long molecular axis was used for the trPOT experiments, in order to maximize the transition rate into the S_1 exciton. The pump energy was chosen to be 2.35 eV in line with earlier reflectance measurements on this 6T film [178], thus somewhat smaller than the computed transition energy for the isolated molecule. The linearly-polarized probe pulse (21.7 eV), created by high harmonics generation (HHG), was incident at an angle of 55° with the electric field oriented along the [001] crystallographic direction (i.e., the y direction), thereby optimizing the photoemission cross-section for molecular emission. The photoelectrons were detected with a time-of-flight momentum microscope, allowing a 4D data cube $I(E_{\text{kin}}, k_x, k_y, t)$ to be recorded. Thus, the photoemission intensity I was measured as a function of the photoelectrons' kinetic energy E_{kin} , their two parallel momentum components k_x and k_y , and the delay time t between the pump and the probe pulses, respectively. Note that in the actual analysis of the data, energies are defined with reference to the Fermi energy E_F , such that an energy value of zero corresponds to electrons emitted from the Fermi level, negative energies indicate occupied states while positive values signalize transiently excited states.

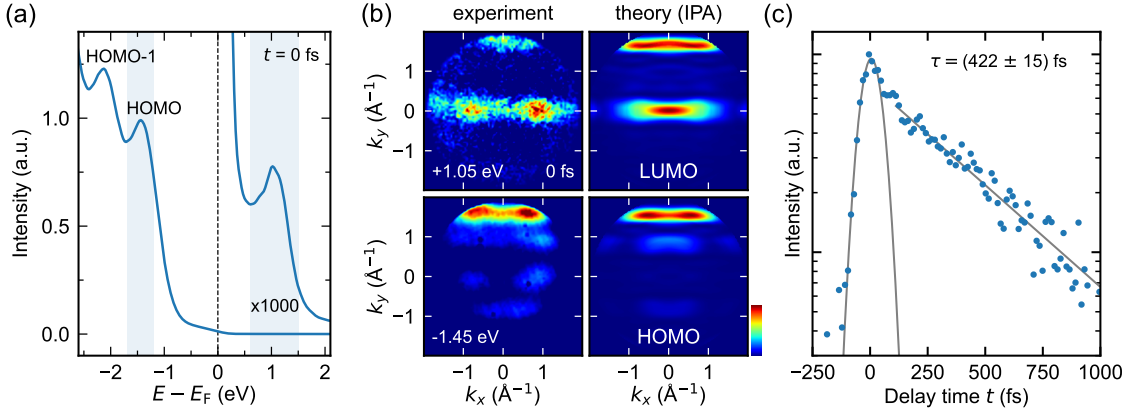


Figure 5.2: (a) Momentum-integrated photoemission spectrum with molecular emission from the HOMO and HOMO-1 below the Fermi energy E_F and the excitonic signature above E_F at $t = 0$ fs. (b) Momentum maps averaged over the blue-shaded energy regions indicated in panel (a) corresponding to the HOMO (lower row) and exciton (at $t = 0$ fs, upper row). The experimental data (left column) are compared to simulations for the HOMO and LUMO, respectively, computed in the independent particle approximation (IPA) for a free-standing monolayer of 6T molecules. (c) Momentum-integrated intensity, averaged over energies between 0.6 and 1.4 eV, as a function of delay time indicating an exponential decay of the exciton with a lifetime of $\tau = (422 \pm 15)$ fs.

An overview of the photoemission data is given in Fig. 5.2a, which shows momentum-integrated spectra at $t = 0$ fs both for occupied states below the Fermi energy E_F and for energies above, the latter enhanced by a factor of 1000 for the sake of clarity. Below E_F , we find the HOMO and HOMO-1 emissions at about -1.5 eV and -2.3 eV, in agreement with a previous study [179]. A momentum map taken around the HOMO peak is shown in the lower left corner of Fig. 5.2b. The comparison with a simulation for a free-standing layer of 6T molecules (lower right corner; using Eq. 3.42 for the HOMO-band only and integrating over all kinetic energies of photoelectrons coming from the band, compare Sec. D.3.3) shows excellent agreement and clearly supports this assignment. It is important to note that the simulation takes into account both the polarization of the probe pulse, which is incident from the negative k_y direction and which gives rise to the “up-down” asymmetry in the maps, as well as the molecular tilt angle of $\pm 32^\circ$ in the molecular film which has been determined by static POT [33, 180].

Above E_F , the pump pulse creates an excitation whose photoemission signature peaks at 1.05 eV. As shown by the delay scan in Fig. 5.2c, we observe a single-exponential decay with a lifetime of (422 ± 15) fs, which is somewhat larger than the 250 fs observed for a single layer of PTCDA molecules on the oxygen-passivated Cu(110) surface [10], presumably owing to the thicker organic film in the present case. The momentum distribution at $t = 0$ fs is shown in the top left corner of Fig. 5.2b. It is characterized by two emission features (major lobes) along the $k_y = 0$ line symmetrically grouped around the Γ point, and another weaker, minor lobe at $k_y \approx 1.7 \text{ \AA}^{-1}$. In a first attempt, we associate this observed momentum pattern with the LUMO of 6T, which is depicted in the top right corner of Fig. 5.2b. For simulating this map, we assumed that an electron populates the

LUMO-band of the free-standing 6T layer, but no interactions whatsoever with the remaining hole are considered⁹⁵ (using Eq. 3.42 for the LUMO-band only, in the same way as before for the HOMO-band). In contrast, the experimental map for 6T shows marked differences to the so-obtained simulated map. While the map employing the independent-particle approximation (IPA) is characterized by two stripe-like features along k_x in the k regions of the major and minor lobes, respectively, the simulation fails to reproduce the observed intensity modulation along the k_x direction in the major lobe region, resulting in an intensity maximum at normal emission, rather than two separated peaks with a minimum at normal emission. A possible origin for this discrepancy could be that electron-hole correlations cannot be ignored for 6T. Furthermore, it needs to be clarified whether an additional LUMO+1 contribution, as predicted for an isolated 6T molecule, could contribute to the deviation between experiment and theory regarding the momentum distribution of the excited-state photoemission. To answer these questions, we have performed *ab initio* simulations on various levels of sophistication, which shall now be shown.

5.3 Computational Results

We have performed density functional theory (DFT) and GW/BSE calculations as well as exPOT simulations for five systems: a monomer, a monolayer trimer, a monolayer tetramer, a periodic free-standing monolayer and, finally, a bilayer hexamer of 6T molecules. Details on the used geometry as well as the computational methods can be found in Sec. 5.6. The geometries can be seen in Fig. 5.5f-j. Before comparing the exPOT simulations to the experimental exciton k-map shown in the top left corner of Fig. 5.2b, we compare key properties of the five systems as obtained from the *ab initio* calculations.

Quasiparticle GW energies can be found in Fig. 5.3. For the monolayer, we plot a path in the b_2 direction of the Brillouin zone – corresponding to the a_2 direction in real space, the direction along which inter-molecular interaction leads to a sizable band dispersion.

The calculated optical absorption spectra for light polarized along the long molecular axis (y direction) are shown in Fig. 5.4. Note that each spectrum was normalized to a maximum value of 1.0 for better comparability.

The monomer spectrum shows a single optically active exciton, while for the trimer and tetramer additional, albeit much weaker, optically active excitons appear. For the monolayer, we observe an overall redshift of the spectrum, which is due to the different computational treatment of the monomer and clusters as opposed to the extended monolayer. For the latter, we used a single-shot G_0W_0 calculation on top of a PBE starting point, while for the former we could afford B3LYP starting points and self-consistent *evGW* corrections. The spectrum of the free-standing monolayer is dominated by two optically active excitons, where the first exciton, S_1 , exhibits a transition dipole moment about twice as large as the one of the next optically active exciton, S_3 . Finally, for the bilayer hexamer system we observe an additional blueshift of the spectrum when compared to the

⁹⁵This photoemission simulation is thus effectively equivalent to the situation detailed below Eq. 3.39, where the LUMO is populated via charge-transfer from the substrate.

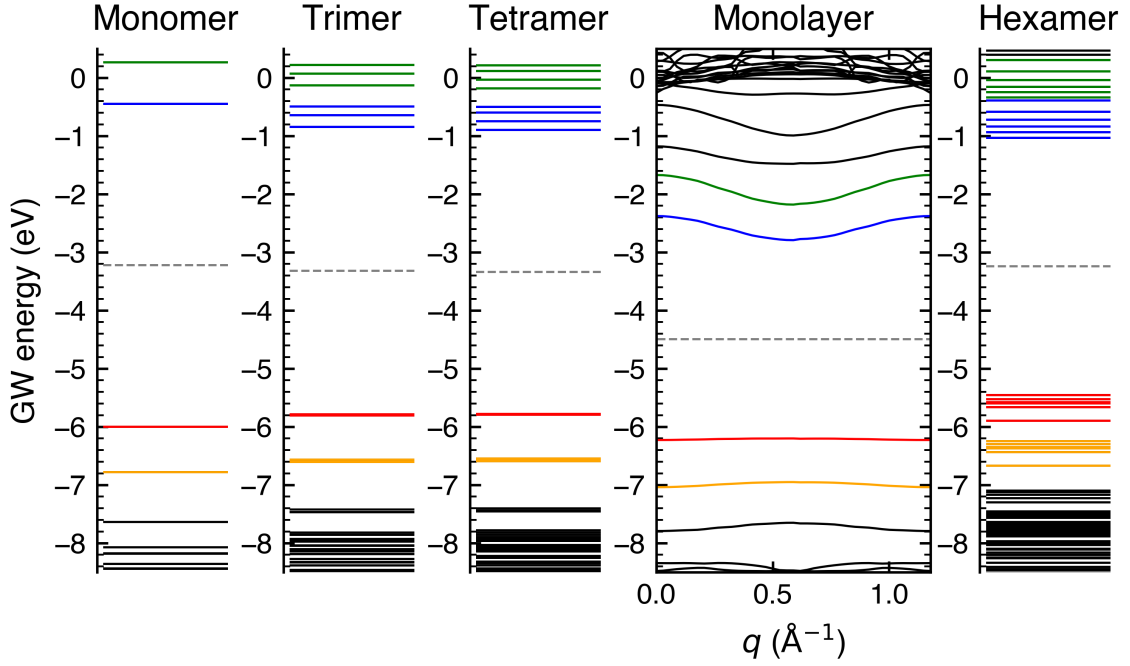


Figure 5.3: GW quasiparticle energy levels of 6T. From left to right, the GW energy levels of a 6T monomer, trimer, tetramer, monolayer and (bilayer) hexamer are shown. Monomer and cluster calculations were performed on the $evGW$ level and the monolayer calculation on the G_0W_0 level. The monolayer band-structure is directly plotted using the GW energies that were used in the BSE and is shown for a path from Γ to Γ_2 in b_2 direction. Cluster-orbitals have been identified with HOMO-1–LUMO+1 of the monomer and accordingly color-coded. Similarly, the related energy bands of the monolayer have been color-coded accordingly. The Fermi level is shown as a dashed gray line.

monomer and other cluster calculations, which can be attributed to the changes in the electronic structure due to the now-present interlayer interaction. Importantly, it can be seen that the spectrum is composed of a multitude of optically active excitons with varying sizes of the transition dipole moment $|d_y|^2$. This complicates the simulation of excited-state photoemission, as detailed below.

The compositions of these optically active excitons are summarized in Table 5.1, where the transition probability from valence orbital v to conduction orbital c in exciton m is given by (compare Eq. C.71)

$$p_{v \rightarrow c}^m = |X_{vc}^m|^2 \quad (5.1)$$

in the cluster and monomer case and

$$p_{v \rightarrow c}^m = \sum_q^{\text{BZ}} |X_{vcq}^m|^2 \quad (5.2)$$

for the periodic monolayer. Specifically, we find that the contribution of the HOMO-1 to LUMO+1 transition shrinks from 8.4% in the monomer, to 6.2% (6.6%) in the tetramer (trimer) and only 2 – 3% in the monolayer. Conversely, going from the monolayer clusters to the full monolayer, the HOMO to LUMO transition grows even more in importance, fully dominating all other contributions

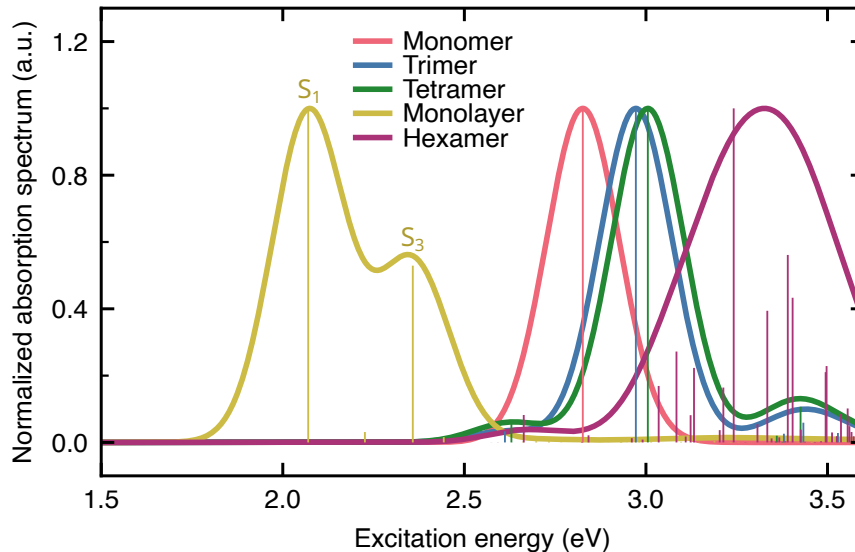


Figure 5.4: Optical absorption spectra of different 6T systems. The spectrum of the monomer is dominated by a single optically active exciton at 2.83 eV, which is also the lowest-energy excitation of the system. For the trimer (tetramer) the most active exciton is the third (fourth) one, located at 2.97 eV (3.00 eV). For the monolayer, the lowest-energy exciton is located at 2.07 eV and is the most optically active one, followed by the third exciton which is located at 2.36 eV. In the hexamer (bilayer) system, the spectrum is composed of a multitude of optically active excitons with the overall most dominant one being located at 3.24 eV. Each vertical line denotes an individual (optically active) exciton, with the exciton’s transition dipole moment $|d_y|^2$ determining the height of the line. The heights have been normalized on a per-system basis such that the brightest exciton of each system has a height of 1.0. Similarly, all spectra are normalized individually to a maximum value of 1.0.

to the excitons shown in Table 5.1. For the hexamer system we picked excitons 12 and 18 as exemplary excitons, since they are both rather low-lying and optically bright. For both, we again find that they are dominated by the HOMO to LUMO transition, with the HOMO-1 to LUMO+1 transition contributing less than 2%. As a technical note regarding this analysis, we point out that, in the case of the many-molecule clusters, there are multiple orbitals with monomer-HOMO character and multiple orbitals with monomer-LUMO character (which can for example be identified by their k-maps via Eq. 3.39). The same has been verified for HOMO-1 and LUMO+1 of the monomer. Thus, when calculating the contribution of a particular transition to a given exciton, e.g., the HOMO to LUMO transition of the tetramer, we sum $p_{v \rightarrow c}^m$ over these orbitals. For the example of the HOMO to LUMO transition of the tetramer, this means that we sum up transitions across four valence and four conduction orbitals (making it a sum of 16 contributions). See also Fig. 5.3 on the identification of energy levels.

It is insightful to analyze the LUMO+1 contributions to the excitons shown in Table 5.1. The parts connected to the HOMO are suppressed by the at least ≈ 30 times more intense HOMO to LUMO transition. Note that this rules out the second option offered at the end of Sec. 5.2 to explain the discrepancy between

the IPA photoemission map of the LUMO and the experimental exciton k-map. Note also, that for the LUMO+1 contribution connected to the HOMO-1, energy conservation demands [34] the emission features to be expected 0.8 eV below the peak at $E - E_F \approx 1.05$ eV (compare Fig. 5.2a and Eq. 3.62). Taking into account the rapidly rising photoemission background when approaching the Fermi level and the predicted (by the monolayer calculation) approximately 20–30 times lower intensity than the main peak (connected to the HOMO), it becomes clear that a possible LUMO+1 contribution from this transition is extremely hard to detect experimentally, thus explaining why it was not found in the experimental exciton photoemission data. The same argument of course then also holds for transitions connected to even lower valence bands/orbitals.

Table 5.1: Properties of low-lying dominant optically active excitons of the monomer, trimer, tetramer, monolayer and hexamer. In addition to the excitation energy, the energy difference to the lowest exciton S_1 of each system is given in parentheses. For each system individually, the transition dipole moment, $|d_y|^2$, in the direction of the light polarization of the optically strongest exciton is normalized to 1. The last four columns contain the transition probabilities from HOMO/HOMO-1 to LUMO/LUMO+1 for each of the excitons.

System	Exciton	Energy (eV)	$ d_y ^2$	H	H-1	H	H-1
				$\downarrow$ L	$\downarrow$ L+1	$\downarrow$ L+1	$\downarrow$ L
Monomer	S_1	2.826	1.000	0.884	0.084	0.000	0.000
Trimer	S_3	2.972 (0.361)	1.000	0.882	0.066	0.007	0.009
Tetramer	S_4	3.005 (0.410)	1.000	0.883	0.062	0.008	0.010
Monolayer	S_1	2.070	1.000	0.931	0.031	0.006	0.008
Monolayer	S_3	2.358 (0.288)	0.529	0.916	0.021	0.025	0.017
Hexamer	S_{12}	3.084 (0.510)	0.272	0.948	0.014	0.023	0.004
Hexamer	S_{18}	3.242 (0.667)	1.000	0.932	0.017	0.021	0.013

5.4 Comparison of exPOT Simulations to Experimental Exciton k-map

As mentioned before, the experimental exciton k-map depicted in the top left corner of Fig. 5.2b is characterized by two emission features (major lobes) along the $k_y = 0$ line that are symmetrically grouped around the Γ point and are centered respectively at $k_{x,\max} \approx \pm 0.85 \text{ \AA}^{-1}$, and another weaker, minor lobe at $k_y \approx 1.7 \text{ \AA}^{-1}$. Note that the presence of a minor lobe at $k_y \approx 1.7 \text{ \AA}^{-1}$ but not at $k_y \approx -1.7 \text{ \AA}^{-1}$ is attributed to the influence of the probe laser’s angle-of-incidence on the photoemission maps. In all our exPOT simulations shown in Fig. 5.5a-e and 5.7a we neglect the polarization prefactor for simplicity, leading to minor lobes at both $k_y \approx 1.7 \text{ \AA}^{-1}$ and $k_y \approx -1.7 \text{ \AA}^{-1}$. Note also, that for all simulated k-maps in this whole chapter we used the PWA.

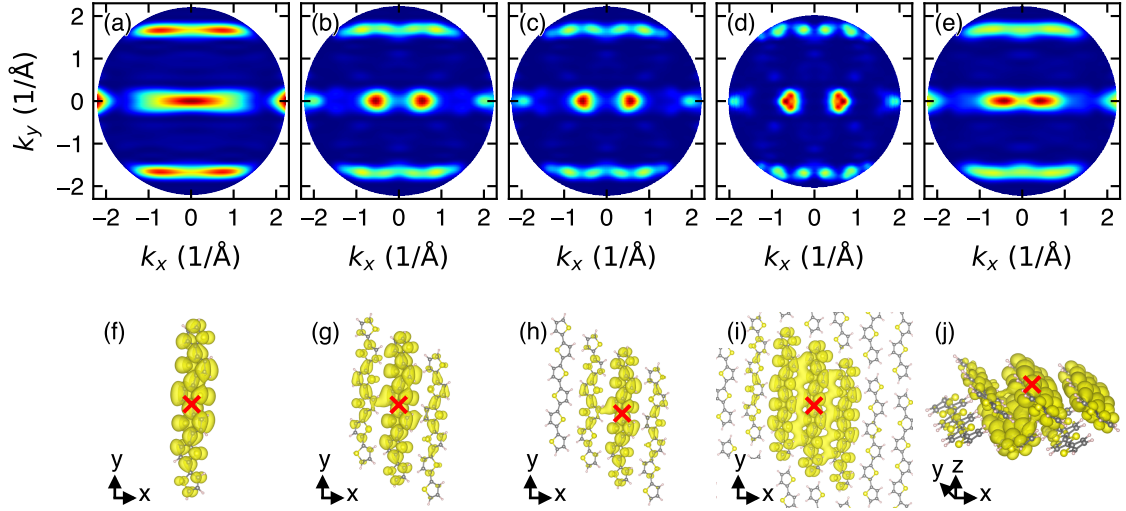


Figure 5.5: Simulated photoemission maps and exciton wave functions. (a) Simulated momentum map for S_1 of the monomer, (b) S_3 of the trimer, (c) S_4 of the tetramer, (d) S_1 of the monolayer and (e) S_{12} of the hexamer. Panels (a)–(d) show emission from the dominant optically bright exciton of each system and show a clear progression towards an increase in the separation between the two intensity peaks along $k_y = 0$ (with trimer and tetramer yielding practically the same separation). For the hexamer, panel (e), S_{12} is one of multiple low-lying bright excitons, as discussed in the text. Panels (f)–(j) show the corresponding fixed-hole electron density $|\chi(\mathbf{r}_e, \mathbf{r}_h = \text{fixed})|^2$ (isosurface at 0.5% of maximum value). The hole has been fixed 0.5 $\text{\AA}$ above a carbon atom connecting the central thiophene rings, as indicated by the red crosses. Panels (f)–(j) were created with VESTA [184].

Let us now take a look at the exPOT simulations (Eq. 3.54 for monomer and clusters and Eq. 3.62 for the periodic monolayer, using energy-integration as detailed in Sec. D.3.3) for the five systems and see if the experimentally observed lobe-structure is reproduced. Note that for monomer, trimer and tetramer, there is a clear optically dominant exciton which has been chosen to calculate the exPOT map of the respective system. For the monolayer, we use S_1 (and S_3) and for the hexamer we use S_{12} , as detailed below. The results are shown in Fig. 5.5 and can be summarized as follows: First, all five systems exhibit photoemission along the $k_y = 0$ line and at $k_y \approx \pm 1.7 \text{ \AA}^{-1}$, already leading to qualitative agreement with the experiment. Second, the monomer does not exhibit the experimental intensity modulation along the $k_y = 0$ line. It exhibits a maximum at the Γ point, while we experimentally find two lobes being symmetrically positioned around the Γ point, with a minimum (along $k_y = 0$) in between. The experimentally observed intensity modulation, however, already appears for the trimer (tetramer), but with a smaller separation of the intensity peaks, located at $k_{x,\text{max}} \approx \pm 0.54 \text{ \AA}^{-1}$ ($k_{x,\text{max}} \approx \pm 0.54 \text{ \AA}^{-1}$) when compared to the experimental positions of $k_{x,\text{max}} \approx \pm 0.85 \text{ \AA}^{-1}$. This value increases to $k_{x,\text{max}} \approx \pm 0.64 \text{ \AA}^{-1}$ in the case of S_1 of the monolayer system. As we can see from Fig. 5.5g-i, the exciton in the trimer, tetramer and periodic monolayer calculation significantly extends over multiple molecules, thus explaining, why the monomer simulation was not able to

reproduce the experimental k-map. Note that the first question posed at the end of Sec. 5.2, has now also been answered: the photoemission modulation along the $k_y = 0$ line is very likely a result of the electron-hole correlation present in the exciton, which has been neglected in the IPA LUMO map shown there.

Notably, the optically bright S_3 exciton of the monolayer (see Fig. 5.7) does also exhibit an intensity modulation along the $k_y = 0$ line, however with an intensity peak appearing at the Γ point. Moreover, for S_1 and S_3 we observe slightly different intensity distributions in the minor lobe region at $k_y \approx \pm 1.7 \text{ \AA}^{-1}$. However, because of the only ~ 0.3 eV higher excitation energy of S_3 and its weaker transition dipole moment compared to S_1 (see Fig. 5.4), the present time-resolved POT experiments are not able to reveal the presence of S_3 .

Of all monolayer *ab initio* calculations, the one involving a full periodic monolayer is the most sophisticated one and (comparing $k_{x,\text{max}}$), as expected, has the best agreement (via S_1) with the experimentally obtained k-map. Note, however, that there remains a small deviation regarding the position of the $k_y = 0$ lobes, for which experimentally a value of $k_{x,\text{max}} \approx \pm 0.85 \text{ \AA}^{-1}$ is found while the monolayer S_1 k-map shows them at $k_{x,\text{max}} \approx \pm 0.64 \text{ \AA}^{-1}$. We attribute this difference to the simplified structural model consisting of only a single 6T layer, while the experiment is performed on four layers of 6T⁹⁶. Unfortunately, *ab initio* GW/BSE calculations for such a four-layer periodic structure (or even a bilayer) are out of reach for computational reasons. This was the motivation for performing the 6T hexamer calculation shown above, where we use a hexamer cluster containing three molecules in the first and three in the second layer (see Appendix 5.6), thereby allowing a first assessment of the influence of additional 6T layers on the exciton k-map. Note that the main absorption peak of the hexamer is composed of several excitons (see Fig. 5.4) and it is not trivial to predict which (possibly: combination, see Sec. 3.3.10 on mixed states) of them corresponds to the excitation created in a pump-probe ARPES experiment of a 4ML system. In an informed guess, we expect the low-lying bright excitons S_{11} and S_{12} to correspond to the experimentally created excitation, both of which exhibit the characteristic double-lobe momentum pattern with only slightly varying $k_{x,\text{max}}$ positions. Choosing S_{12} as an exemplary exciton, as it is the lowest-lying exciton with appreciable oscillator strength, we can see from Fig. 5.5e that it again exhibits the double-lobe momentum pattern along the $k_y = 0$ line, however with a small change in $k_{x,\text{max}}$. Unfortunately, the lobes are shifted towards $k_{x,\text{max}} \approx \pm 0.42 \text{ \AA}^{-1}$, a smaller value than what was observed for the other systems. There are many possible reasons for this⁹⁷: first, since we expect interlayer interactions to be the deciding factor in shifting $k_{x,\text{max}}$ to the experimentally observed value, we can expect the geometry of the second

⁹⁶Note that we rule out problems related to exciton superposition states that may be probed at pump-probe time delays smaller than the dephasing time (compare Sec. 3.3.10 on mixed states and superposition states), since the k-map within the chosen energy window showed little time-dependence, as already mentioned before. Additionally, a combination of S_1 and S_3 in terms of a mixed state has been tested but lead to an additional (small) decrease of $k_{x,\text{max}}$, such that we also rule out such a mixed state as the explanation for the discrepancy.

⁹⁷Although theoretically possible, we omit here the possibility that a 2ML sample would in experiments show a $k_{x,\text{max}}$ as small as what was obtained from the hexamer. Since the periodic monolayer calculation shows a value of $k_{x,\text{max}} \approx \pm 0.64 \text{ \AA}^{-1}$ and the 4ML experiment gives a value of $k_{x,\text{max}} \approx \pm 0.85 \text{ \AA}^{-1}$, we expect a 2ML experiment to exhibit a value within or close to these two boundary cases.

layer relative to the first layer to be crucial. And even though the hexamer geometry is based on the experimentally obtained structure of a 6T multilayer (crystal) systems, already small deviations from the experimental geometry (here: 4ML) could become important. Due to the high computational cost of the corresponding GW/BSE calculations, photoemission simulations for additional geometries have been postponed to future work. Second, looking at the fixed-hole exciton wave function (compare Eq. 2.214) of S_{12} depicted in Fig. 5.5j, we can see high electron density at the right molecule in the upper layer, indicating that the exciton would possibly extend over more than three molecules in that layer if the cluster was larger. “Forcing” the exciton into a too small cluster will likely affect the interaction between the molecular layers and is a likely second source for the deviation from the experimental k-map. Unfortunately, GW/BSE calculations for larger clusters were too expensive at the current time and are again left for future work. To conclude, even though $k_{x,\max}$ went into the wrong direction, the important result here is that the presence of the second layer indeed affected the position of the maxima, thus strengthening our assumption that using a single periodic layer of 6T causes the discrepancy between theory and experiment.

5.5 Summary

To summarize, we have seen that the distinct momentum pattern obtained from a pump-probe ARPES experiment of a four-monolayer thick film of 6T molecules could not be reproduced by a photoemission simulation that disregards the electron-hole correlation in the optically-excited state. In contrast, this correlation is explicitly accounted for in the exPOT formalism and we found that exPOT photoemission simulations already show good agreement with the experiment when employing a small monolayer cluster of only three molecules as a model system. The best agreement with the experimental momentum map was achieved via exPOT simulations using a periodic monolayer of 6T molecules, where the remaining disagreement is likely due to the use of a single monolayer instead of the experimental four-monolayer geometry.

5.6 Computational Details

In the following, we provide details of the *ab initio* calculations underlying this chapter, where we first focus on gas-phase systems (monomer and clusters) and then detail the calculations involving the free-standing molecular monolayer.

5.6.1 Monomer and Clusters

In this section, we provide details of our GW/BSE calculations for an isolated 6T molecule, a cluster containing three and one containing four molecules, as well as for a cluster of six molecules. The geometries of the monomer, trimer and tetramer system were obtained by cutting out one/three/four molecules along the a_2 direction from the periodic monolayer shown in Fig. 5.6, such that these can be regarded as monolayer clusters. In contrast, the hexamer cluster is a bilayer cluster. In its first layer, it is simply the trimer system mentioned before. To these

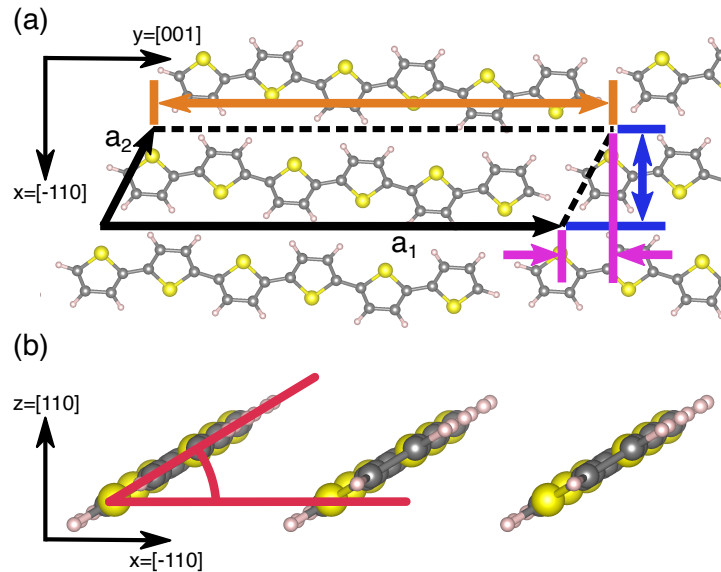


Figure 5.6: (a) Top-down view of the monolayer. The unit cell vectors are shown in black, where a_2 determines the row-slip (purple) of 2.807 Å. The row-distance d (blue) equals 5.335 Å, and the unit cell length (orange) is 25.258 Å. (b) Side view of the monolayer. The molecules are tilted (red) by 31.5° relative to the xy -plane. Created with VESTA [184].

three molecules, we then added three additional molecules as a second layer, based on the herringbone-like arrangement found experimentally in Ref. [183]. That is, for each molecule of the first layer (rotated by +31.5° against the layer plane), we created a molecule in the second layer which is rotated by −31.5° against the layer plane and shifted by about half of the cell length in a_2 direction ($0.49|a_2|$) and by 3.785 Å in z direction (see Fig. 5.5j).

In a first step, we performed single-point ground-state density functional theory (DFT) calculations using ORCA 5.0.4 [143, 144] with the 6-311G* Gaussian-orbital basis set [185, 186] and the B3LYP hybrid functional [69, 70]. The resulting Kohn-Sham orbitals and energies then served as the basis for the GW calculation. For this second step, we employed the FIESTA code [145]. Specifically, we performed an iterative, self-consistent correction of the Kohn-Sham energies (*evGW*) while keeping the wave functions unchanged. For a single 6T molecule, we explicitly corrected 10 occupied (valence) and 10 unoccupied (conduction) orbitals. Orbitals beyond there were rigidly shifted by the correction that was applied to the HOMO-9/LUMO+9. For the trimer/tetramer/hexamer calculation, we explicitly corrected 30/40/60 occupied and 30/40/60 unoccupied orbitals.

In the third step, we solved the (static) Bethe-Salpeter equation (BSE) within the Tamm-Dancoff approximation (TDA, see below), Eq. 2.213. Using again the FIESTA code, we iteratively diagonalized the BSE Hamiltonian. This way, we calculated the first 20 excitons of the monomer, trimer and tetramer system, where we constructed the BSE Hamiltonian by including all valence orbitals up to 20 eV below the HOMO and all conduction orbitals up to 20 eV above the LUMO. This resulted in the use of 72 valence and 135 conduction orbitals in the single-molecule calculation, 218 valence and 381 conduction orbitals in the trimer calculation and 291 valence and 507 conduction orbitals in the tetramer calculation. Similarly, for

the hexamer system we calculated the first 60 excitons, where we used 10 eV as the orbital-inclusion cutoff, leading to the inclusion of 281 valence orbitals and 319 conduction orbitals. Note that this smaller cutoff was chosen for computational reasons. Tests with the trimer system showed that using this smaller cutoff does not lead to significant changes in the momentum maps of low-lying excitons. In particular, this applies to those excitons dominated by HOMO to LUMO contributions, which are the excitons of interest here (where we identify the first three valence/conduction orbitals of the trimer with the monomer’s HOMO and LUMO). This demonstrates that the use of this somewhat smaller cutoff value for the hexamer system is well justified. In all cases, we used the TDA, since test calculations with the monomer showed the de-excitations’ total weight to be less than 2% of that of the excitations in the BSE eigenvector of S_1 . That is, we found:

$$\sum_{v,c} |X_{v,c}^{S_1}|^2 > 50 \sum_{v,c} |Y_{v,c}^{S_1}|^2 \quad (5.3)$$

Also, the excitations (see also Table 5.1 for the absolute size of the dominant excitations) were found to change by less than a percentage point when employing the TDA, that is (employing equal normalization for comparability):

$$\begin{aligned} \sum_{v,c} |X_{v,c}^{S_1}|^2 &= 1 \\ \sum_{v,c} |X_{v,c}^{S_1 \text{ TDA}}|^2 &= 1 \\ \left| |X_{v,c}^{S_1}|^2 - |X_{v,c}^{S_1 \text{ TDA}}|^2 \right| &< 0.01 \quad \forall v, c \end{aligned} \quad (5.4)$$

5.6.2 Periodic 6T Layer

This section summarizes details of our *ab initio* GW/BSE calculations for a free-standing, periodic monolayer of 6T. Its geometry is based on the experimentally determined structure of a 6T crystal [183]. We use a skewed unit cell containing one molecule per cell as depicted in Fig. 5.6. Just as in the cluster case, we perform a series of DFT, GW and BSE calculations to get all the quantities required by the exPOT formalism, Eq. 3.62.

For the first step, the ground-state DFT calculations, we used QUANTUM ESPRESSO (PWSCF v.7.2) [150–152], employing the PBE functional [66], ONCV pseudopotentials and a plane-wave energy cutoff of 70 Ry for wave functions and 280 Ry for the density. To avoid spurious interactions between repeated slabs in the z direction, the unit cell height was set to 28.525 Å, which corresponds to a vacuum layer of 25.521 Å. Additionally, we employed a truncation scheme for the Coulomb interaction [168]. For this and all upcoming steps, unless stated otherwise, we utilized a $2 \times 8 \times 1$ BZ mesh.

Steps two and three, the GW and (static) BSE calculations, were performed using BERKELEYGW 4.0 [36, 95, 104] using the slab truncation scheme [104]. Before performing the GW step, we employed BERKELEYGW’s PARABANDS tool to calculate *stochastic conduction pseudo-bands* [187] to reduce the calculation times and the scaling of the subsequent GW/BSE calculation. We protected 27 conduction bands, which were then utilized for the construction of the BSE Hamiltonian. The

remaining conduction bands were compressed into 520 pseudo-bands, resulting in a total of 620 bands (including the 73 valence bands). The actual GW calculation was then conducted at the G_0W_0 level (and without changing the orbitals), where we used the generalized plasmon pole model [95]. For faster convergence of the G_0W_0 energies with respect to the BZ mesh, we used the nonuniform neck subsampling (NNS) technique [169]. Additionally, for faster convergence with respect to the number of empty bands, we used the static remainder approach of Ref. [170] (“exact_static_ch” flag set to 1). As a substep, we calculated the static inverse dielectric function by employing a cutoff energy of 20 Ry for reciprocal lattice vectors and summing over 500 bands. Finally, we obtained the G_0W_0 energies of 27 valence and 27 conduction bands by summing again over 500 bands and using the same plane-wave cutoff as before. Then, for use in the ensuing BSE calculation, we recalculated the static inverse dielectric function applying the same settings as above, but without the NNS subsampling.

For solving the BSE, we considered 27 valence and 27 conduction bands in the construction of the direct and exchange kernel matrix. Note that for solving the BSE, we calculated wave functions on a finer BZ mesh, $10 \times 40 \times 1$, and interpolated the G_0W_0 corrections and the direct and exchange kernel to the finer grid (interpolating from the 27 coarse valence and 27 coarse conduction wave functions to 20 fine valence and 22 fine conduction wave functions). Then, by fully diagonalizing the BSE Hamiltonian in the Tamm-Dancoff approximation, Eq. 2.215, and restricting ourselves to excitations with center-of-mass momentum $\mathbf{Q} = 0$, we obtained the exciton energies and eigenvectors for optical excitations.

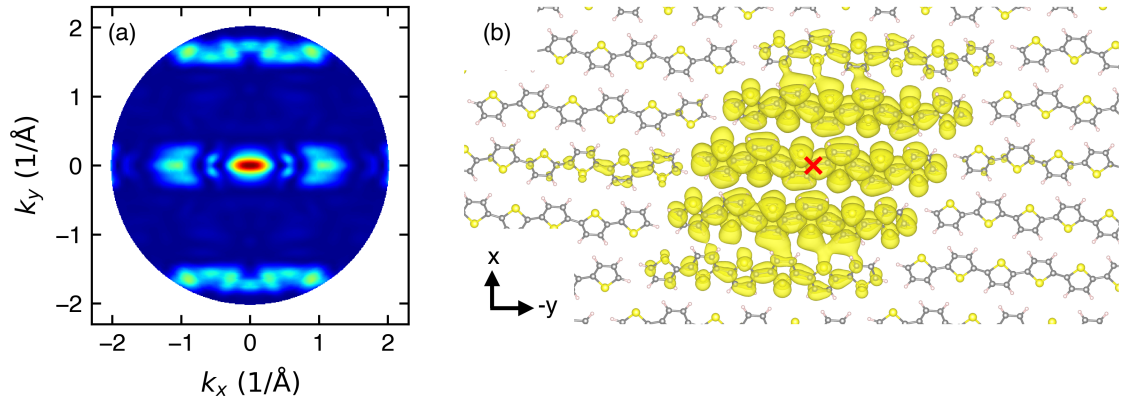


Figure 5.7: In analogy to Fig. 5.5: (a) simulated momentum map for S_3 of the monomer and (b) the corresponding fixed-hole electron density $|\chi(\mathbf{r}_e, \mathbf{r}_h = \text{fixed})|^2$ (isosurface at 0.5% of maximum value). The hole has been fixed 0.5 $\text{\AA}$ above a carbon atom connecting the central thiophene rings, as indicated by the red crosses. Panel (b) was created with VESTA [184].

6 Exciton Photoemission of a Type-II Organic Hetero-Interface

6.1 Introduction

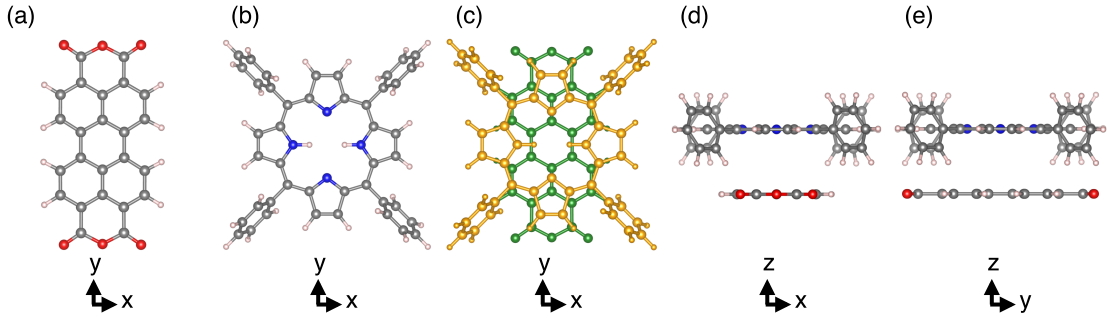


Figure 6.1: Molecular structure of the studied systems. (a) and (b) show respectively the isolated PTCDA and H2TPP molecules. (c) Top (d) front and (e) side view of the PTCDA/H2TPP dimer. For clearer visibility the PTCDA molecule is colored green and the H2TPP molecule is colored orange in (c). Atomic colors in (a), (b), (d), (e): hydrogen:white, carbon:gray, nitrogen:blue, oxygen:red. Note that H2TPP's phenyl rings are twisted, forming a propeller conformation. Created with VESTA [184].

Charge transfer (CT) excitons are highly relevant not only in naturally occurring processes like photosynthesis [188], but also in practical applications like organic photovoltaics [189], such that the study of related phenomena like CT exciton transport in solids or the recombination process poses a promising endeavor. As a powerful experimental technique, trARPES can be used to study the formation and decay of CT excitons by measuring momentum-space fingerprints of the excited state as a function of the pump-probe delay time.

In this chapter, photoemission momentum maps (k-maps) are simulated for a model hetero-organic interface system. We choose PTCDA and H2TPP as the molecules forming the interface since the specific level alignment of the two molecules makes the existence of low-energy charge transfer (CT) excitons very likely. As shown below, the system indeed exhibits two distinct low-energy CT excitons, making it a promising test system for the study of ultrafast exciton formation and decay dynamics via ultrafast trARPES experiments. Experimentally,

such an interface can be realized by adsorbing a (or multiple) film(s) of PTCDA on a Cu(001)-2O substrate [10], followed by the deposition of an H2TPP molecular layer. Since the calculations in this chapter are performed on a gas-phase theory level and for a single PTCDA/H2TPP dimer, we choose one particular dimer geometry which is expected to mimic the geometry of extended films. The individual molecules as well as the chosen dimer geometry can be found in Fig. 6.1.

Note that the usage of molecular clusters as a first stepping stone towards a full simulation of extended molecular layers is motivated by the findings of Chapter 5. As was shown there, already photoemission simulations involving small molecular clusters can be able to reproduce experimental momentum patterns of extended molecular layers with qualitative agreement. Crucially, it was found that the used molecular cluster must be large enough to sufficiently account for intermolecular interactions. In our current system, the interaction between neighboring PTCDA molecules and neighboring H2TPP molecules is expected to be less relevant than the interaction between the tilted 6T molecules of Chapter 5, thus justifying the usage of a single molecule from each molecular layer.

We begin by focusing on quasiparticle GW energies and show how the energy levels of the dimer are related to those of the monomer systems. In agreement with this assignment of the dimer orbitals we then identify the low-energy excitons of the dimer as CT excitons and the energetically higher-lying excitons as Frenkel excitons. Finally, we analyze photoemission fingerprints of the various dimer excitons and show how the experimentally-observed photoemission signal may change under a decay from the optically active Frenkel excitons to the optically dark CT excitons.

6.2 Quasiparticle GW Energy Levels

Having performed the necessary *ab initio* calculations (details can be found in Sec. 6.6), we start the analysis of the dimer system with a comparison of the GW quasiparticle energies obtained for it, as compared to GW energies of an isolated PTCDA molecule and an isolated H2TPP molecule, Fig. 6.2. First, comparing the two monomer systems, we find a *type-II level alignment* of the PTCDA and H2TPP frontier orbitals, that is, we find the following energetic order: HOMO of PTCDA < (HOMO-1 and) HOMO of H2TPP < LUMO of PTCDA < LUMO of H2TPP. Based on this ordering, and assuming little hybridization in the dimer orbitals (such that each dimer orbital in the relevant energetic domain is effectively an orbital of one of the monomers), we can expect the dimer's HOMO to sit on the H2TPP molecule, while its LUMO should sit on the PTCDA molecule. As shown in the center of Fig. 6.2, this is in fact the orbital structure we found (via Kohn-Sham DFT + GW) for the dimer: using Loewdin population analysis, each dimer orbital was partially assigned to the PTCDA or H2TPP molecule, with the result that the orbitals in the shown energy range of [-8 eV, 0 eV] are all mostly located on only one of the two molecules, with the HOMO and HOMO-1 being located on the H2TPP molecule and the LUMO on PTCDA. Note that, for each dimer orbital, the sum of PTCDA and H2TPP contributions shown is not 100%, which is an artifact resulting from the omission of atomic orbitals contributing less than 0.1% to the dimer orbital. In addition to the energetic ordering, by looking at the

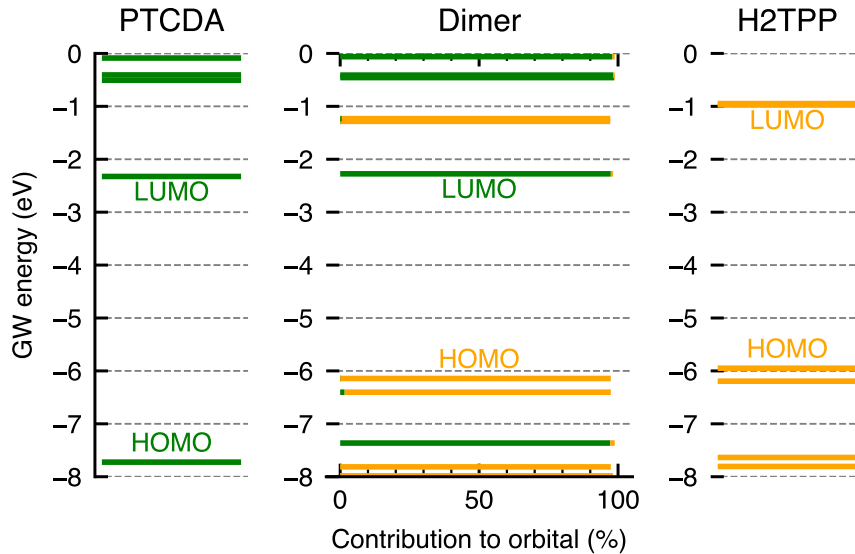


Figure 6.2: GW orbital energies of PTCDA, PTCDA/H2TPP dimer and H2TPP. The GW quasiparticle energies are shown on the left (green) for the PTCDA monomer and on the right (orange) for the H2TPP monomer. The orbital energies of the dimer are shown in the middle, where the vertical line corresponding to each orbital has been colored based on a Löwdin population analysis, thereby showing what percentage of the orbital is sitting at the PTCDA (green) or the H2TPP (orange) molecule.

orbital's wave functions, the HOMO and HOMO-1 of the dimer can respectively be identified with the HOMO and HOMO-1 of H2TPP, and the dimer's LUMO can be identified with the LUMO of PTCDA. Note additionally, since they will become relevant later, that the HOMO-2 of the dimer can be identified with the HOMO of PTCDA and the (almost degenerate) LUMO+1 and LUMO+2 of the dimer can respectively be identified with the (almost degenerate) LUMO and LUMO+1 of H2TPP.

6.3 Frenkel and CT Excitons

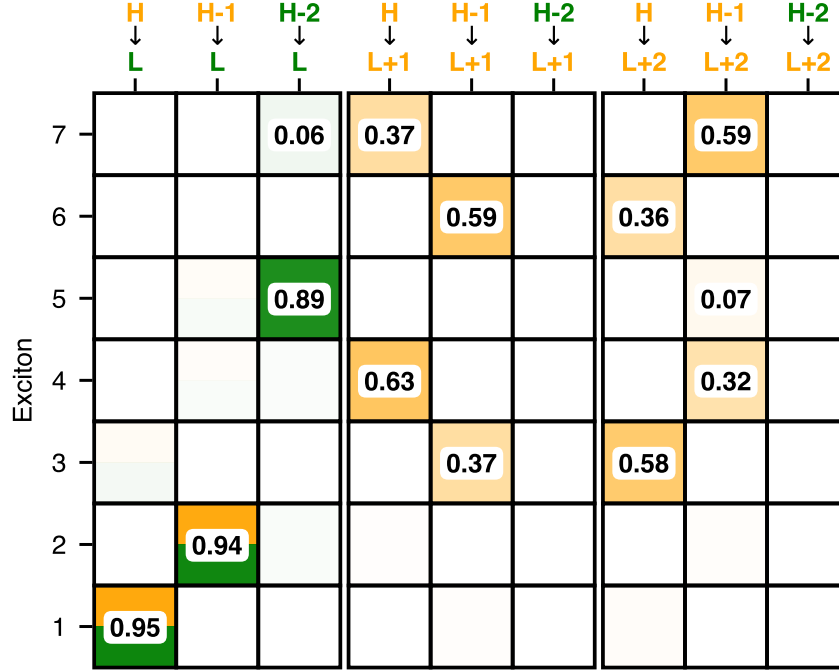


Figure 6.3: Composition of dimer excitons. For the first 7 excitons (m) of the dimer (rows), the composition in terms of valence to conduction transitions ($v \rightarrow c$) given by the Bethe-Salpeter equation (BSE) eigenvector via $|X_{v,c}^m|^2$ is shown. Each column corresponds to a specific transition, where the names of the dimer orbitals have been colored based on Fig. 6.2: orbitals mostly located on PTCDA are colored green, orbitals mostly located on H2TPP are orange. Here, “L” refers to the dimer’s LUMO, “H” to the HOMO, “L+1” to the LUMO+1, and so on. For each exciton m and transition $v \rightarrow c$, the corresponding field is colored by the location of the valence orbital (upper half) and conduction orbital (lower half), where the opacity is determined by the strength of the transition in the exciton, $|X_{v,c}^m|^2$. If the transition strength is larger than 0.05, its value is explicitly written into the field. As can be seen from the figure, excitons 1 and 2 (S_1 and S_2) are CT excitons with the electron being located on PTCDA and the hole being in both cases located on the H2TPP molecule (in the HOMO and HOMO-1 orbital, respectively), while the other five excitons are Frenkel excitons, with exciton 5 (S_5) being located on PTCDA and the other four being located on H2TPP.

With the dimer’s HOMO and HOMO-1 being located on H2TPP and the LUMO on PTCDA, we expect the system to exhibit low-energy charge-transfer (CT) excitons. Having computed the low-energy eigenstates of the BSE Hamiltonian (see Sec. 6.6.3), the composition of the dimer’s first 7 excitonic states is shown in Fig. 6.3. In particular, the contribution of the valence to conduction transition $v \rightarrow c$ for each exciton m is given by the (absolute square of the) corresponding eigenvector element $|X_{v,c}^m|^2$ (compare Sec. 5.3). Note that, for a given exciton m ,

the sum of the elements can be larger than 1, since we did not use the Tamm-Dancoff approximation, and the BSE eigenvector including de-excitations $\{Y_{v,c}^m\}$ is normalized to (compare Eq. C.71):

$$\sum_{v,c} |X_{v,c}^m|^2 - \sum_{v,c} |Y_{v,c}^m|^2 = 1 \quad (6.1)$$

Note however, that $\sum_{v,c} |X_{v,c}^m|^2$ is usually not much larger than 1, because de-excitations usually contribute much less to the exciton. In fact, due to their rather small contribution to the excitons under consideration (see Table 6.5) and since they are not directly included in the exPOT formalism Eq. 3.54, such de-excitations are not further analyzed here. Focusing on the composition of the excitons in terms of excitations $v \rightarrow c$, we can then see from Fig. 6.3, that the two lowest-energy excitons S_1 and S_2 are indeed CT excitons: S_1 is dominated by the HOMO to LUMO transition, such that the hole is located on H2TPP while the electron sits on PTCDA. For S_2 we get the same results, just with the hole residing in the HOMO-1 instead of the HOMO.

The next five excitons are all Frenkel-type excitons, each located on a single molecule only, with S_5 being located on PTCDA and the other four on H2TPP. As mentioned above, we can identify the dimer orbitals with orbitals of the monomer system (see Fig. 6.2). Consequently, the five Frenkel-type excitons of the dimer system can also be identified with excitons of the respective monomer system. In particular, S_5 of the dimer corresponds to S_1 of the PTCDA monomer system, which is an almost pure HOMO to LUMO transition ($|X_{v,c}^m|^2 \approx 0.997$ for $v = \text{HOMO}$, $c = \text{LUMO}$ and $m = S_1$ of PTCDA). Similarly, S_3 , S_4 , S_6 and S_7 of the dimer can respectively be identified with S_1 , S_2 , S_3 and S_4 of the H2TPP monomer system, which can be seen when comparing with Fig. 6.6.

6.4 Momentum-Space Fingerprints of Excitons

Having determined that S_1 and S_2 are CT excitons, the next question is how to access them in a measurement and obtain an unambiguous experimental fingerprint of their CT character. Table 6.1 summarizes the low-energy excitons of the monomer systems and the dimer. In particular, we can see that the S_1 and S_2 CT excitons of the dimer are optically almost dark, that is, the transition dipole moments are very small in all directions. The first bright exciton of the dimer is the S_5 exciton, which lies ≈ 0.75 eV above the dimer's S_1 and has above been identified with the lowest-lying exciton, S_1 , of the PTCDA monomer. Additionally, another ≈ 0.5 – 0.65 eV higher in energy we find that the dimer's S_6 and S_7 (which have been identified with H2TPP's S_3 and S_4) are optically very bright. These effects arising from the strengths of the transition dipoles can also be seen in the optical absorption spectra shown in Fig. 6.4, where we can clearly identify the dimer's absorption peaks with those of the monomer systems.

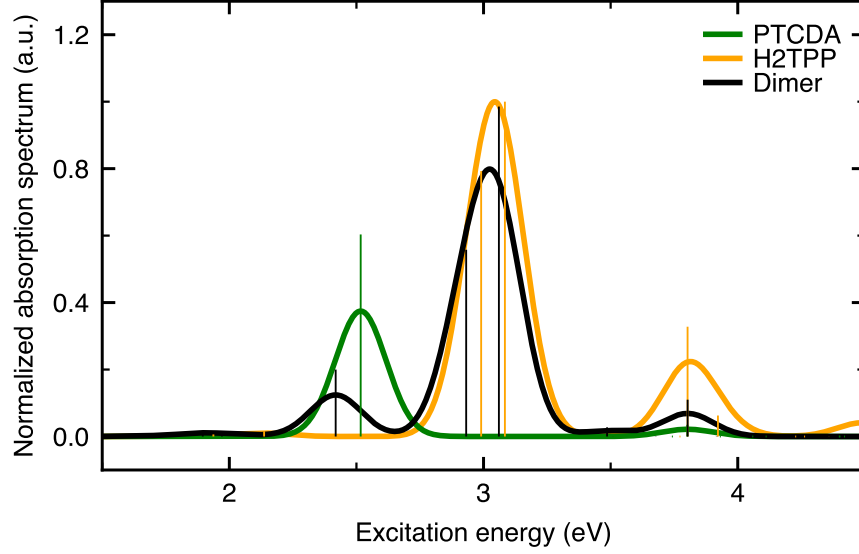


Figure 6.4: Optical absorption spectra of PTCDA, H2TPP and the dimer. In the shown energy-window, the PTCDA monomer's spectrum is dominated by a single absorption peak which is given by the optically bright S_1 exciton (2.52 eV) of PTCDA. For the H2TPP monomer we see a very dominant absorption peak produced by the S_3 (2.99 eV) and S_4 (3.08 eV) excitons of H2TPP, followed by a higher-energy smaller peak which is dominated by the S_7 (3.80 eV) exciton. For the dimer, we find an absorption peak related to its S_5 (2.42 eV) exciton, a very high peak related to its S_6 (2.93 eV) and S_7 (3.06 eV) excitons and a minor peak related to its S_{18} (3.80 eV) exciton. For each optically active exciton, a vertical line is shown, whose height is given by the exciton's transition dipole moment $|d_x|^2 + |d_y|^2 + |d_z|^2$ (relative to the ground state), where arbitrary units have been chosen such that the highest line has a height of 1.0. Similarly, spectra have been normalized such that the maximal height is 1.0. Note that, in contrast to Fig. 5.4, the vertical lines have been normalized collectively and also the spectra have been normalized collectively. Note that the highest calculated exciton of the dimer is S_{20} , which has an excitation energy of 3.92 eV (PTCDA: S_{20} at 5.73 eV; H2TPP: S_{20} at 4.76 eV), such that possible absorption peaks beyond this energy have been neglected from the spectrum.

Let us now focus again on the question of how to access the CT excitons in a pump-probe ARPES experiments. Since they are both optically dark, we need to pump the system to one of the optically bright excitons, hoping that energetic relaxation results in a population of S_1 and/or S_2 . Before distinguishing possible pathways for a pump-probe experiment, a few comments are adequate: First, note that we can see from Table 6.1 that the transition dipole of all optically active excitons are in-plane ($|d_z|^2 \approx 0$), – and in fact also each almost purely in x or y direction – thus suggesting the use of a normal-incidence pump light with an appropriately chosen polarization direction (or an s-polarized non-normal-incidence pump light in combination with an appropriate azimuthal orientation relative to the sample). Second, as detailed in Ref. [34] and below Eq. 3.54, the photoelectrons emitted from a given exciton m may exhibit various kinetic energies which are determined by the energetic positions of the valence orbitals which contribute to the exciton m .

Table 6.1: Exciton energies and transition dipoles for PTCDA monomer, H2TPP monomer, and dimer. As in Fig. 6.4, the transition dipole moments have been normalized (for all systems together), such that the largest value becomes 1.0 (see S_4 of H2TPP).

System	Exciton	Excitation Energy (eV)	$ d_x ^2$	$ d_y ^2$	$ d_z ^2$
PTCDA	S_1	2.517	0.000	0.603	0.000
PTCDA	S_2	3.533	0.000	0.000	0.000
H2TPP	S_1	1.937	0.006	0.000	0.000
H2TPP	S_2	2.137	0.000	0.016	0.000
H2TPP	S_3	2.991	0.793	0.000	0.000
H2TPP	S_4	3.084	0.000	1.000	0.000
H2TPP	S_5	3.439	0.000	0.000	0.000
Dimer	S_1	1.669	0.003	0.000	0.000
Dimer	S_2	1.895	0.000	0.015	0.000
Dimer	S_3	1.971	0.003	0.000	0.000
Dimer	S_4	2.147	0.000	0.004	0.000
Dimer	S_5	2.418	0.000	0.200	0.000
Dimer	S_6	2.932	0.558	0.000	0.000
Dimer	S_7	3.060	0.000	0.985	0.000
Dimer	S_8	3.245	0.000	0.000	0.000

The momentum distribution for a given kinetic energy – corresponding to valence orbital v – is, on the other hand, determined by the dominant conduction orbitals, that is, the conduction orbitals $\{c\}$ which are connected to the valence orbital v via a large element of the (absolute square of the) BSE eigenvector, $|X_{v,c}^m|^2$. Third, the following discussion describes how photoemission from pure exciton states is expected to be observed experimentally. In the case of statistical mixtures (for example of S_1 and S_2 after relaxation, S_6 and S_7 briefly after the pump pulse or any of the states involved in a possible decay pathway), the exPOT formalism can still be used to disentangle the photoemission signal, see Sec. 3.3.10. Coherent superposition states are however beyond the reach of the exPOT formalism presented in Sec. 3.3. Thus, whenever the system enters a coherent superposition state, the application of the formalism becomes problematic, until dephasing of the state has occurred. In principle, any particular stage in the decay pathway may even be more short-lived than the dephasing time, thus possibly (if the state at that stage is a superposition state) making it inaccessible to the formalism. The estimation of decay pathways, exciton lifetimes and dephasing times thus may become crucial to predict experimental outcomes. Fourth, the upcoming discussion neglects a possibly substantial energy broadening of the probe pulse used in ultrafast trARPES experiments, which would energetically “smear out” the discussed photoemission data, possibly even leading to overlaps of otherwise energetically separated signals.

As a first pathway to reach the CT excitons, we discuss the optical excitation of S_5 , followed by a relaxation to S_1 or S_2 . As can be seen from Fig. 6.3 these three excitons are all dominated by a single transition, where in all three cases,

the electron sits in the dimer's LUMO. In the S_5 , the hole resides in the HOMO-2, while in S_1 and S_2 it respectively sits in the HOMO and HOMO-1. Thus, if we first occupy the S_5 via the pump pulse ($\Omega_{\text{pump}} \approx 2.42$ eV) and then transition to the S_1 (S_2), neglecting possible intermediary populations of other excitons, we can expect to obtain k-maps derived by the dimer's LUMO (which is PTCDA's LUMO), however at changing kinetic energies: using a probe energy ω , photoemission from the S_5 should result in a LUMO k-map at $E_{\text{kin}} = \omega - 4.95$ eV (compare Eq. 3.54 and Table 6.4), while photoemission from the S_1 (S_2) results in a LUMO k-map at $E_{\text{kin}} = \omega - 4.47$ eV ($E_{\text{kin}} = \omega - 4.51$ eV). Given that the k-map of the LUMO is only mildly dependent on the kinetic energy (compare Fig. 6.5), such a transition from S_5 to S_1 (S_2) would be experimentally observed as an energetic blueshift(!) of the exciton photoemission signal by 0.47 eV (0.44 eV), while the photoemission angular distribution (k-map) would remain mostly unchanged. More intuitively, this pathway can be understood as first creating an electron-hole pair on PTCDA (corresponding to PTCDA's S_1 exciton), followed by a transition of the hole from PTCDA onto the H2TPP molecule (equivalently: followed by an electron of H2TPP hopping onto PTCDA and filling the hole there, leaving a hole on H2TPP). In this transition, the electron in the excited state remains in the same orbital all the time (PTCDA's LUMO), while the hole transitions (from PTCDA's HOMO to H2TPP's HOMO or HOMO-1, depending on whether we transition to S_1 or S_2) Note that there is also a minor HOMO-1 to LUMO+2 contribution to S_5 (see Fig. 6.3). If visible (compare the HOMO-1 to LUMO+1 transition of 6T discussed in Chapter 5) experimentally, it would appear as the LUMO+2 k-map (which is H2TPP's LUMO+1), located 0.96 eV above the main peak and should disappear via the transition to S_1 or S_2 .

Other possible pathways consist in first exciting S_6 ($\Omega_{\text{pump}} \approx 2.93$ eV) or S_7 ($\Omega_{\text{pump}} \approx 3.06$ eV) and then relaxing to the low-energy CT excitons. Photoemission from S_6 would be visible in terms of two signals: a LUMO+1 k-map at $E_{\text{kin}} = \omega - 3.47$ eV and an $\approx 40\%$ less intense LUMO+2 k-map at $E_{\text{kin}} = \omega - 3.21$ eV. Similarly, photoemission from S_7 would be visible in terms of two signals: a LUMO+2 k-map at $E_{\text{kin}} = \omega - 3.34$ eV and an, again, $\approx 40\%$ less intense LUMO+1 k-map at $E_{\text{kin}} = \omega - 3.08$ eV. Through relaxation to S_1 or S_2 , these signals would disappear, with the LUMO k-map at the energies given above appearing. Thinking again intuitively, in S_6 and S_7 we first create an electron-hole pair on H2TPP. In the relaxation, the electron would then transition onto the PTCDA molecule (from H2TPP's LUMO and LUMO+1 to PTCDA's LUMO), while the hole remains on H2TPP and partially remains in the same orbital (it sits initially in HOMO and HOMO-1 of H2TPP and afterward in either of them, depending on whether we transition to S_1 or S_2).

Regarding the pathways involving a relaxation from S_6 or S_7 to the low-energy CT excitons, note that, as can be seen from Fig. 6.5, the dimer's LUMO (PTCDA's LUMO), LUMO+1 and LUMO+2 (LUMO and LUMO+1 of H2TPP) have very similar k-maps, except that the LUMO+1's k-map is rotated by 90° relative to that of the LUMO+2 (and of the LUMO, in the chosen dimer geometry). Note additionally, that PTCDA orders on the Cu(001)-2O substrate suggested in the introduction in two rotational orientations that differ by a 90° in-plane rotation, such that photoemission from the PTCDA's LUMO orbitals can be expected to be correspondingly averaged [10]. As detailed above, a decay from S_6 or S_7 to the CT

excitons is expected to show a transition from a LUMO+1 and LUMO+2 signal to a LUMO signal. The time-dependent evolution of the observed photoemission intensity angular distribution in such a decay thus strongly depends on the relative orientation of the H2TPP molecules and the PTCDA molecules in the interface structure of the experimental sample. If the H2TPP molecules were oriented as in Fig. 6.1 then the observed angular distribution would only change minimally, while a rotation of the H2TPP molecules relative to the PTCDA molecules could lead to a clear change – a rotation – of measured k-maps during the decay.

In principle, we can think of exciting even higher-lying excitons and analyze what photoemission signal to expect from them. This is not done here, however, since S_6 and S_7 already demand a quite high pump-energy, possibly already higher than what we expect to be able to produce in planned pump-probe experiments.

We conclude with three remarks: first, we have already established that a treatment that takes into account the true, experimentally-observed relative rotational orientation of the PTCDA layer and the H2TPP layer is crucial for a comparison of the above analysis to experimental results. To further improve on the provided analysis, it is however also important to take into account the true relative position of PTCDA molecules and H2TPP molecules and the fact that H2TPP has a larger area (when lying flat) than PTCDA, such that within some surface area there are likely less H2TPP molecules than PTCDA molecules present. Having established the existence of CT excitons in the isolated dimer systems, it is crucial to incorporate all these effects to determine the exact form of the multilayer's exciton wave functions and the corresponding photoemission signals. A cluster-based or periodic treatment based on a realistic interface structure (possibly also including multiple, differently-rotated H2TPP molecules per unit cell) is therefore advisable for further theoretical analysis of the system. Based on our experience with the 6T molecule, compare Chapter 5, a periodic treatment seems more promising here, since cluster calculations there could only be performed with up to six molecules, while the periodic treatment was possible using a 2×8 Brillouin zone mesh.

Second, note that an additional aspect to take into account is the geometry of the multilayer system. When employing the structure suggested in the introduction, the uppermost layer of the system would be the H2TPP layer, followed by the PTCDA layer(s) (and then the substrate). Now, as detailed above, photoemission from the CT excitons S_1 and S_2 , as well as the Frenkel-type exciton S_5 is dominated by emission of electrons from the LUMO, which is located on the PTCDA molecule and thus not in the uppermost layer. As a result, the assumption of a plane-wave final state may become problematic (see Sec. 3.3.7) and could thus necessitate the use of more sophisticated photoelectron states, see Sec. 3.3.4.

Lastly, the above discussion is of course not able to *predict the decay pathway* that the optically pumped PTCDA/H2TPP heterostructure will take. We have however seen in Chapter 5, that experimentally observed energy- and angular photoemission intensity distributions of trARPES experiments can be well-understood with our exPOT formalism. Based on the above analysis of photoemission fingerprints of the various excitons of the heterostructure we are thus already well-prepared to analyze trARPES data and *assign a decay pathway* to it.

6.5 Summary

To summarize, we have seen that an isolated dimer consisting of a single PTCDA and a single H2TPP molecule (in the geometry shown in Fig. 6.1) exhibits two distinct low-energy CT excitons. Though they are optically dark, excitation of higher-lying Frenkel-type excitons followed by a decay could make them accessible to pump-probe ARPES experiments. Such decay pathways are predicted to be observable via distinct k-maps appearing and disappearing at distinct energies, determined by the involved excitons (where an analysis in terms of the exPOT formalism is possible within the usual constraints, as discussed in Sec. 6.4).

Thus, the system constitutes a promising candidate for the analysis of CT excitons via ultrafast trARPES experiments. In order to further solidify the framework presented here, additional theoretical analysis in terms of cluster calculations or calculations using a realistic interface structure and periodic-boundary-conditions as well as an analysis of the discussed decay dynamics in terms of exciton lifetimes and dephasing times may therefore be worthwhile and are kept as future work.

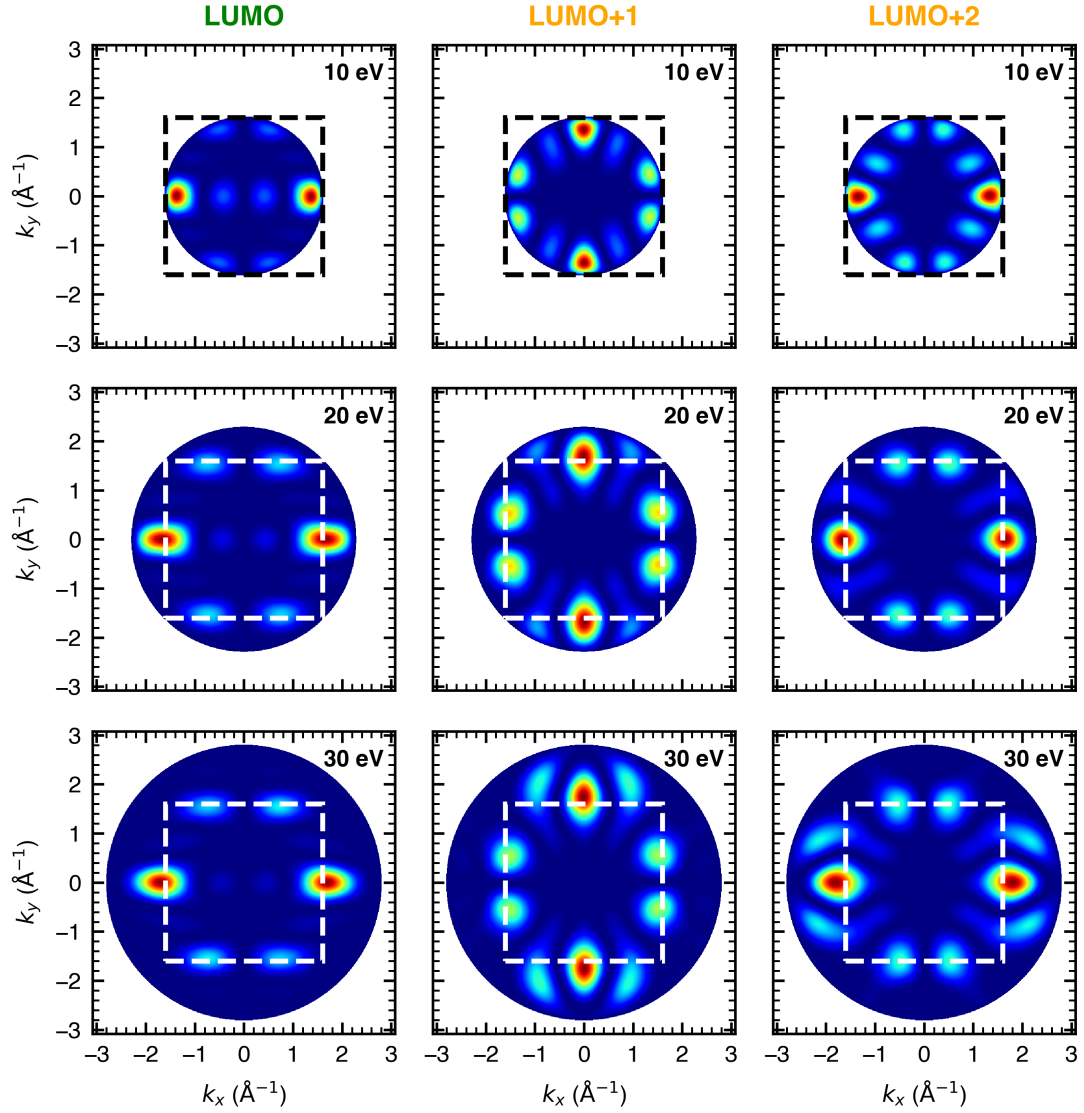


Figure 6.5: Photoemission momentum maps of the PTCDA/H2TPP dimer’s LUMO (first column), LUMO+1 (second column) and LUMO+2 (third column) at kinetic energies of 10 eV (first row), 20 eV (second row) and 30 eV (third). Orbital names are colored according to their assignment to the individual molecules (green: PTCDA, orange:H2TPP). A dashed square (black in first row, white in second and third row) is plotted above each k-map with the sides located at $k_x = \pm 1.6 \text{ \AA}^{-1}$ parallel to the k_y axis and $k_y = \pm 1.6 \text{ \AA}^{-1}$ parallel to the k_x axis for simpler comparison of different orbitals and kinetic energies. The k-maps shown here were calculated as $|\mathcal{F}[\varphi_c](\mathbf{k})|^2$, with $\mathbf{k}$ vectors on the hemisphere defined by the respective kinetic energy (compare text below Eq. 3.54 and the description of photoemission pathways given in Sec. 6.4). The probe-polarization prefactor has been left out and maps are individually normalized to a maximum value of 1.

6.6 Computational Details

This section provides details on the density functional theory (DFT) and GW/BSE calculations performed for (i) an isolated PTCDA molecule, (ii) an isolated H2TPP

molecule and (iii) an isolated dimer composed of one PTCDA and one H2TPP molecule. These calculations have been performed in a very similar fashion as the 6T monomer and cluster calculations presented in Sec. 5.6.1.

Throughout all three systems, ORCA 5.0.4 [143, 144] was used for ground-state DFT calculations, where in all cases, the B3LYP hybrid functional [69, 70] was used in combination with the Grimme D3 dispersion correction with the Becke-Johnson damping scheme [73, 74]. As a basis, we again used the 6-311G* Gaussian-orbital basis set [185, 186].

6.6.1 PTCDA

Focusing first on the PTCDA monomer calculation, the initial molecular geometry was taken from the MOLECULAR ORBITAL DATABASE [190]. After an additional geometry optimization with ORCA (using “TightOpt” convergence thresholds) – the optimized geometry is shown in Fig. 6.1(a) – the Kohn-Sham wave functions and energies obtained for the converged geometry (which barely changed from the initial geometry) then served as a basis for the GW calculation. Using the FIESTA code [145], we iteratively corrected (*evGW*) the first 20 valence and first 20 conduction orbital energies, while leaving the Kohn-Sham wave functions unchanged, until self-consistency was achieved. Orbital energies beyond the HOMO-19/LUMO+19 were rigidly shifted by the HOMO-19/LUMO+19 correction, respectively. A small selection of quasiparticle GW energies can be found in Table 6.2.

Finally, to obtain the system’s excitonic states, we used the FIESTA code to solve the (static) BSE, Eq. 2.210, based on the GW energies and Kohn-Sham wave functions. Since the small system size (as compared to the 6T hexamer cluster of Sec. 5.6.1) allowed for it, we did not use the Tamm-Dancoff approximation (TDA) and therefore also included de-excitations in the exciton wave function (compare Eq. 2.212). The BSE Hamiltonian was constructed using a 100 eV inclusion cutoff for valence- and conduction orbitals, leading to the usage of 69 valence- and 383 conduction orbitals. By iterative diagonalization of the BSE Hamiltonian, we then obtained the first 20 excitons of the PTCDA monomer.

Table 6.2: GW quasiparticle energies of the PTCDA monomer.

Orbital	Energy (eV)
HOMO-1	-9.443
HOMO	-7.724
LUMO	-2.325
LUMO+1	-0.507

6.6.2 H2TPP

For the H2TPP monomer the completely same procedure and computational settings as for the PTCDA monomer were used, making a separate description unnecessary. Just note that the 100 eV inclusion cutoff used for the construction

of the BSE Hamiltonian resulted in the usage of 112 valence- and 691 conduction orbitals.

The optimized geometry is shown in Fig. 6.1(b).

A small selection of quasiparticle GW energies can be found in Table 6.3. Note that we can understand the orbital energies of H2TPP in more detail via the following symmetry consideration: neglecting briefly the tilt of the phenyl rings, the presence of the two central hydrogen atoms reduces H2TPP’s symmetry from D_{4h} to D_{2h} and thus breaks apart otherwise degenerate molecular orbitals. In reality, due to the tilt of the phenyl rings, the geometry can only be seen as approximately D_{2h} -symmetric or “even more approximately” D_{4h} -symmetric. Note however, that for molecular orbitals with little density on the phenyl rings and the central hydrogens, the approximate D_{4h} symmetry leads to almost degenerate orbitals, as is the case for LUMO and LUMO+1 of H2TPP.

As reference for the main text, the composition of the H2TPP monomer’s first four excitons is given in Fig. 6.6.

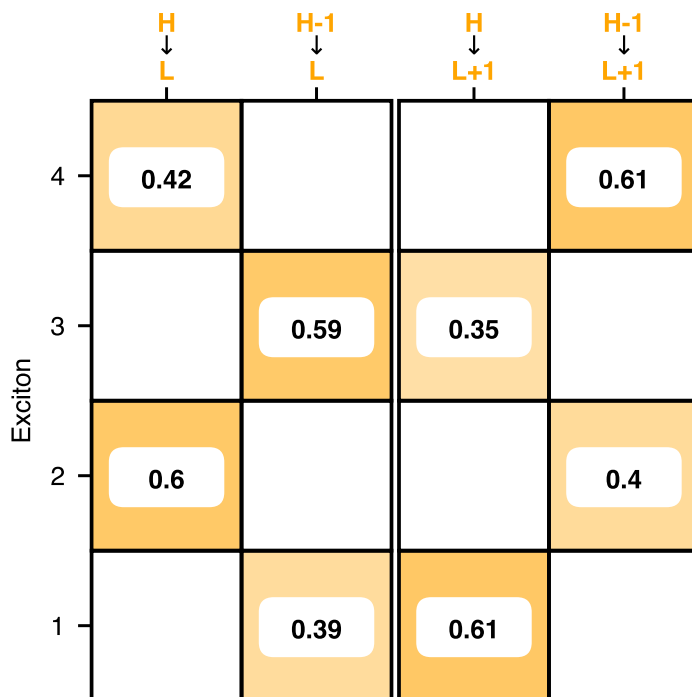


Figure 6.6: Composition of H2TPP’s excitons. In analogy to Fig. 6.3, but now only for the H2TPP molecule and in terms of its (monomer) orbital labels (compare right side of Fig. 6.2).

6.6.3 PTCDA/H2TPP Dimer

For the construction of the dimer, we used the monomer geometries of PTCDA and H2TPP calculated above and aligned the molecules by PTCDA’s short axis and H2TPP’s central hydrogen-hydrogen axis. Next, all internal degrees of freedom within each molecule were frozen, rendering them rigid. Finally, while prohibiting translations in the x- and y direction and while prohibiting rotations, the distance

Table 6.3: GW quasiparticle energies of the H2TPP monomer.

Orbital	Energy (eV)
HOMO-2	-7.636
HOMO-1	-6.194
HOMO	-5.949
LUMO	-0.974
LUMO+1	-0.948
LUMO+2	0.865

between the molecules (z direction) was optimized using the RIIGID code [191, 192] (created by the author of this thesis as part of his PhD). The so-obtained geometry is shown in Fig. 6.1(c)-(e). The distance between the flat PTCDA molecule and the flat porphyrin core of the H2TPP molecule was thereby obtained as 3.967 Å.

Using the Kohn-Sham wave functions and energies obtained for the optimized dimer geometry, we then again performed a self-consistent *evGW* correction with the FIESTA code. We again explicitly corrected 20 valence and 20 conduction orbital energies, while rigidly shifting the remaining orbital energies and leaving wave functions unchanged. A selection of quasiparticle GW energies can be found in Table 6.4.

Employing again the FIESTA code, we used a 50 eV orbital inclusion cutoff for the construction of the (static) BSE Hamiltonian (resulting in the usage of 182 valence and 646 conduction orbitals), which we then again iteratively diagonalized, again not using the TDA, to obtain the first 20 excitons of the dimer system. As a reference for the main text, the overall weight of the de-excitations of selected excitons is shown in Table 6.5.

Table 6.4: GW quasiparticle energies of the PTCDA/H2TPP dimer.

Orbital	Energy (eV)
HOMO-3	-7.814
HOMO-2	-7.364
HOMO-1	-6.402
HOMO	-6.143
LUMO	-2.276
LUMO+1	-1.284
LUMO+2	-1.233
LUMO+3	-0.457

Table 6.5: Weight of de-excitations of low-energy excitons of the PTCDA/H2TPP dimer.

Exciton	$\sum_{v,c} Y_{v,c}^m ^2$
S_1	0.001
S_2	0.003
S_3	0.007
S_4	0.007
S_5	0.019
S_6	0.055
S_7	0.069
S_8	0.002

7 Conclusion

We have successfully extended and implemented the framework of *photoemission orbital tomography for excitons* (exPOT) to periodic systems, thereby allowing for *ab initio* simulations of trARPES experiments involving materials that are highly relevant for real-world optoelectronic devices but have until now been out of reach of the formalism. Notable examples of systems that have as a result become accessible to exPOT are 2D semiconductors, molecular layers in which the intermolecular interaction leads to a sizable band dispersion (in the order of a few tenths of an eV) and systems where substrate-adsorbate interactions are important. While the examples shown in this text focus on optically bright excitons, our approach is also suited for excitons with finite center-of-mass momentum, thereby bridging the gap between *ab initio* many-body theory and experimentally measurable momentum-resolved spectra.

Focusing first on 2D semiconductors, photoemission from monolayer hexagonal boron nitride (hBN), Chapter 4, served as a proof of concept for the extension of the exPOT formalism to extended systems using periodic boundary conditions. We have seen how the exPOT formalism leads to distinct photoemission intensity patterns for photoemission from a pure excitonic state, with the photoemission energy dispersion being governed by the hole states. Conversely, the photoemission matrix element is given by a linear combination of Fourier-transformed conduction-band wave functions, weighted by components of the exciton's Bethe-Salpeter equation (BSE) eigenvector. This way, a direct link between the photoemission intensity and *ab initio* quantities obtained from GW/BSE calculations is formed. By simulating photoemission from a two-dimensional subspace of degenerate excitons, we have additionally shown how the pump pulse's polarization determines which specific excitonic state within this subspace is created by the absorption of the pump pulse, leading to a direct influence of the pump polarization on fine details of the exciton photoemission angular distribution.

While the hBN example serves as a more didactical example for our formalism, a comparison to experimental data was necessary to assess the viability of the approximations made throughout the derivation shown in Chapter 3. In Chapter 5 we therefore compared exPOT simulations to experimental data obtained in trARPES experiments involving four layers of sexithiophene (6T) molecules adsorbed on a crystalline substrate. Photoemission simulations from excitons of a free-standing periodic layer were able to reproduce the experimentally obtained photoelectron momentum patterns, therefore proving the suitability of our formalism for practical applications. In particular, we showed that the electron-hole correlation of the excited state created by the pump pulse must be included in the simulation in order to reproduce the distinct experimental momentum pattern. We also performed photoemission simulations based on molecular clusters, which

also showed good agreement with the experimental momentum pattern. Quantitative agreement with experimental data was however best for the free-standing monolayer-based simulation, thus confirming that molecular clusters can be used as a first estimate for exciton photoemission from extended systems, while a periodic treatment is advisable when inter-molecular interactions lead to a sizable band dispersion.

Finally, in Chapter 6, we simulated exciton photoemission from a dimer consisting of a single PTCDA and a single H2TPP molecule, serving as a first step towards the investigation of photoemission from charge-transfer (CT) excitons in type-II organic hetero-interfaces. We found that the dimer exhibits two distinct, low-energy CT excitons which are optically dark. Higher-energy Frenkel-type excitons have, however, been found to be optically active such that the system may first be pumped to these excitons, which subsequently decay into the CT exciton states. The PTCDA-H2TPP interface is therefore found to be a promising candidate for trARPES studies of CT exciton dynamics and more sophisticated photoemission simulations based on the realistic interface structure are commendable.

To conclude, we have seen that the exPOT formalism for periodic systems is capable of reproducing and explaining experimental trARPES photoemission data on a microscopic level by providing a direct bridge between photoemission intensities and *ab initio* quantities. Further, our theoretical analysis has shown the predictive strength of exPOT for the planning of state-of-the-art experiments on novel materials. In total, our formalism thus provides not only a sophisticated framework for the analysis of experimental data but also a powerful tool for streamlining material selection and determining key experimental parameters in frontier trARPES studies.

A Mathematical Background

Die Physik ist für die Physiker eigentlich viel zu schwer.

— David Hilbert

[Reid. *Hilbert*. Springer Verlag, 1996, S. 127.]

A.1 Hilbert Spaces

This section introduces single- and many-particle states and Hilbert spaces, as they are used throughout this text. Additional details on many-electron states can for example be found Chapter 6 of Ref. [42] or in Refs. [50, 75]. The used notions of direct sums and tensor products can also be found in Refs. [86, 193, 194]. Details on the Bloch theorem and periodic boundary conditions can for example be found in Refs. [113, 195]. A treatment of theoretical surface science can be found in Ref. [196].

A.1.1 One-Electron States

We begin with the Hilbert space⁹⁸ of a single electron, which is the vector space whose vectors correspond to the physically allowed states of a single electron. In the following we will show how we can obtain an orthonormal basis (ONB) of this Hilbert space, which then allows us to express any physically allowed state as a (unique) linear combination of the basis vectors. For clarity, we first treat electrons as spinless particles and then add spin in a second step. The Hilbert space of physically allowed spinless states is then given by:

$$L^2(\mathbb{R}^3) = \left\{ \varphi : \mathbb{R}^3 \rightarrow \mathbb{C} \mid \int_{\mathbb{R}^3} |\varphi(\mathbf{r})|^2 d^3r < \infty \right\} \quad (\text{A.1})$$

The norm of a state from $L^2(\mathbb{R}^3)$ is defined as

$$\|\varphi\| = \left(\int_{\mathbb{R}^3} d^3r |\varphi(\mathbf{r})|^2 \right)^{1/2}, \quad (\text{A.2})$$

thereby allowing for the interpretation of $|\varphi|^2$ as a spatial probability-distribution (by *normalizing* the wave functions to $\|\varphi\| = 1$). Two states are said to be orthog-

⁹⁸A *Hilbert space* is a complete inner-product space [197]. For simplicity, we do not consider completeness throughout this section.

onal, if their inner product (which induces the above norm)

$$\langle \varphi_a | \varphi_b \rangle = \int_{\mathbb{R}^3} d^3r \varphi_a^*(\mathbf{r}) \varphi_b(\mathbf{r}) \quad (\text{A.3})$$

is zero.

In general, an ONB⁹⁹ of any Hilbert space can be found by obtaining the eigenvectors of any Hermitian operator that acts on it¹⁰⁰. In the main text we will typically use the eigenvectors of the Kohn-Sham (KS) Hamiltonian (see Sec. 2.2.4) which consists of the kinetic energy operator and some scalar external potential v . This operator acts on $L^2(\mathbb{R}^3)$ (unless we use spin-density functional theory where it also acts on spin, see below) and as such its eigenvectors – which we obtain by solving the corresponding Schrödinger equation – form an ONB of this space. Note that this also holds true when using hybrid functionals in the GKS formalism, where the Hamiltonian then additionally contains the (Hermitian) Fock exchange operator (see Sec. 2.2.5). We distinguish in the following between *gas-phase systems*, where the atomic region is restricted to a small spatial region and *periodic surface systems* (throughout the text simply called *periodic systems*), where the atomic region extends infinitely in a plane, see Sec. 2.1.1.

Gas-Phase Systems

In the case of gas-phase systems, the atomic region is spatially confined to a small volume (in our case a molecule or a molecular cluster). The *bound states* of the system are then given by wave functions that are solutions of the Schrödinger equation (in real space), *vanish at infinity* (boundary condition for Schrödinger equation) and are elements of $L^2(\mathbb{R}^3)$. They are typically heavily localized in the atomic region, quickly vanishing at distance. In addition to the bound states, the Schrödinger equation admits *scattering solutions* or *scattering states*, whose wave functions do not vanish at infinity [38]. That is, the scattering states are *non-normalizable* and are thus not elements of $L^2(\mathbb{R}^3)$. They can instead be “normalized” via the Dirac delta function, see Ref. [198].

The bound states and the scattering states¹⁰¹ together then form an ONB¹⁰² of $L^2(\mathbb{R}^3)$ [129] (see in particular Chapters 2 and 10 in Ref. [129] on the completeness of scattering states in combination with bound states). In fact, $L^2(\mathbb{R}^3)$ can be written as the direct sum (see Def. 7) of a subspace spanned by the bound states and a subspace spanned by the scattering states [129].

⁹⁹ Where eigenvectors in degenerate subspace can always be chosen to be orthogonal.

¹⁰⁰Strictly speaking, the operator must be *self-adjoint*, see Ref. [198]. As is common in physics literature, we do not distinguish between these notions here and throughout this text. See also Footnote 101 on additional complications regarding the basis expansion.

¹⁰¹ Strictly speaking, a scattering state cannot be a basis element of $L^2(\mathbb{R}^3)$, since it does not lie in that space. We will not further discuss this in the upcoming text, but note that we can alleviate this nuisance by using the *rigged Hilbert space* construction [198]. Just like the bound states are eigenstates with corresponding eigenvalues – which form the point spectrum – of the Hamiltonian, we can then treat the scattering states as eigenstates with corresponding eigenvalues – which form the continuous spectrum – of the Hamiltonian. Note also, that throughout this whole text – including the main sections – we usually write basis sums via discrete indices for simplicity, even though the basis may in fact also contain a continuous part, see Appendix A.2.

¹⁰²With orthonormalization as discussed below. See also Footnote 99.

Lastly, for later comparison, the orthonormalization (with respect to Eq. A.3) of the basis states shall be given. Denoting bound states as $\{\varphi_n\}$ and scattering states as $\{\varphi_{\mathbf{k}}\}$, it reads (compare Refs. [129, 198]):

$$\begin{aligned}\langle \varphi_n | \varphi'_n \rangle &= \delta_{n,n'} \\ \langle \varphi_{\mathbf{k}} | \varphi_{\mathbf{k}'} \rangle &= \delta(\mathbf{k} - \mathbf{k}') \\ \langle \varphi_n | \varphi_{\mathbf{k}} \rangle &= 0\end{aligned}\tag{A.4}$$

Periodic Systems

In the case of infinitely extended surfaces, the atomic region stretches over an infinite area in two directions but a finite interval in the third direction (which we choose as the z direction). As detailed in Sec. 2.1.1 we additionally assume the atomic/nuclear structure to be *in-plane periodic*. As a result the effective potential v in Kohn-Sham density functional theory (KS-DFT) is also in-plane periodic (see also Sec. 2.2.6), or, more generally (to also include the GKS scheme), the one-particle Hamiltonian commutes with the in-plane translation operators. That is, we define a *surface unit cell* and denote its in-plane unit cell vectors by $\mathbf{a}_1$ and $\mathbf{a}_2$ (area A_c), such that the potential satisfies (generally: the Hamiltonian commutes with translations built from $\mathbf{a}_1$ and $\mathbf{a}_2$):

$$\begin{aligned}v(\mathbf{r} + \mathbf{a}_1) &= v(\mathbf{r}) \\ v(\mathbf{r} + \mathbf{a}_2) &= v(\mathbf{r})\end{aligned}\tag{A.5}$$

This unit cell is then infinitely repeated in both in-plane directions to form an infinite surface. This is the kind of system we use for simulations of photoemission from adsorbates on crystalline surfaces, where the sample is modeled by an infinitely extended (in the in-plane direction) atomically thin (in the z direction) substrate with the adsorbate sitting on top (see Sec. 2.1.1 for details).

Let us now find the solutions of the Schrödinger equation for such a Hamiltonian, which then again form an ONB of $L^2(\mathbb{R}^3)$. To begin with, the infinite surface's in-plane symmetry allows us to use Bloch's theorem, which states that the solutions of the one-particle Schrödinger equation in a periodic potential (generally: if the Hamiltonian commutes with lattice translations) are given by (can be chosen as) [195]:

$$\varphi_{n,\mathbf{q}}(\mathbf{r}) = e^{i\mathbf{q}\cdot\mathbf{r}} u_{n,\mathbf{q}}(\mathbf{r}),\tag{A.6}$$

with u exhibiting the same periodicity as the surface atomic structure, the unit-cell's in-plane periodicity. Since the atomic structure is only in-plane periodic, the Bloch functions are indexed by an *in-plane Bloch momentum*¹⁰³ $\mathbf{q}$ ($q_z = 0$).

Based on Bloch's theorem, we now know how the solutions of the Schrödinger equation look like. To actually calculate them, we now additionally invoke in-plane periodic boundary conditions, which are in this context also known as *Born-von Kármán periodic* (BvK) boundary conditions [195]. That is, we define a finite

¹⁰³Note that the Bloch momentum is at this point a complex-valued vector! Only when invoking the periodic (or twisted) boundary conditions does it become real-valued [195].

surface area¹⁰⁴ consisting of N_1 and N_2 in-plane repetitions of the unit cell (respectively, per direction) and demand solutions of the Schrödinger equation to be periodic at the edges of this surface, that is:

$$\begin{aligned}\varphi(\mathbf{r} + N_1 \mathbf{a}_1) &= \varphi(\mathbf{r}) \\ \varphi(\mathbf{r} + N_2 \mathbf{a}_2) &= \varphi(\mathbf{r})\end{aligned}\tag{A.7}$$

This finite area can be understood as a cutout from the infinite surface (which can be built from it via infinite repetitions in both in-plane directions) and is from now on called the *BvK area* and its surface area is denoted by A . Via the above boundary condition, we thus only find a subset of solutions of the Schrödinger equation, namely those that exhibit the demanded periodicity: starting from Eq. A.6 and additionally invoking this in-plane periodic boundary conditions via the BvK area, we then find that the allowed solutions are the Bloch functions with Bloch momenta on the discrete grid (using the reciprocal lattice vectors $\mathbf{b}_1, \mathbf{b}_2$):

$$\mathbf{q} = \sum_{i=1}^2 \frac{n_i}{N_i} \mathbf{b}_i, \text{ with } n_i = 0, 1, \dots, N_i - 1\tag{A.8}$$

Note that we can restrict ourselves to $\{\mathbf{q}\}$ from the first Brillouin zone or any other primitive cell of the reciprocal lattice without loss of generality [195]. With this in mind, we then simply say that $\mathbf{q}$ is from the Brillouin zone and assume some volume has been chosen and is used consistently. Of course, if we want a complete basis of $L^2(\mathbb{R}^3)$, we not only need this subset of solutions of Schrödinger equation, but *all of its solutions*. We will get back to this later. For now, let us work on this smaller grid of allowed Bloch momenta.

The boundary condition used in z direction then depends on the searched states. To calculate the *bound solutions* of the Schrödinger equation we could in principle invoke vanishing boundary conditions in the z direction. For computational reasons (we can then use the same code packages that are used for bulk calculations), however, we calculate them in practice in a roundabout way by using the *repeated slab approach* in combination with periodic boundary conditions in z direction. First, note that our atomic system is not periodic in z direction! It can be thought of as being confined to a small interval in z direction, with *bound states* quickly falling off outside that interval. Let us now choose a bigger interval, that encloses the bound states, such that they are effectively zero (except for quickly vanishing tails) outside that interval (in practice: enclose the atomic region and add vacuum above and below it to form the slab¹⁰⁵). We position our coordinate system such that this interval starts at $z = 0$ and ends at $z = L$. Defining $\mathbf{a}_3$ to point in the positive z direction and have length L , we then *artificially repeat the atomic structure in z direction*, such that the resulting potential satisfies:

$$v(\mathbf{r} + \mathbf{a}_3) = v(\mathbf{r})\tag{A.9}$$

¹⁰⁴In this text we use the word (BvK) *area* to refer to both, a spatial region of the infinite surface (the exact position does not matter due to periodicity), and the surface area of that region. It is clear from the context which of the two is meant.

¹⁰⁵Due to z periodicity, only the total amount of vacuum matters, not how much of it was put at either side individually. For simplicity, we often assume in the following text that the vacuum is spread symmetrically, that is, the atomic structure is in the middle of the slab and bound states vanish at $z = 0$ and $z = L$. A deviation from this convention is trivial.

The potential is then periodic in all three dimensions (generally: the Hamiltonian now also commutes with translations built additionally via $\mathbf{a}_3$) and the corresponding three-dimensional unit-cell (unit-cell vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$) is known as the *slab*. This approach is known as the repeated slab approach, since the atomic structure is now given by its structure inside the slab-like unit cell and is periodic in all three unit-cell directions. We then use this artificial potential (or: artificial Hamiltonian) and search for solutions of the Schrödinger equation that share the same periodicity in z direction,

$$\varphi(\mathbf{r} + \mathbf{a}_3) = \varphi(\mathbf{r}), \quad (\text{A.10})$$

and vanish in the vacuum region between two repetitions of the atomic structure. Note that the vacuum used in the calculation must therefore be large enough to allow the wave functions to vanish in between two repetitions of atomic structure (states that do not vanish in between two repetitions would describe spurious interactions between the repetitions.). To make sure the wave functions vanish in it, we use in practice not only a large vacuum ($> 10 \text{ \AA}$ in total) but also additional decoupling techniques, see Secs. 5.6.2 and 4.6. On the z interval $[0, L]$, the so-obtained states should then be practically identical to the bound states we would have obtained by using vanishing boundary conditions! Outside that interval they of course vastly differ, with the “real” bound states featuring quickly decaying tails, while the so-obtained states are repeated periodically. When instead setting the so-obtained states (manually) to zero outside $[0, L]$ they are then practically (and, for our purposes, sufficiently) identical to the “real” bound states for all $z \in \mathbb{R}$. When performing integrals over $z \in \mathbb{R}$ and the integrand contains a bound state – calculated as described above – we can then restrict the integration to $z \in [0, L]$.

Having found a way to calculate the system’s bound states, we next focus on its *scattering states*. They can be found by using the same treatment for the in-plane directions, but invoking scattering boundary conditions in the z direction. We will not go further into their calculation. Details can for example be found in Refs. [127, 128, 130] and in Sec. 3.3.4.

As mentioned before, when invoking the in-plane periodic boundary conditions Eq. A.7 we only find a subset of all solutions of the Schrödinger equation, namely those with Bloch momenta given by Eq. A.8. A way of obtaining all solutions is then to calculate bound- and scattering states as described above and taking the *thermodynamic limit* $N_1, N_2 \rightarrow \infty$. In this limit, the boundary conditions of Eq. A.7 cease to be a restriction on the wave functions and we thus obtain all solutions of the Schrödinger equation (stated differently: by increasing N_1 and N_1 we can obtain an “arbitrarily complete” set of orthonormal functions). As can be seen from Eq. A.8, this limit is accompanied by the grid of allowed Bloch momenta becoming infinitely dense, such that the allowed momenta become effectively continuous (but still restricted to the Brillouin zone without loss of completeness [195]). All the bound and scattering states for all the (continuously spaced) Bloch momenta then together form an ONB¹⁰⁶ of $L^2(\mathbb{R}^3)$. Thus, any physically allowed

¹⁰⁶The states are delta normalized (see below), since these states, bound and scattering states alike, are all non-normalizable and thus not physically allowed states of a single electron – that is, they are not elements of $L^2(\mathbb{R}^3)$. This is not a surprise, since the model system we are working with – an infinitely extended surface – is unphysical in itself. Still, they form a complete ONB and (subsets of them) can be used for (quadrature) integrations, see Appendix B.3. See also Footnotes 99 and 101.

state can then be written by a (unique) linear combination of these states.

For completeness, we shall again give the orthonormalization (with respect to Eq. A.3). Denoting the bound states as $\{\varphi_{n,\mathbf{q}}\}$ with in-plane Bloch momentum $\mathbf{q}$ and band index n and the scattering states as $\varphi_{\mathbf{k}}$ (compare Refs. [127, 128, 130]), we write (compare Eq. A.4):

$$\begin{aligned}\langle\varphi_{n,\mathbf{q}}|\varphi_{n',\mathbf{q}'}\rangle &= \delta_{n,n'}\delta(\mathbf{q}-\mathbf{q}') \\ \langle\varphi_{\mathbf{k}}|\varphi_{\mathbf{k}'}\rangle &= \delta(\mathbf{k}-\mathbf{k}') \\ \langle\varphi_{n,\mathbf{q}}|\varphi_{\mathbf{k}}\rangle &= 0\end{aligned}\tag{A.11}$$

Lastly, note that it will occasionally become useful to remember that on its inside, a macroscopically sized but finite surface (think of it like a cutout from the infinite surface) closely resembles the infinite surface! In particular, we can expect its bound states to closely resemble (in the inner region and above and below that inner region) those of the infinite surface, except near the lateral sides of the finite surface (and of course beyond those edges, where they should vanish). To see this explicitly, let us assume that the finite surface is composed of N_1 and N_2 (both macroscopically large) repetitions of the surface unit cell. Since we are only interested in its interior region, the shape in fact does not matter, so this is not a restriction. Additionally, we demand wave functions to satisfy periodic boundary conditions Eq. A.7 at the lateral sides. While this may be seen as a restriction on the wave functions, note that this condition becomes irrelevant in the thermodynamic limit $N_1, N_2 \rightarrow \infty$. Thus, already for macroscopic systems, we can expect that it effectively does not affect wave functions on the interior. Finally, note that on its inside, the system appears translationally invariant, which only breaks down in the small region near its edges. Thus, to good approximation, the situation is the same as in the case of an infinite surface with enforced periodic boundary conditions on a finite (BvK) region and the bound states of the finite surface should – in the interior region – thus closely resemble Bloch orbitals Eq. A.6 with Bloch momenta given by Eq. A.8.

Spin

Until now, we have treated electrons as spinless particles. We now include spin in our formulation: since electrons are spin-1/2 particles, electronic spin is described via the Hilbert space $\mathbb{C}^2$, where we, by convention, choose the physical states of *spin-up in z direction*, $|\uparrow\rangle$, and *spin-down in z direction*, $|\downarrow\rangle$, as our (orthonormal) basis of $\mathbb{C}^2$. Physically allowed one-electron states are thus elements of the position-spin Hilbert space:

$$\mathcal{H}_1 = L^2(\mathbb{R}^3) \otimes \mathbb{C}^2\tag{A.12}$$

This is the Hilbert-space *tensor product* of $L^2(\mathbb{R}^3)$ and $\mathbb{C}^2$, which is abstractly constructed in the following (basis-dependent) way (compare Chapter 17 in Ref. [86]):

Def. 6. Let V and W be two Hilbert spaces over $\mathbb{K}$. Let $\{|v_i\rangle\}_i$ and $\{|w_i\rangle\}_i$ be bases of the spaces, respectively. Then, the *tensor product Hilbert space* $V \otimes W$ is a vector space over $\mathbb{K}$ and is spanned by the basis $\{|v_i\rangle \otimes |w_j\rangle\}_{i,j}$. Additionally,

we define the *tensor product of vectors*, where, if $|v\rangle \in V$ and $|w\rangle \in W$ and

$$\begin{aligned} |v\rangle &= \sum_i c_i |v_i\rangle \\ |w\rangle &= \sum_j d_j |w_j\rangle, \end{aligned}$$

we write

$$|v\rangle \otimes |w\rangle \equiv \sum_{i,j} c_i d_j |v_i\rangle \otimes |w_j\rangle,$$

thus obtaining an element of $V \otimes W$. Note that the basis elements of $V \otimes W$ are initially defined in a symbolic fashion (for every pair $(|v_i\rangle, |w_j\rangle)$ of basis elements from V and W , there is a basis element in $V \otimes W$ which we denote by $|v_i\rangle \otimes |w_j\rangle$). The tensor product of vectors then tells us how elements of V and W are related to elements of $V \otimes W$. To make it a Hilbert space, the inner product on $V \otimes W$ is then defined for $|v\rangle, |\tilde{v}\rangle \in V$ and $|w\rangle, |\tilde{w}\rangle \in W$ as

$$\langle v, w | \tilde{v}, \tilde{w} \rangle_{V \otimes W} \equiv \langle v | \tilde{v} \rangle_V \langle w | \tilde{w} \rangle_W,$$

where we introduced notation $|v, w\rangle \equiv |v\rangle \otimes |w\rangle$. Trivially, if the bases of V and W are orthonormal bases, then so is the obtained basis of $V \otimes W$.

In the present case, we use $\{\varphi_i\}$ as an ONB of $L^2(\mathbb{R}^3)$ and $\{\uparrow, \downarrow\}$ as an ONB of $\mathbb{C}^2$ (both are vector spaces over $\mathbb{C}$). Then the tensor-product Hilbert space is spanned by an ONB that we obtain by combining all basis elements of $L^2(\mathbb{R}^3)$ with all basis elements of $\mathbb{C}^2$ ($s = \uparrow, \downarrow$):

$$\{|\varphi_i\rangle \otimes |s\rangle\}, \quad (\text{A.13})$$

where $|\varphi_i\rangle \otimes |s\rangle$ describes the state of an electron in the *spatial state/orbital* φ_i with *spin* s . States of the form $|\varphi\rangle \otimes |\uparrow\rangle$ and $|\varphi\rangle \otimes |\downarrow\rangle$ for a generic spatial state φ are known as *pure spin-up* and *pure spin-down* orbitals. A generic state in this space is then given by

$$\begin{aligned} |\psi\rangle &= \sum_i \sum_{s=\uparrow, \downarrow} c_{i,s} |\varphi_i\rangle \otimes |s\rangle \\ &= \sum_i \sum_{s=\uparrow, \downarrow} c_{i,s} |\varphi_i, s\rangle, \end{aligned} \quad (\text{A.14})$$

where we used the compact notation of Def. 6 in the second line. Projecting onto $\langle \mathbf{r}, s |$ (which is a vector in the tensor-product space), we get:

$$\psi(\mathbf{r}, s) \equiv \langle \mathbf{r}, s | \psi \rangle = \sum_i c_{i,s} \varphi_i(\mathbf{r}) \quad (\text{A.15})$$

It is then common to write the projections on $s = \uparrow$ and $s = \downarrow$ for a given position $\mathbf{r}$ as a column vector¹⁰⁷:

$$\tilde{\psi}(\mathbf{r}) = \begin{pmatrix} \psi(\mathbf{r}, \uparrow) \\ \psi(\mathbf{r}, \downarrow) \end{pmatrix} = \begin{pmatrix} \sum_i c_{i,\uparrow} \varphi_i(\mathbf{r}) \\ \sum_i c_{i,\downarrow} \varphi_i(\mathbf{r}) \end{pmatrix} \quad (\text{A.16})$$

¹⁰⁷Viewed differently, we do not project onto a spin-state at all and simply use coordinate-representation in the chosen spin-basis, with the first/second coordinate corresponding to the spin up/down basis element.

Such generic states are known as *spinor orbitals*.

Lastly, note that the inner product (and the induced norm) is usually expressed via the spin-position basis:

$$\begin{aligned}\langle\psi_a|\psi_b\rangle &= \sum_{s=\uparrow,\downarrow} \int_{\mathbb{R}^3} d^3r \langle\psi_a|\mathbf{r}, s\rangle \langle\mathbf{r}, s|\psi_b\rangle \\ &= \sum_{s=\uparrow,\downarrow} \int_{\mathbb{R}^3} d^3r \psi_a^*(\mathbf{r}, s) \psi_b(\mathbf{r}, s)\end{aligned}\tag{A.17}$$

To conclude, note that we in practice (in the main text) usually find our one-electron basis states using Kohn-Sham density functional theory (DFT). Instead of first searching for solutions of a spin-independent Schrödinger equation and then simply adding spin on top (which corresponds to KS-DFT as presented in Sec. 2.2.4), we may from the beginning work with a Hamiltonian that is nontrivial in spin-space (as in *spin-density functional theory*) to obtain an ONB of position-spin space in terms of spinor orbitals. An overview of the different ways in which spin can be treated in KS-DFT is given near the end of Sec. 2.2.4.

A.1.2 Many-Electron States

Denoting the one-electron (spin-position) Hilbert space introduced above as $\mathcal{H}_1$, the Hilbert space $\mathcal{H}_N$ of N electrons is then simply given by the tensor product of N one-electron Hilbert spaces, which is commonly written as:

$$\mathcal{H}_N = \mathcal{H}_1^{\otimes N}\tag{A.18}$$

An ONB of this Hilbert space can be constructed as shown above. That is, if $\{\phi_i\}$ is an ONB of $\mathcal{H}_1$, then an ONB of $\mathcal{H}_N$ can be constructed by taking all possible combinations of N one-electron basis elements:

$$\{|\phi_{i_1}\rangle \otimes |\phi_{i_2}\rangle \otimes \cdots \otimes |\phi_{i_N}\rangle\} = \{|\phi_{i_1}, \phi_{i_2}, \dots, \phi_{i_N}\rangle\}\tag{A.19}$$

where we again used the compact notation of Def. 6. An arbitrary N -electron state in this space is then again a (normalizable, see Footnote 101) linear combination of these basis states.

Note that this is not yet the Hilbert space we work with in practice, since we need to additionally satisfy the *symmetrization postulate*, which says for electrons (which are fermions), that only antisymmetric N -electron states are physically allowed [42, 50, 75]. Let us first define the *antisymmetrization operator* $\hat{\mathcal{A}}$: if ψ_1, ψ_2 etc. are arbitrary elements of $\mathcal{H}_1$, so, arbitrary one-electron states, then $|\psi_1, \psi_2, \dots, \psi_N\rangle$ is an element of $\mathcal{H}_N$ (see tensor-product of vectors in Def. 6). The antisymmetrization operator then acts on this state as:

$$\begin{aligned}\hat{\Pi} |\psi_1, \psi_2, \dots, \psi_N\rangle &\equiv |\psi_{\Pi(1)}, \psi_{\Pi(2)}, \dots, \psi_{\Pi(N)}\rangle \\ \hat{\mathcal{A}} &\equiv \frac{1}{\sqrt{N!}} \sum_{\Pi} (-1)^{|\Pi|} \hat{\Pi} \\ |\psi_1, \psi_2, \dots, \psi_N\rangle_A &\equiv \hat{\mathcal{A}} |\psi_1, \psi_2, \dots, \psi_N\rangle \\ &= \frac{1}{\sqrt{N!}} \sum_{\Pi} (-1)^{|\Pi|} \hat{\Pi} |\psi_1, \psi_2, \dots, \psi_N\rangle,\end{aligned}\tag{A.20}$$

where the sum runs over all $N!$ permutations of $\{1, 2, \dots, N\}$ and $|\Pi|$ is the *number of transpositions* in the permutation. Note that we can immediately see

$$|\psi_1, \psi_2, \dots, \psi_i, \dots, \psi_j, \dots, \psi_N\rangle_A = -|\psi_1, \psi_2, \dots, \psi_j, \dots, \psi_i, \dots, \psi_N\rangle_A, \quad (\text{A.21})$$

since swapping two orbitals simply adds one transposition to each permutation and thus an overall -1 sign. In the same way we directly find [75]:

$$\hat{\Pi}\hat{\mathcal{A}} = \hat{\mathcal{A}}\hat{\Pi} = (-1)^{|\Pi|}\hat{\mathcal{A}} \quad (\text{A.22})$$

For reference, also note the action of the antisymmetrizer on the tensor product of a one-electron state ψ and an antisymmetrized N -electron state $|\psi_1, \psi_2, \dots, \psi_N\rangle_A$:

$$\begin{aligned} \hat{\mathcal{A}}|\psi\rangle \otimes |\psi_1, \psi_2, \dots, \psi_N\rangle_A &= \frac{1}{\sqrt{N!}} \sum_{\Pi} (-1)^{|\Pi|} \hat{\mathcal{A}}\hat{\Pi} |\psi, \psi_1, \psi_2, \dots, \psi_N\rangle \\ &= \sqrt{N!} |\psi, \psi_1, \psi_2, \dots, \psi_N\rangle_A, \end{aligned} \quad (\text{A.23})$$

where, in the first line, we implicitly replaced the N -electron permutation operator by the equivalent $N+1$ -electron permutation operator (which only mixes the last N states, without the first one).

The space $\mathcal{H}_N^A$ of antisymmetric N -electron states is then obtained from $\mathcal{H}_N$ by using the latter's ONB and antisymmetrizing each element of that basis to form a complete set of states in $\mathcal{H}_N^A$, which is then given by:

$$\{|\phi_{i_1}, \phi_{i_2}, \dots, \phi_{i_N}\rangle_A\} \quad (\text{A.24})$$

Note that $\mathcal{H}_N^A$ is a subspace of $\mathcal{H}_N$ and inherits the inner product that it needs to be a Hilbert space. The state $|\psi_1, \psi_2, \dots, \psi_N\rangle_A$ is then an element of $\mathcal{H}_N^A$ and is interpreted as the state of an N -electron system, with one electron in state ψ_1 , one electron in ψ_2 and so on. From Eq. A.21, we find that antisymmetric N -electron states spanning $\mathcal{H}_N^A$ cannot contain any two identical one-electron states – a result famously known as the *Pauli principle* (e.g., for $N=2$, $|\phi_i, \phi_i\rangle_A = 0$). Additionally, we can see from Eq. A.22 that two antisymmetric N -electron states built from the same one-electron states but in a different order/permutation, are identical, except for a possible global phase difference of -1 , and thus represent the same physical state, such that we can drop all but one of those states from the set $\{|\phi_{i_1}, \phi_{i_2}, \dots, \phi_{i_N}\rangle_A\}$ without losing completeness in $\mathcal{H}_N^A$. With these points in mind, an ONB of $\mathcal{H}_N^A$ is then given by [42] (orthonormality follows through from the original basis):

$$: \{|\phi_{i_1}, \phi_{i_2}, \dots, \phi_{i_N}\rangle_A, \ i_1 < i_2 < \dots < i_N\} \quad (\text{A.25})$$

Note that at this point we must know a way to index the one-particle orbitals to allow for a unique ordering of them, which we then use consistently. This can for example be done by ordering them energetically (with some “tie-breaker” in the case of a degeneracy) and will become very relevant in the next section.

While not treated here explicitly, note that the electron-nuclear states of Sec. 2.1 (in particular also before invoking the Born-Oppenheimer approximation) can be constructed in the same fashion, by first constructing a nuclear Hilbert space (via tensor products) and then building the tensor product between the nuclear and the electronic Hilbert space.

A.1.3 Fock Space

Using the ordered one-electron states, the (orthonormal) basis elements of $\mathcal{H}_N^A$ can also be written as¹⁰⁸

$$|n_1, n_2, \dots\rangle \equiv \left| \prod_i \phi_i^{n_i} \right\rangle_A, \quad (\text{A.26})$$

with

$$\begin{aligned} n_i &= 0 \text{ or } 1 \\ \sum_i n_i &= N, \end{aligned} \quad (\text{A.27})$$

where the first condition stems from the Pauli principle mentioned above and the second condition is needed to restrict ourselves to N -electron states.

When dropping the second condition, we obtain the (orthonormal) *occupancy number basis* of the *Fock space*, which is the Hilbert space obtained from building the *direct sum* of the 0-electron- (vacuum)¹⁰⁹, 1-electron-, 2-electron-, etc. Hilbert spaces [75]:

$$F = \bigoplus_{N=0}^{\infty} \mathcal{H}_N^A, \quad (\text{A.28})$$

where we use the (basis-dependent) definition of the direct sum of Hilbert spaces¹¹⁰:

Def. 7. Let V and W be two Hilbert spaces over $\mathbb{K}$. Let $\{|v_i\rangle\}_i$ and $\{|w_i\rangle\}_i$ be bases of the spaces, respectively. Then, the *direct sum Hilbert space* $V \oplus W$ is a vector space over $\mathbb{K}$ and is spanned by the union of the bases of V and W into one set forming the basis of $V \oplus W$. Additionally, we *define* the *direct sum of vectors*, where, if $|v\rangle_V \in V$ and $|w\rangle_W \in W$ and

$$\begin{aligned} |v\rangle_V &= \sum_i c_i |v_i\rangle_V \\ |w\rangle_W &= \sum_j d_j |w_j\rangle_W, \end{aligned}$$

we write

$$|v\rangle_V \oplus |w\rangle_W \equiv \sum_i c_i |v_i\rangle_{V \oplus W} + \sum_j d_j |w_j\rangle_{V \oplus W},$$

thus obtaining an element of $V \oplus W$ (where we temporarily added indices to clearly show which spaces the vectors belong to). Note that the basis elements of $V \oplus W$ are initially defined in a symbolic fashion (For every basis element $|v_i\rangle_V$ of V , there is a basis element of $V \oplus W$, which we denote by $|v_i\rangle_{V \oplus W}$. The same goes for the basis elements of W). The direct sum of vectors then tells

¹⁰⁸Where we introduce compact notation $|\prod_i \phi_i^{n_i}\rangle_A \equiv |\phi_{i_1}, \phi_{i_2}, \dots\rangle_A$, where $n_i = 1$ for all orbitals included on the right and $n_i = 0$ else.

¹⁰⁹Note that the vacuum state is *not* the zero vector of the Fock space.

¹¹⁰While a basis-dependent formulation is not the most elegant one, it fits our purposes. It is easily seen that this definition fulfills the properties of a direct sum as given in Chapter 17 in Ref. [86].

us how elements of V and W are related to elements of $V \oplus W$. To make it a Hilbert space, the inner product on $V \oplus W$ is then defined for $|v\rangle, |\tilde{v}\rangle \in V$ and $|w\rangle, |\tilde{w}\rangle \in W$ as

$$\langle v + w | \tilde{v} + \tilde{w} \rangle_{V \oplus W} \equiv \langle v | \tilde{v} \rangle_V + \langle w | \tilde{w} \rangle_W,$$

where we introduced notation $|v + w\rangle \equiv |v\rangle \oplus |w\rangle$. Trivially, if the bases of V and W are orthonormal bases, then so is the obtained basis of $V \oplus W$.

Note that, since the basis of the Fock space is simply the combination of all individual basis sets (of the 0-electron, 1-electron, etc. Hilbert spaces) into one, a generic vector in the Fock space is simply given by a (direct) sum of a 0-electron, a 1-electron etc. state (linear coefficients can be absorbed into the individual N -electron states). The Fock space is thus able to describe quantum systems with a variable particle number (we talked here about electrons, but these concepts can of course also be used for other types of particles). We can traverse between Fock-space sectors with different numbers of particles via the *creation operator* [75]

$$\hat{a}_\alpha^\dagger |n_1, n_2, \dots\rangle = (-1)^{\sum_{\beta=1}^{\alpha-1} n_\beta} |n_1, n_2, \dots, n_\alpha + 1, \dots\rangle \delta_{n_\alpha, 0} \quad (\text{A.29})$$

which adds an electron in orbital α and the *annihilation operator* [75]

$$\hat{a}_\alpha |n_1, n_2, \dots\rangle = (-1)^{\sum_{\beta=1}^{\alpha-1} n_\beta} |n_1, n_2, \dots, n_\alpha - 1, \dots\rangle \delta_{n_\alpha, 1} \quad (\text{A.30})$$

which removes an electron from orbital α . Note that the creation operator destroys the state (via the Pauli principle) if $n_\alpha = 1$ while the annihilation operator destroys it if $n_\alpha = 0$. Occasionally we also use the *particle-number operator* [75]:

$$\begin{aligned} \hat{n}_\alpha |n_1, n_2, \dots\rangle &\equiv \hat{a}_\alpha^\dagger \hat{a}_\alpha |n_1, n_2, \dots\rangle \\ &= n_\alpha |n_1, n_2, \dots\rangle \end{aligned} \quad (\text{A.31})$$

For reference, note also the relation between the antisymmetrizer and the creation operator:

$$\begin{aligned} \hat{\mathcal{A}} |\phi_\alpha\rangle \otimes |\phi_{i_1}, \phi_{i_2}, \dots, \phi_{i_N}\rangle_A &= \sqrt{N!} |\phi_\alpha, \phi_{i_1}, \phi_{i_2}, \dots, \phi_{i_N}\rangle_A \\ &= \sqrt{N!} (-1)^{\sum_{\beta=1}^{\alpha-1} n_\beta} |n_1, n_2, \dots, n_\alpha + 1, \dots\rangle \delta_{n_\alpha, 0} \\ &= \sqrt{N!} \hat{a}_\alpha^\dagger |n_1, n_2, \dots\rangle, \end{aligned} \quad (\text{A.32})$$

where we used Eqs. A.23, the Pauli principle and A.21.

To conclude, note that, since it can describe states with a variable number of particles, the Fock space can be used for the study of open quantum systems or, for example, in effective theories when working with quasiparticles (where for example a physical N -electron system can be described via a state containing zero, one or multiple excitons, see Sec. 2.4.4). In the other parts of this text we routinely use operators defined on the Fock space (creation/annihilation operators or the Hamiltonian of Eq. 2.121), which allows us to efficiently traverse between N -electron and $N \pm 1$ -electron states. We however never create superposition states of different-electron-number states from the different sectors of the Fock space!

A.1.4 Operators in First and Second Quantization

To conclude, we briefly show the action of one-particle and two-particle operators on the antisymmetrized N -electron Hilbert space $\mathcal{H}_N^A$. Details can for example be found in Refs. [42, 75].

One-Particle Operators

A linear operator $\hat{O}$ is termed a one-particle or single-particle operator if it is of the form:

$$\hat{O} = \sum_{i=1}^N \hat{o}_i, \quad (\text{A.33})$$

where the $\{\hat{o}_i\}$ (acting on $\mathcal{H}_N$) are in principle all the same operator $\hat{o}$ (acting on $\mathcal{H}_1$) and only differ in the “position” they act on. That is, for a simple product state in $\mathcal{H}_N$ (thus not an element of $\mathcal{H}_N^A$), we have:

$$\hat{o}_i (|\psi_1\rangle \otimes |\psi_2\rangle \otimes \cdots \otimes |\psi_i\rangle \otimes \cdots \otimes |\psi_N\rangle) = |\psi_1\rangle \otimes |\psi_2\rangle \otimes \cdots \otimes \hat{o} |\psi_i\rangle \otimes \cdots \otimes |\psi_N\rangle \quad (\text{A.34})$$

It is then trivial to see that $\hat{O}$ and the permutation operator $\hat{\Pi}$ commute and thus that also $\hat{O}$ and $\hat{\mathcal{A}}$ commute! Thus, we have (using Eq. A.20):

$$\begin{aligned} \hat{O} |\psi_1, \psi_2, \dots, \psi_N\rangle_A &= \hat{O} \hat{\mathcal{A}} |\psi_1, \psi_2, \dots, \psi_N\rangle \\ &= \hat{\mathcal{A}} \sum_{i=1}^N \hat{o}_i |\psi_1, \psi_2, \dots, \psi_N\rangle \\ &= \sum_{i=1}^N \hat{\mathcal{A}} (|\psi_1\rangle \otimes |\psi_2\rangle \otimes \cdots \otimes \hat{o} |\psi_i\rangle \otimes \cdots \otimes |\psi_N\rangle), \end{aligned} \quad (\text{A.35})$$

where we used linearity of $\hat{\mathcal{A}}$ to get to the last line. Action of $\hat{O}$ on a generic state in $\mathcal{H}_N^A$ follows equivalently by expanding it in the basis Eq. A.25 and using linearity of $\hat{O}$.

Note, that the fact that $\hat{O}$ and $\hat{\mathcal{A}}$ commute leads to simple and well known expressions like (compare Eq. 2.26):

$$\begin{aligned} \langle \{\mathbf{r}\} |_A \sum_{i=1}^N \hat{\mathbf{p}}_i |\Psi\rangle &= \langle \{\mathbf{r}\} |_A \hat{\mathcal{A}} \sum_{i=1}^N \hat{\mathbf{p}}_i |\Psi\rangle \\ &= \sum_{i=1}^N \langle \{\mathbf{r}\} | \hat{\mathbf{p}}_i \hat{\mathcal{A}} |\Psi\rangle \\ &= \sum_{i=1}^N -i \nabla_i \langle \{\mathbf{r}\} | \hat{\mathcal{A}} |\Psi\rangle \\ &= \sum_{i=1}^N -i \nabla_i \langle \{\mathbf{r}\} |_A |\Psi\rangle, \end{aligned} \quad (\text{A.36})$$

where we used that the antisymmetrizer is Hermitian [126]. The same holds for the two-particle operators below, see for example Eq. 2.28.

The formulation shown above is known as the *first-quantized* formulation of the operator $\hat{O}$. Equivalently, its action on $\mathcal{H}_N^A$ can be written in *second quantization* as:

$$\begin{aligned}\hat{O} &= \sum_{i,j} O_{i,j} \hat{a}_i^\dagger \hat{a}_j \\ O_{i,j} &= \langle \phi_i | \hat{O} | \phi_j \rangle,\end{aligned}\tag{A.37}$$

for any orthonormal basis $\{\phi_i\}$ of $\mathcal{H}_1$ with corresponding creation and annihilation operators. Notably, if we started with an M -electron operator $\hat{O} = \sum_{i=1}^M \hat{o}_i$ with $M \neq N$, the resulting second-quantized version would look the same! In other words, the second-quantized expression directly has a well-defined meaning on the whole Fock space Eq. A.28! The same holds for the two-particle operators and the electronic Hamiltonian shown below.

An example of such a single-particle operator can be found in Eq. 2.9 or in Eq. 3.19.

Two-Particle Operators

We often also encounter two-particle linear operators of the form¹¹¹:

$$\begin{aligned}\hat{O} &= \frac{1}{2} \sum_{i=1}^N \sum_{j=1, j \neq i}^N o(\hat{\mathbf{r}}_i, \hat{\mathbf{r}}_j), \\ o(\hat{\mathbf{r}}_i, \hat{\mathbf{r}}_j) &= o(\hat{\mathbf{r}}_j, \hat{\mathbf{r}}_i)\end{aligned}\tag{A.38}$$

We can trivially see that $\hat{O}$ again commutes with $\hat{\Pi}$ and $\hat{\mathcal{A}}$, such that:

$$\begin{aligned}\hat{O} |\psi_1, \psi_2, \dots, \psi_N\rangle_A &= \hat{O} \hat{\mathcal{A}} |\psi_1, \psi_2, \dots, \psi_N\rangle \\ &= \sum_{i=1}^N \sum_{j=1, j \neq i}^N \hat{\mathcal{A}} o(\hat{\mathbf{r}}_i, \hat{\mathbf{r}}_j) |\psi_1, \psi_2, \dots, \psi_N\rangle\end{aligned}\tag{A.39}$$

Note that $o(\hat{\mathbf{r}}_i, \hat{\mathbf{r}}_j) |\psi_1, \psi_2, \dots, \psi_N\rangle$ is in general not a simple product state anymore but rather a linear combination of product states. More importantly for us, the action of $\hat{O}$ on $\mathcal{H}_N^A$ can be written in second quantization as:

$$\begin{aligned}\hat{O} &= \frac{1}{2} \sum_{i,j,k,l} O_{i,j,k,l} \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k \\ O_{i,j,k,l} &= \sum_{s=\uparrow,\downarrow} \sum_{s'=\uparrow,\downarrow} \int_{\mathbb{R}^3} d^3r \int_{\mathbb{R}^3} d^3r' \phi_i^*(\mathbf{r}, s) \phi_j^*(\mathbf{r}', s') \phi_k(\mathbf{r}, s) \phi_l(\mathbf{r}', s') o(\mathbf{r}, \mathbf{r}')\end{aligned}\tag{A.40}$$

¹¹¹Note that we restrict ourselves to spin-independent interactions, which is the type of two-particle operators we explicitly treat in the main text, see Eq. 2.11.

Electronic Hamiltonian

To conclude this section, we write the electronic Hamiltonian of Eq. 2.42:

$$\begin{aligned}\hat{H}_e &= \sum_i^N \hat{h}_i + \frac{1}{2} \sum_{i=1}^N \sum_{j=1, j \neq i}^N \frac{1}{|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|} \\ \hat{h}_i &= \frac{1}{2} \hat{p}_i^2 - \sum_{k=1}^K \frac{Z_k}{|\hat{\mathbf{r}}_i - \mathbf{R}_k|}\end{aligned}\quad (\text{A.41})$$

in second quantization. For the single-particle term we find:

$$\begin{aligned}\sum_i^N \hat{h}_i &= \sum_{i,j} \langle \phi_i | \hat{h} | \phi_j \rangle \hat{a}_i^\dagger \hat{a}_j \\ &= \sum_{i,j} \int dx \phi_i^*(x) \left[-\frac{\nabla^2}{2} - \sum_{k=1}^K \frac{Z_k}{|\mathbf{r} - \mathbf{R}_k|} \right] \phi_j(x) \hat{a}_i^\dagger \hat{a}_j \\ &= \int dx \hat{\Psi}^\dagger(x) \left[-\frac{\nabla^2}{2} - \sum_{k=1}^K \frac{Z_k}{|\mathbf{r} - \mathbf{R}_k|} \right] \hat{\Psi}(x),\end{aligned}\quad (\text{A.42})$$

where we used the notation of Eq. 2.4 and the quantum field operators Eq. 2.119. For the two-particle term we similarly get:

$$\begin{aligned}\frac{1}{2} \sum_{i=1}^N \sum_{j=1, j \neq i}^N \frac{1}{|\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|} &= \frac{1}{2} \sum_{i,j,k,l} \int dx dx' \phi_i^*(x) \phi_j^*(x') \phi_k(x) \phi_l(x') \frac{1}{|\mathbf{r} - \mathbf{r}'|} \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k \\ &= \frac{1}{2} \int dx dx' \frac{1}{|\mathbf{r} - \mathbf{r}'|} \hat{\Psi}^\dagger(x) \hat{\Psi}^\dagger(x') \hat{\Psi}(x') \hat{\Psi}(x)\end{aligned}\quad (\text{A.43})$$

A.2 Notation for Basis Expansions

Throughout this text, we routinely encounter expansions in terms of or summations over one-electron basis sets. See for example the definition of quantum field operators in Eq. 2.119:

$$\hat{\Psi}(x) = \sum_i \phi_i(x) \hat{a}_i \quad (\text{A.44})$$

We usually write these expansions in terms of summations over discrete one-electron states/orbitals. Now, as is detailed in Appendix A.1.1, a one-electron basis set can be obtained by solving a one-particle Schrödinger equation (usually via Kohn-Sham DFT) and the resulting basis set generally contains scattering states belonging to the continuous spectrum. For the case of an infinite surface, even the basis states we call “bound” states are indexed by a continuous Bloch momentum. As a result, when using such a one-electron basis, expressions like the discrete summation have to be understood in a symbolic way while the exact expression would also contain an integral over the continuously indexed eigenvectors

[198]. For example (assuming orthonormality and Dirac delta normalization as in Ref. [198] or Eq. A.4), the quantum field operators become:

$$\hat{\Psi}(x) = \sum_i \phi_i(x) \hat{a}_i + \int da \phi_a(x) \hat{a}_a \quad (\text{A.45})$$

In principle the same also goes for expansions via many-electron states, compare for example Eq. 2.129.

A.3 Functionals

We start from the usual definition of a (scalar-valued) functional, given e.g. in Ref. [197]:

Def. 8. Let V be a vector space over a field $\mathbb{K}$ (usually $\mathbb{R}$ or $\mathbb{C}$). A *functional* on V is a map^a

$$F: V \rightarrow \mathbb{K}, \quad v \mapsto F[v].$$

^aIn a weaker definition, a functional may also be defined only over a subset of elements of some vector space. Note also that in the main text we usually do not explicitly mention the domain of the functionals we work with for simplicity.

An important class of functionals are those defined on vector spaces consisting of functions (e.g. $L^2(\mathbb{R}^3)$), that is mappings that assign a complex (or real, since $\mathbb{R} \subset \mathbb{C}^{112}$) number to a function and can thus be thought of as “functions of functions”. Based on the definition given in Refs. [47, 77, 199], we define the functional derivative for such functionals of functions:

Def. 9. Let $(V, \|\cdot\|)$ be a normed vector space of functions with domain Ω and let F be a functional on V . Let $f_0 \in V$ be a function. We define the *variation* of F under a change $\delta f \in V$ of the function as

$$\delta F[f_0, \delta f] = F[f_0 + \delta f] - F[f_0].$$

If there exists a g , such that for any δf we have^a

$$\delta F[f_0, \delta f] = \int_{\Omega} dx g(x) \delta f(x) + o(\|\delta f\|),$$

then we say that F is *differentiable* at f_0 , call g the *functional derivative* of F at f_0 and write $g(x) = \left. \frac{\delta F}{\delta f(x)} \right|_{f_0}$.

^aHere we use *little-o* notation (compare Ref. [200]): “ $+o(\|\delta f\|)$ ” means that we add a functional G of δf that falls faster than linearly when approaching $\delta f = 0$ (from any direction), that is $\lim_{\delta f \rightarrow 0} \frac{G[\delta f]}{\|\delta f\|} = 0$. Note that far from $\delta f = 0$, the behavior of $G[\delta f]$ is irrelevant.

Notice, that this definition is somewhat incomplete, because we did not specify what g actually is. This allows us to apply the definition to a wider range of

¹¹²Strictly speaking $\mathbb{R}$ is embedded in $\mathbb{C}$.

functionals. A natural choice would be to assume g to be an element of the same vector space V as f_0 . This is for example the case if V is the Hilbert space $L^2(\mathbb{R}^3)$ with the inner product $\langle u|v \rangle = \int_{\mathbb{R}^3} d^3r u^*(\mathbf{r})v(\mathbf{r})$ and F is *Fréchet differentiable* at f_0 .¹¹³ However, this definition also allows for g to be an ordinary function outside V or even the symbolic kernel of a distribution, for example the Dirac delta “function” of the delta distribution.

Using the functional derivative of Def. 9 we can expand/calculate a functional in the vicinity (i.e. for small δf) of a function f_0 by neglecting the $o(\|\delta f\|)$ term, such that the variation δF in Def. 9 is linear in δf , hence why we also call this expansion the *linear approximation* of the functional F in the vicinity of f_0 . Note that we can also go beyond the linear approximation by performing a *Taylor series* expansion of $F[f_0 + \delta f]$, see Ref. [47].

Finally, note that we call a function f_c a *critical point* of the functional F , if the functional derivative of F vanishes at f_c :

$$g(x) = \left. \frac{\delta F}{\delta f(x)} \right|_{f_c} = 0 \quad (\text{A.46})$$

For real-valued functionals F , the global minimizer (often also simply called the “global minimum”) $\arg \min_{f \in V} F[f]$ is such a critical point [47] (assuming differentiability of F at the global minimum) hence why the search for critical points becomes very relevant in practice, see for example Sec. 2.2. That is, we search for functions that satisfy Eq. A.46, compare for example Eq. 2.85. Using Def. 9 this may equivalently be formulated as a search for functions that satisfy

$$\delta F[f_c, \delta f] = o(\|\delta f\|), \quad (\text{A.47})$$

which we symbolically – compare for example Eq. 2.84 – often simply write as:

$$\delta F = 0 \quad (\text{A.48})$$

A.4 Fourier Transformation

This section lists the Fourier-transform conventions used throughout this text. A central equation underlying this section is give by Eq. B.14:

$$\frac{1}{2\pi} \int_{\mathbb{R}} dx e^{ikx} = \delta(k) \quad (\text{A.49})$$

A.4.1 Convention for Position Arguments

Plane waves

The plane waves $\{|\mathbf{k}\rangle\}$,

$$\langle \mathbf{r} | \mathbf{k} \rangle = (2\pi)^{-3/2} e^{i\mathbf{k} \cdot \mathbf{r}}, \quad (\text{A.50})$$

¹¹³ F is Fréchet differentiable at f_0 if there exists a continuous linear functional A , such that $\delta F[f_0, \delta f] = A[\delta f] + o(\|\delta f\|)$ [200, 201]. But if V is a Hilbert space with an inner product $\langle u|v \rangle$ that is antilinear in the first argument and linear in the second argument, the Riesz representation theorem [197] tells us that for every continuous linear functional A (i.e. for every element of the continuous dual space V^*), there exists a unique element $h \in V$, satisfying $A[v] = \langle h|v \rangle \forall v \in V$. In our example of $V = L^2(\mathbb{R}^3)$, we can then identify h^* as the functional derivative of F at f_0 . And for $V = L^2(\mathbb{R}^3)$, if $h \in V$, then trivially $h^* \in V$.

are the solutions of the single-electron (spinless) Schrödinger equation in free space ($V = 0$, compare Appendix A.1.1) and form an orthonormal basis of $L^2(\mathbb{R}^3)$, where the chosen normalization/prefactor ensures simple Dirac delta normalization (which ensures simple expressions throughout the text, e.g. $\mathbb{1}_{L^2(\mathbb{R}^3)} = \int_{\mathbb{R}^3} d^3k |\mathbf{k}\rangle \langle \mathbf{k}|$, see also Ref. [198])

$$\langle \mathbf{k} | \mathbf{k}' \rangle = \delta(\mathbf{k} - \mathbf{k}'), \quad (\text{A.51})$$

as can be seen by comparing to Eq. A.49. We also refer to the plane waves as *momentum eigenstates*, since they are common eigenstates of the momentum operators $\hat{p}_x$, $\hat{p}_y$ and $\hat{p}_z$.

Continuous Fourier Transformation

Since the plane waves form a basis of $L^2(\mathbb{R}^3)$, any physical (spinless) state (see Appendix A.1.1) can be expanded in them. Given a physical (spinless one-electron) state $|\varphi\rangle$ we can expand this state in the plane-waves or in the position basis (or, of course, any other basis) and the “expansion coefficients” are related via (using $\langle \mathbf{r} | \mathbf{r}' \rangle = \delta(\mathbf{r} - \mathbf{r}')$ such that $\mathbb{1}_{L^2(\mathbb{R}^3)} = \int_{\mathbb{R}^3} d^3r |\mathbf{r}\rangle \langle \mathbf{r}|$):

$$\begin{aligned} \mathcal{F}[\varphi](\mathbf{k}) &\equiv \langle \mathbf{k} | \varphi \rangle \\ &= \int_{\mathbb{R}^3} d^3r \langle \mathbf{k} | \mathbf{r} \rangle \langle \mathbf{r} | \varphi \rangle \\ &= (2\pi)^{-3/2} \int_{\mathbb{R}^3} d^3r e^{-i\mathbf{k} \cdot \mathbf{r}} \varphi(\mathbf{r}) \end{aligned} \quad (\text{A.52})$$

and

$$\begin{aligned} \varphi(\mathbf{r}) &= \langle \mathbf{r} | \varphi \rangle \\ &= \int_{\mathbb{R}^3} d^3k \langle \mathbf{r} | \mathbf{k} \rangle \langle \mathbf{k} | \varphi \rangle \\ &= (2\pi)^{-3/2} \int_{\mathbb{R}^3} d^3k e^{i\mathbf{k} \cdot \mathbf{r}} \mathcal{F}[\varphi](\mathbf{k}) \end{aligned} \quad (\text{A.53})$$

Here, $\mathcal{F}[\varphi]$ denotes the *Fourier transform* of the wave function φ , where we use the symmetric normalization for the Fourier transformation Eq. A.52 and the back-transformation Eq. A.53 of wave functions.

Note that, while we introduced it in terms of physical states, the Fourier transform and back-transformation can also be applied to non-normalizable states¹¹⁴ we meet throughout this text. That is, we find for the position state $|\mathbf{r}'\rangle$:

$$\begin{aligned} f_{\mathbf{r}'}(\mathbf{r}) &\equiv \langle \mathbf{r} | \mathbf{r}' \rangle = \delta(\mathbf{r} - \mathbf{r}') \\ \mathcal{F}[f_{\mathbf{r}'}](\mathbf{k}) &= (2\pi)^{-3/2} e^{-i\mathbf{k} \cdot \mathbf{r}'}, \end{aligned} \quad (\text{A.54})$$

where we can use Eq. A.49 (simply integrating over $\mathbf{k}$ instead of $\mathbf{r}$) to verify that the back-transformation leads again to $\delta(\mathbf{r} - \mathbf{r}')$. Similarly, we find for the momentum eigenstate (plane wave) $|\mathbf{k}'\rangle$:

$$\begin{aligned} f_{\mathbf{k}'}(\mathbf{r}) &\equiv \langle \mathbf{r} | \mathbf{k}' \rangle = (2\pi)^{-3/2} e^{i\mathbf{k}' \cdot \mathbf{r}} \\ \mathcal{F}[f_{\mathbf{k}'}](\mathbf{k}) &= \delta(\mathbf{k} - \mathbf{k}') \end{aligned} \quad (\text{A.55})$$

¹¹⁴See also Footnote 101

Using the linearity of the Fourier transform Eq. A.52 then also allows us to Fourier-transform the bound Bloch state $|\varphi_{n,\mathbf{q}}\rangle$ (compare Appendix B.2):

$$\begin{aligned}
\varphi_{n,\mathbf{q}}(\mathbf{r}) &= \sum_{\mathbf{G}} c_{n,\mathbf{q},\mathbf{G}}(z) e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}_{\parallel}} \\
\mathcal{F}[\varphi](\mathbf{k}) &= (2\pi)^{-3/2} \sum_{\mathbf{G}} \int_{\mathbb{R}^2} d^2r_{\parallel} e^{i(\mathbf{q}+\mathbf{G}-\mathbf{k}_{\parallel})\cdot\mathbf{r}_{\parallel}} \int_{\mathbb{R}} dz e^{-ik_z z} c_{n,\mathbf{q},\mathbf{G}}(z) \\
&= 2\pi \sum_{\mathbf{G}} \left[(2\pi)^{-2} \int_{\mathbb{R}^2} d^2r_{\parallel} e^{i(\mathbf{q}+\mathbf{G}-\mathbf{k}_{\parallel})\cdot\mathbf{r}_{\parallel}} \right] \left[(2\pi)^{-1/2} \int_{\mathbb{R}} dz e^{-ik_z z} c_{n,\mathbf{q},\mathbf{G}}(z) \right] \\
&= 2\pi \sum_{\mathbf{G}} \delta(\mathbf{q} + \mathbf{G} - \mathbf{k}_{\parallel}) \mathcal{F}[c_{n,\mathbf{q},\mathbf{G}}](k_z), \tag{A.56}
\end{aligned}$$

where we used Eq. A.49 and introduced the one-dimensional equivalent of the Fourier transform Eq. A.52.

Discrete Fourier Transformation

We routinely encounter functions that repeat periodically over a surface unit cell (see Appendix A.1.1 for details):

$$\begin{aligned}
u(\mathbf{r} + \mathbf{a}_1) &= u(\mathbf{r}) \\
u(\mathbf{r} + \mathbf{a}_2) &= u(\mathbf{r}) \tag{A.57}
\end{aligned}$$

Based on the in-plane reciprocal lattice vectors $\{\mathbf{G}\}$ (compare Eq. D.41 and only sum over $i = 1, 2$), such a function can be written as:

$$u(\mathbf{r}) = \sum_{\mathbf{G}} c(\mathbf{G}, z) e^{i\mathbf{G}\cdot\mathbf{r}} \tag{A.58}$$

Conversely, the expansion coefficients can be obtained via:

$$c(\mathbf{G}, z) = \frac{1}{A_c} \int_{A_c} d^2r_{\parallel} e^{-i\mathbf{G}\cdot\mathbf{r}} u(\mathbf{r}) \tag{A.59}$$

Comparing with Eq. A.52 and Eq. A.53 shows obvious similarities (although the prefactor has now been chosen antisymmetrically) and we refer to the expressions shown here as the *discrete Fourier transformation* and back-transformation. Trivially, the above expressions can also be extended to functions that are periodic in all three directions (which we encounter in the repeated-slab approach, see Appendices A.1.1 and D.2.3)

A.4.2 Convention for Time Arguments

We also routinely encounter time-dependent functions, for which we choose the common antisymmetric Fourier-transformation normalization condition for the transformation between time t and frequency ω . Additionally, we follow the sign-convention of Ref. [77]. Denoting the time-dependent function by f and its Fourier-transform by $\tilde{f}$ it reads:

$$\begin{aligned}
\tilde{f}(\omega) &= \int_{\mathbb{R}} dt e^{i\omega t} f(t) \\
f(t) &= \frac{1}{2\pi} \int_{\mathbb{R}} d\omega e^{-i\omega t} \tilde{f}(\omega) \tag{A.60}
\end{aligned}$$

B Density Functional Theory

B.1 Ground-State Density of an Infinite Surface

In Kohn-Sham density functional theory (KS-DFT), the ground-state electron density of a finite system takes the form (see Eq. 2.100):

$$n(\mathbf{r}) = \sum_{s=\uparrow,\downarrow} \sum_{i=1}^N |\phi_i(\mathbf{r}, s)|^2 \quad (\text{B.1})$$

In the context of an infinitely extended surface, these occupied orbitals are in-plane (bound) Bloch orbitals indexed by the continuous Bloch momentum from the Brillouin zone (see Appendix A.1.1). We can explicitly transform the above equation for the density to an appropriate expression for the infinite surface by starting from a macroscopic but finite surface and performing the thermodynamic limit. This derivation also serves as a recipe for other quantities occurring throughout this text. As argued in Appendix A.1.1, the bound states (for our physical systems, the occupied states are of course bound states) of such a system are in the interior region, to good approximation, Bloch functions with Bloch momenta given by Eq. A.8. Let us denote the surface area of the finite surface as $A = N_1 N_2 A_c$, where A_c is the area of the surface unit cell and N_1 and N_2 are respectively the number of repetitions of the unit cell (= number of Bloch momenta) forming the finite surface. In the interior region, the density then simply reads (for a gapped system with only fully filled/empty bands)

$$\begin{aligned} n(\mathbf{r}) &= \sum_{s=\uparrow,\downarrow} \sum_n^{\text{occ.}} \sum_{\mathbf{q}}^{\text{BZ}} |\phi_{n,\mathbf{q}}(\mathbf{r}, s)|^2 \\ &= \sum_{s=\uparrow,\downarrow} \sum_n^{\text{occ.}} \sum_{\mathbf{q}}^{\text{BZ}} |u_{n,\mathbf{q}}(\mathbf{r}, s)|^2, \end{aligned} \quad (\text{B.2})$$

with normalization

$$\sum_{s=\uparrow,\downarrow} \int_{A_c} d^2 r_{\parallel} \int_{\mathbb{R}} dz |u_{n,\mathbf{q}}(\mathbf{r}, s)|^2 = \frac{1}{N_1 N_2}, \quad (\text{B.3})$$

such that:

$$\begin{aligned}
\int_{A_c} d^2 r_{\parallel} \int_{\mathbb{R}} dz n(\mathbf{r}) &= \sum_{s=\uparrow,\downarrow} \sum_n^{occ.} \sum_{\mathbf{q}}^{BZ} \int_{A_c} d^2 r_{\parallel} \int_{\mathbb{R}} dz |u_{n,\mathbf{q}}(\mathbf{r}, s)|^2 \\
&= \sum_n^{occ.} \sum_{\mathbf{q}}^{BZ} \frac{1}{N_1 N_2} \\
&= \sum_n^{occ.} 1
\end{aligned} \tag{B.4}$$

Since the area of the 2D Brillouin zone is $A_{BZ} = \frac{(2\pi)^2}{A_c}$, the Brillouin zone area per Bloch momentum is $\frac{(2\pi)^2}{A}$ and the density can be written as:

$$n(\mathbf{r}) = \frac{A}{(2\pi)^2} \sum_{s=\uparrow,\downarrow} \sum_n^{occ.} \sum_{\mathbf{q}}^{BZ} \frac{(2\pi)^2}{A} |u_{n,\mathbf{q}}(\mathbf{r}, s)|^2 \tag{B.5}$$

Changing the normalization of the orbitals to

$$\sum_{s=\uparrow,\downarrow} \int_{A_c} d^2 r_{\parallel} \int_{\mathbb{R}} dz |u_{n,\mathbf{q}}(\mathbf{r}, s)|^2 = \frac{A_c}{(2\pi)^2}, \tag{B.6}$$

this becomes:

$$n(\mathbf{r}) = \sum_{s=\uparrow,\downarrow} \sum_n^{occ.} \sum_{\mathbf{q}}^{BZ} \frac{(2\pi)^2}{A} |u_{n,\mathbf{q}}(\mathbf{r}, s)|^2 \tag{B.7}$$

In the thermodynamic limit we then obtain the electron density of the infinite surface as:

$$n(\mathbf{r}) = \sum_{s=\uparrow,\downarrow} \sum_n^{occ.} \int_{BZ} d^2 q |u_{n,\mathbf{q}}(\mathbf{r}, s)|^2 \tag{B.8}$$

Note that the new normalization we chose, Eq. B.6 is needed to ensure simple (without prefactors) Dirac delta normalization of the Bloch states (see Appendix. B.2) and results in the simple form of the density in the thermodynamic limit. We of course retain (number of electrons in unit cell equals number of spin-bands, as is well known from band formation):

$$\begin{aligned}
\int_{A_c} d^2 r_{\parallel} \int_{\mathbb{R}} dz n(\mathbf{r}) &= \sum_{s=\uparrow,\downarrow} \sum_n^{occ.} \int_{BZ} d^2 q \int_{A_c} d^2 r_{\parallel} \int_{\mathbb{R}} dz d^3 r |u_{n,\mathbf{q}}(\mathbf{r}, s)|^2 \\
&= \sum_n^{occ.} \int_{BZ} d^2 q \frac{A_c}{(2\pi)^2} \\
&= \sum_n^{occ.} A_{BZ} \frac{A_c}{(2\pi)^2} \\
&= \sum_n^{occ.} 1
\end{aligned} \tag{B.9}$$

Note also, that we can now explicitly see that the electron density is surface-periodic. Lastly, note that this expression for the density holds for all of the infinite surface! While the expression Eq. B.7 only held for the interior region of a finite surface, the infinite surface has no ends, so the final expression holds everywhere.

B.2 Normalization of Bound In-Plane Bloch States

This section is concerned with the normalization of (KS) Bloch orbitals. We restrict ourselves in the following discussion to spatial orbitals for simplicity, since the spatial dependence is where normalization complications arise as a result of the thermodynamic limit. The discussion can trivially be extended to spatial-spin product orbitals and to spinor orbitals (compare Eq. B.6).

The “bound” states of an infinite atomic surface are described in Appendix A.1.1 as in-plane Bloch functions (with Bloch momenta in the surface Brillouin zone) that vanish in the vacuum far above and below the surface:

$$\begin{aligned}\varphi_{n,\mathbf{q}}(\mathbf{r}) &= e^{i\mathbf{q}\cdot\mathbf{r}} u_{n,\mathbf{q}}(\mathbf{r}) \\ u_{n,\mathbf{q}}(\mathbf{r} + \mathbf{a}_1) &= u_{n,\mathbf{q}}(\mathbf{r}) \\ u_{n,\mathbf{q}}(\mathbf{r} + \mathbf{a}_2) &= u_{n,\mathbf{q}}(\mathbf{r}) \\ \lim_{z \rightarrow \pm\infty} u_{n,\mathbf{q}}(\mathbf{r}_{\parallel} + \mathbf{e}_z z) &= 0\end{aligned}\tag{B.10}$$

They are non-normalizable and thus no elements of $L^2(\mathbb{R}^3)$ and we instead “normalize” them via the Dirac delta, see Eq. A.11:

$$\langle \varphi_{n,\mathbf{q}} | \varphi_{n',\mathbf{q}'} \rangle = \delta_{n,n'} \delta(\mathbf{q} - \mathbf{q}')\tag{B.11}$$

The aim of this section is to show how this normalization determines the normalization of the in-plane periodic functions $\{u_{n,\mathbf{q}}\}$.

To begin, note that thanks to its periodicity, we can expand $u_{n,\mathbf{q}}$ in a Fourier series over the in-plane reciprocal lattice vectors (compare Eq. (3.34) in Ref. [130]):

$$u_{n,\mathbf{q}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{n,\mathbf{q},\mathbf{G}}(z) e^{i\mathbf{G}\cdot\mathbf{r}_{\parallel}}\tag{B.12}$$

Now, insert this into the overlap of two Bloch states:

$$\begin{aligned}\langle \varphi_{n,\mathbf{q}} | \varphi_{n',\mathbf{q}'} \rangle &= \int_{\mathbb{R}^3} d^3r \varphi_{n,\mathbf{q}}^*(\mathbf{r}) \varphi_{n',\mathbf{q}'}(\mathbf{r}) \\ &= \int_{\mathbb{R}^3} d^3r e^{i(\mathbf{q}' - \mathbf{q})\cdot\mathbf{r}_{\parallel}} u_{n,\mathbf{q}}^*(\mathbf{r}) u_{n',\mathbf{q}'}(\mathbf{r}) \\ &= \sum_{\mathbf{G},\mathbf{G}'} \int_{\mathbb{R}} dz c_{n,\mathbf{q},\mathbf{G}}^*(z) c_{n',\mathbf{q}',\mathbf{G}'}(z) \int_{\mathbb{R}^2} d^2r_{\parallel} e^{i(\mathbf{q}' - \mathbf{q})\cdot\mathbf{r}_{\parallel}} e^{i(\mathbf{G}' - \mathbf{G})\cdot\mathbf{r}_{\parallel}}\end{aligned}\tag{B.13}$$

Using the (2D version of the) expression

$$\frac{1}{2\pi} \int_{\mathbb{R}} dx e^{ikx} = \delta(k),\tag{B.14}$$

we find:

$$\langle \varphi_{n,\mathbf{q}} | \varphi_{n',\mathbf{q}'} \rangle = \sum_{\mathbf{G}, \mathbf{G}'} \int_{\mathbb{R}} dz c_{n,\mathbf{q},\mathbf{G}}^*(z) c_{n',\mathbf{q}',\mathbf{G}'}(z) (2\pi)^2 \delta(\mathbf{q}' - \mathbf{q} + \mathbf{G}' - \mathbf{G}) \quad (\text{B.15})$$

Using further that the Bloch momenta are restricted to the Brillouin zone, the Dirac delta function's argument can only vanish if $\mathbf{q} = \mathbf{q}'$ and $\mathbf{G} = \mathbf{G}'$, such that we get:

$$\begin{aligned} \langle \varphi_{n,\mathbf{q}} | \varphi_{n',\mathbf{q}'} \rangle &= \sum_{\mathbf{G}, \mathbf{G}'} \int_{\mathbb{R}} dz c_{n,\mathbf{q},\mathbf{G}}^*(z) c_{n',\mathbf{q}',\mathbf{G}'}(z) (2\pi)^2 \delta(\mathbf{q}' - \mathbf{q}) \delta_{\mathbf{G}', \mathbf{G}} \\ &= \sum_{\mathbf{G}} \int_{\mathbb{R}} dz c_{n,\mathbf{q},\mathbf{G}}^*(z) c_{n',\mathbf{q},\mathbf{G}}(z) (2\pi)^2 \delta(\mathbf{q}' - \mathbf{q}) \end{aligned} \quad (\text{B.16})$$

To continue, note that we can identify part of this expression as the overlap of two periodic functions:

$$\begin{aligned} \int_{A_c} d^2 r_{\parallel} \int_{\mathbb{R}} dz u_{n,\mathbf{q}}^*(\mathbf{r}) u_{n',\mathbf{q}}(\mathbf{r}) &= \sum_{\mathbf{G}, \mathbf{G}'} \int_{\mathbb{R}} dz c_{n,\mathbf{q},\mathbf{G}}^*(z) c_{n',\mathbf{q},\mathbf{G}'}(z) \int_{A_c} d^2 r_{\parallel} e^{i(\mathbf{G}' - \mathbf{G}) \cdot \mathbf{r}_{\parallel}} \\ &= A_c \sum_{\mathbf{G}} \int_{\mathbb{R}} dz c_{n,\mathbf{q},\mathbf{G}}^*(z) c_{n',\mathbf{q},\mathbf{G}}(z), \end{aligned} \quad (\text{B.17})$$

where A_c is the area of the surface unit cell. Inserting this into Eq. B.16 we thus find:

$$\langle \varphi_{n,\mathbf{q}} | \varphi_{n',\mathbf{q}'} \rangle = \frac{(2\pi)^2}{A_c} \delta(\mathbf{q}' - \mathbf{q}) \int_{A_c} d^2 r_{\parallel} \int_{\mathbb{R}} dz u_{n,\mathbf{q}}^*(\mathbf{r}) u_{n',\mathbf{q}}(\mathbf{r}) \quad (\text{B.18})$$

Finally, if we demand the orthonormalization of Eq. B.11 for the full Bloch state, then the periodic parts must be normalized such that their overlap becomes:

$$\int_{A_c} d^2 r_{\parallel} \int_{\mathbb{R}} dz u_{n,\mathbf{q}}^*(\mathbf{r}) u_{n',\mathbf{q}}(\mathbf{r}) = \delta_{n,n'} \frac{A_c}{(2\pi)^2} \quad (\text{B.19})$$

B.3 Brillouin-Zone Sampling

We have shown that the (Kohn-Sham) ground-state electron density of an infinitely-extended surface takes the form of Eq. B.8 (assuming only fully filled and completely empty bands):

$$n(\mathbf{r}) = \sum_{s=\uparrow,\downarrow} \sum_n^{\text{occ.}} \int_{\text{BZ}} d^2 q |u_{n,\mathbf{q}}(\mathbf{r}, s)|^2, \quad (\text{B.20})$$

where the $\{u_{n,\mathbf{q}}\}$ are normalized (here and below) according to Eq. B.19. Trivially, the density is periodic with the surface unit-cell:

$$\begin{aligned} n(\mathbf{r} + \mathbf{a}_1) &= n(\mathbf{r}) \\ n(\mathbf{r} + \mathbf{a}_2) &= n(\mathbf{r}) \end{aligned} \quad (\text{B.21})$$

In practice, we can of course not calculate an infinite number of solutions of the Schrödinger equation. Instead, we only calculate solutions at a finite number of Bloch momenta. The used choice of Bloch momenta is known as the *Brillouin zone sampling*. The density inside the surface unit cell can then approximately be calculated using a finite set of Bloch momenta and numerical quadrature of the integral [46]:

$$n(\mathbf{r}) \approx \sum_{s=\uparrow,\downarrow} \sum_n^{\text{occ.}} \sum_{\mathbf{q}}^{\text{BZ}} w_{\mathbf{q}} |u_{n,\mathbf{q}}(\mathbf{r}, s)|^2 \quad (\text{B.22})$$

For example, when using the Γ -centered¹¹⁵ grid of Eq. A.8 – which corresponds to the allowed Bloch momenta when enforcing periodic boundary conditions Eq. A.7 – the integral is approximated by a sum over $N_1 N_2$ Bloch momenta (A_c is the surface unit-cell's area):

$$n(\mathbf{r}) \approx \sum_{s=\uparrow,\downarrow} \frac{(2\pi)^2}{N_1 N_2 A_c} \sum_n^{\text{occ.}} \sum_{\mathbf{q}}^{\text{BZ}} |u_{n,\mathbf{q}}(\mathbf{r}, s)|^2 \quad (\text{B.23})$$

This can be understood as dividing the Brillouin zone into equally sized cubic sectors and assuming the Bloch states within each sector to be approximately constant. Trivially, this approximation can then be improved by increasing the number of used Bloch momenta until convergence is achieved. Note also, that we have already encountered this expression in Eq. B.7: it is the electron density in the interior region of a macroscopic but finite surface, whose electron density can intuitively be understood to converge to that of the infinite surface when increasing its size via N_1 and N_2 (see comments in Appendix A.1.1 for details).

Alternatively, such quadratures are also routinely performed using shifted (off- Γ) but still regular (and rectilinear, in coordinates of the $\{\mathbf{b}_i\}$) Brillouin zone grids, which can be understood as using Bloch functions that satisfy *twisted boundary conditions*¹¹⁶ ($\phi(\mathbf{r} + N_1 \mathbf{a}_1, s) = e^{i\theta} \phi(\mathbf{r}, s)$, etc.). Lastly, integral quadrature may be performed via irregular sampling of the Brillouin zone which generally requires good understanding of the considered system.

While we have shown it above for the case of the electron density, this techniques can of course be also used in other occasions where integrals over the Brillouin zone are met.

¹¹⁵We call a BZ sampling Γ -centered if it contains Γ . Otherwise, we call it *off*- Γ .

¹¹⁶Note that we above and in Appendix A.1.1 focused on periodic boundary conditions since they are a standard choice and since our practical calculations of the electron density used a Γ -centered sampling of the Brillouin zone. We could have, however, equivalently worked with twisted boundary conditions, which – as the periodic boundary conditions – become obsolete in the limit $N_1, N_2 \rightarrow \infty$.

C Many-Body Perturbation Theory

C.1 Bethe-Salpeter Equation

C.1.1 Derivation of BSE in Matrix Form

Our goal in this section is to derive a form of the Bethe-Salpeter equation (BSE) for practical calculations. Based on various typical approximations, we will introduce the *BSE Hamiltonian* as a matrix in Kohn-Sham (KS) representation, whose diagonalization then allows us to construct the two-particle correlation function L (in the electron-hole time-ordering, see Sec. 2.4).

Throughout this section, indices i, j, k, l run over valence and conduction orbitals, while v only runs over valence- and c only over conduction orbitals. Indices a, b, d, e run over all pairs (v, c) and (c, v) . The same holds for the primed indices like v' .

Transition to Kohn-Sham Representation

We start with the BSE in the GW- and static approximation, Eq. 2.208:

$$L(x_1, x_2, x_{1'}, x_{2'}, \omega) = L_0(x_1, x_2, x_{1'}, x_{2'}, \omega) + \int d(x_3, x_4, x_5, x_6) L_0(x_1, x_4, x_{1'}, x_3, \omega) K(x_3, x_5, x_4, x_6) L(x_6, x_2, x_5, x_{2'}, \omega) \quad (\text{C.1})$$

Using the completeness of the KS orbitals, we can expand the quantities inside the BSE in them¹¹⁷, which we call a transition of the equation from position-spin representation to KS representation (basis change). Let $\{\phi_i\}$ be the set of KS orbitals, forming a complete and orthonormal one-particle basis. Then the set $\{\psi_{i,j}\}$, with

$$\psi_{i,j}(x, y) = \phi_i(x)\phi_j^*(y), \quad (\text{C.2})$$

¹¹⁷ Note that it is not trivially clear that these quantities can be expanded via (tensor products of) the basis functions of $L^2(\mathbb{R}^3) \otimes \mathbb{C}^2$, after all we never examined which function spaces they, for example L , belongs to. We will not go into detail here and simply assume that such an expansion is possible. In fact, we will go a step further and assume that sums over orbitals can be truncated, such that only a finite number of orbitals is needed for a satisfactory expansion such that we can work with finitely-sized matrices and vectors. In particular, we assume that only bound states are needed in the expansion while scattering states can be neglected (compare Appendix A.1.1). This is implicitly assumed throughout this derivation.

forms a complete and orthonormal two-particle basis¹¹⁸ (with i and j running independently over the one-particle basis set), where orthonormality of the two-particle orbitals follows from orthonormality of the KS orbital:

$$\begin{aligned} \int d(x, y) \psi_{i,j}(x, y) \psi_{k,l}^*(x, y) &= \int d(x, y) \phi_i(x) \phi_j^*(y) \phi_k^*(x) \phi_l(y) \\ &= \delta_{i,k} \delta_{j,l} \end{aligned} \quad (\text{C.3})$$

Note also:

$$\begin{aligned} \psi_{i,j}(x, y) &= \phi_i(x) \phi_j^*(y) \\ &= (\phi_j(y) \phi_i^*(x))^* \\ &= \psi_{j,i}^*(y, x) \end{aligned} \quad (\text{C.4})$$

We now start with L , which we write as (the preceding i is motivated by the Lehmann representation Eq. 2.192 of the exact L):

$$L(x_1, x_2, x_{1'}, x_{2'}, \omega) = i \sum_{(i,j),(k,l)} L_{k,l}^{i,j}(\omega) \psi_{i,j}(x_1, x_{1'}) \psi_{k,l}^*(x_{2'}, x_2) \quad (\text{C.5})$$

Next comes the non-interacting electron-hole propagator L_0 , which we write accordingly:

$$L_0(x_1, x_2, x_{1'}, x_{2'}, \omega) = i \sum_{(i,j),(k,l)} L_{k,l}^{i,j}(\omega) \psi_{i,j}(x_1, x_{1'}) \psi_{k,l}^*(x_{2'}, x_2) \quad (\text{C.6})$$

Entering these into the BSE, we get:

$$\begin{aligned} i \sum_{(i,j),(k,l)} L_{k,l}^{i,j}(\omega) \psi_{i,j}(x_1, x_{1'}) \psi_{k,l}^*(x_{2'}, x_2) &= \\ &= i \sum_{(i,j),(k,l)} L_{0,k,l}^{i,j}(\omega) \psi_{i,j}(x_1, x_{1'}) \psi_{k,l}^*(x_{2'}, x_2) \\ &\quad - \int d(x_3, x_4, x_5, x_6) \sum_{(i,j),(k,l)} L_{0,k,l}^{i,j}(\omega) \psi_{i,j}(x_1, x_{1'}) \psi_{k,l}^*(x_3, x_4) \\ &\quad \quad K(x_3, x_5, x_4, x_6) \sum_{(i',j'),(k',l')} L_{k',l'}^{i',j'}(\omega) \psi_{i',j'}(x_6, x_5) \psi_{k',l'}^*(x_{2'}, x_2) \end{aligned} \quad (\text{C.7})$$

Expanding the (static) interaction kernel K as

$$K(x_3, x_5, x_4, x_6) = i \sum_{(i,j),(k,l)} K_{k,l}^{i,j} \psi_{i,j}(x_3, x_4) \psi_{k,l}^*(x_6, x_5) \quad (\text{C.8})$$

and using orthonormality of the two-particle orbitals, we get:

$$\begin{aligned} \sum_{(i,j),(k,l)} L_{k,l}^{i,j}(\omega) \psi_{i,j}(x_1, x_{1'}) \psi_{k,l}^*(x_{2'}, x_2) &= \\ &= \sum_{(i,j),(k,l)} L_{0,k,l}^{i,j}(\omega) \psi_{i,j}(x_1, x_{1'}) \psi_{k,l}^*(x_{2'}, x_2) \\ &\quad - \sum_{(i,j),(k,l)} \sum_{(i',j'),(k',l')} L_{0,k,l}^{i,j}(\omega) K_{i',j'}^{k,l} L_{k',l'}^{i',j'}(\omega) \psi_{i,j}(x_1, x_{1'}) \psi_{k',l'}^*(x_{2'}, x_2) \end{aligned} \quad (\text{C.9})$$

¹¹⁸We mean here that it is a basis of square-normalizable functions of two spin and position indices. This is why antisymmetrization is not relevant here, compare Appendix A.1.2.

Renaming indices, we get:

$$\begin{aligned}
& \sum_{(i,j),(k,l)} L_{k,l}^{i,j}(\omega) \psi_{i,j}(x_1, x_{1'}) \psi_{k,l}^*(x_{2'}, x_2) = \\
& = \sum_{(i,j),(k,l)} L_0^{i,j}(\omega) \psi_{i,j}(x_1, x_{1'}) \psi_{k,l}^*(x_{2'}, x_2) \\
& - \sum_{(i,j),(k,l)} \sum_{(i',j'),(k',l')} L_0^{i,j}(\omega) K_{i',j'}^{k',l'} L_{k,l}^{i',j'}(\omega) \psi_{i,j}(x_1, x_{1'}) \psi_{k,l}^*(x_{2'}, x_2) \quad (C.10)
\end{aligned}$$

Using again that the two-particle orbitals are orthogonal, a comparison of expansion coefficients gives us:

$$L_{k,l}^{i,j}(\omega) = L_0^{i,j}(\omega) - \sum_{(i',j'),(k',l')} L_0^{i,j}(\omega) K_{i',j'}^{k',l'} L_{k,l}^{i',j'}(\omega) \quad (C.11)$$

Alternative Form of BSE

Before continuing, we consider the BSE Eq. C.1 in an alternative form. From Eqs. 2.192 and 2.196 we can see that the exact L and L_0 satisfy the following symmetry relation:

$$\begin{aligned}
L(x_1, x_2, x_{1'}, x_{2'}, \omega) &= L(x_2, x_1, x_{2'}, x_{1'}, -\omega) \\
L_0(x_1, x_2, x_{1'}, x_{2'}, \omega) &= L_0(x_2, x_1, x_{2'}, x_{1'}, -\omega) \quad (C.12)
\end{aligned}$$

Inserting this into Eq. C.1, we find:

$$\begin{aligned}
L(x_2, x_1, x_{2'}, x_{1'}, -\omega) &= L_0(x_2, x_1, x_{2'}, x_{1'}, -\omega) + \int d(x_3, x_4, x_5, x_6) \\
& L_0(x_4, x_1, x_3, x_{1'}, -\omega) K(x_3, x_5, x_4, x_6) L(x_2, x_6, x_{2'}, x_5, -\omega) \quad (C.13)
\end{aligned}$$

Renaming $1 \leftrightarrow 2$ and $-\omega \rightarrow \omega$ to get:

$$\begin{aligned}
L(x_1, x_2, x_{1'}, x_{2'}, \omega) &= L_0(x_1, x_2, x_{1'}, x_{2'}, \omega) + \int d(x_3, x_4, x_5, x_6) \\
& L(x_1, x_6, x_{1'}, x_5, \omega) K(x_3, x_5, x_4, x_6) L_0(x_4, x_2, x_3, x_{2'}, \omega) \quad (C.14)
\end{aligned}$$

Renaming further $4 \leftrightarrow 6$ and $3 \leftrightarrow 5$, we get:

$$\begin{aligned}
L(x_1, x_2, x_{1'}, x_{2'}, \omega) &= L_0(x_1, x_2, x_{1'}, x_{2'}, \omega) + \int d(x_3, x_4, x_5, x_6) \\
& L(x_1, x_4, x_{1'}, x_3, \omega) K(x_5, x_3, x_6, x_4) L_0(x_6, x_2, x_5, x_{2'}, \omega) \\
& = L_0(x_1, x_2, x_{1'}, x_{2'}, \omega) + \int d(x_3, x_4, x_5, x_6) \\
& L(x_1, x_4, x_{1'}, x_3, \omega) K(x_3, x_5, x_4, x_6) L_0(x_6, x_2, x_5, x_{2'}, \omega), \quad (C.15)
\end{aligned}$$

where we used $K(x_5, x_3, x_6, x_4) = K(x_3, x_5, x_4, x_6)$ (compare Eq. 2.207 and use $v(x, y) = v(y, x)$ and $W(x, y) = W(y, x)$, see below). Thus, using the same procedure that lead to Eq. C.11, we get:

$$L_{k,l}^{i,j}(\omega) = L_0^{i,j}{}_{k,l}(\omega) - \sum_{(i',j'),(k',l')} L_{k',l'}^{i,j}(\omega) K_{i',j'}^{k',l'} L_0^{i',j'}{}_{k,l}(\omega) \quad (\text{C.16})$$

We will use this second form of the BSE to simplify the upcoming calculation of L . Our final expression for L , Eq. C.89, again satisfies Eq. C.12 (as does the approximated form of L_0 we use below, Eq. C.17).

Eliminating (v, v) and (c, c) Contributions

We continue by examining L_0 in more details. Expressing G_1 in a quasiparticle-approximation-like form (compare Eq. 2.167) but with KS wave functions $\{\phi_i\}$ instead of quasiparticle (QP) wave functions and neglecting the finite imaginary part¹¹⁹ of the QP energies $\{\varepsilon_i^{QP}\}$ and setting the QP renormalization factors to 1¹²⁰, we find (compare Eq. 2.196, which is based on the exact G_1) [36, 118]:

$$\begin{aligned} L_0(x_1, x_2, x_{1'}, x_{2'}, \omega) &= i \sum_{v,c} \frac{\phi_c(x_1) \phi_v(x_2) \phi_v^*(x_{1'}) \phi_c^*(x_{2'})}{\omega - (\varepsilon_c^{QP} - \varepsilon_v^{QP}) + i\eta} \\ &\quad - \frac{\phi_v(x_1) \phi_c(x_2) \phi_c^*(x_{1'}) \phi_v^*(x_{2'})}{\omega + (\varepsilon_c^{QP} - \varepsilon_v^{QP}) - i\eta} \\ &= i \sum_{(v,c)} \frac{\psi_{c,v}(x_1, x_{1'}) \psi_{c,v}^*(x_{2'}, x_2)}{\omega - (\varepsilon_c^{QP} - \varepsilon_v^{QP}) + i\eta} \\ &\quad - \frac{\psi_{v,c}(x_1, x_{1'}) \psi_{v,c}^*(x_{2'}, x_2)}{\omega + (\varepsilon_c^{QP} - \varepsilon_v^{QP}) - i\eta} \end{aligned} \quad (\text{C.17})$$

Comparing with Eq. C.6, we find that $L_0^{i,j}{}_{k,l}(\omega) = 0$ except for:

$$\begin{aligned} L_0^{v,c}{}_{v,c}(\omega) &= \frac{-1}{\omega + (\varepsilon_c^{QP} - \varepsilon_v^{QP}) - i\eta} \\ L_0^{c,v}{}_{c,v}(\omega) &= \frac{1}{\omega - (\varepsilon_c^{QP} - \varepsilon_v^{QP}) + i\eta} \end{aligned} \quad (\text{C.18})$$

From Eq. C.11 we then find

$$L_{k,l}^{v,v'}(\omega) = L_0^{v,v'}{}_{k,l}(\omega) - \sum_{(i',j'),(k',l')} L_0^{v,v'}{}_{k',l'}(\omega) K_{i',j'}^{k',l'} L_{k,l}^{i',j'}(\omega) = 0, \quad (\text{C.19})$$

and similarly:

$$L_{k,l}^{c,c'}(\omega) = 0 \quad (\text{C.20})$$

Using Eq. C.16 we additionally get:

$$\begin{aligned} L_{v,v'}^{i,j}(\omega) &= 0 \\ L_{c,c'}^{i,j}(\omega) &= 0 \end{aligned} \quad (\text{C.21})$$

¹¹⁹This is needed for R to be Hermitian, see Eq. C.39.

¹²⁰See Ref. [112] for the interplay of the renormalization factors and the frequency-dependence of W in the BSE kernel.

We can thus restrict index pairs in Eq. C.11 to combinations (v, c) and (c, v) , thus writing the BSE as

$$L_b^a(\omega) = L_0^a{}_b(\omega) - \sum_{d,e} L_0^a{}_e(\omega) K_d^e L_b^d(\omega), \quad (\text{C.22})$$

where the indices appearing in the equation are the combinations (v, c) and (c, v) , flattened into a single index. Before continuing, note that the (v, v) and (c, c) sector is not present in L_0 as a consequence of how the quasiparticle states have been constructed in Eq. 2.174, where we did not include quasiholes in conduction orbitals and quasielectrons in valence orbitals.

For convenience, we now express Eq. C.22 as a matrix equation. For a generic matrix A , we introduce the (block matrix) notation:

$$A = \left(\begin{array}{c|cc} & (v', c') & (c', v') \\ \hline (v, c) & A_{v',c'}^{v,c} & A_{c',v'}^{v,c} \\ (c, v) & A_{v',c'}^{c,v} & A_{c',v'}^{c,v} \end{array} \right) \quad (\text{C.23})$$

Note that the upper index thus is the row-index and the lower one the column-index. We leave the order of rows in the $\{(v, c)\}$ sector arbitrary, however, demand that the $\{(c, v)\}$ sector is ordered accordingly. That is, if (v_m, c_n) is the p -th element in the ordered set $\{(v, c)\}$ (p -th row), then (c_n, v_m) is the p -th element in the ordered set $\{(c, v)\}$ ($N+p$ -th row; N is defined below). This will become useful later. Additionally, we demand the same order for the columns (primed indices), as is used for the rows (this is needed to write the BSE via matrix products). The BSE then becomes:

$$L(\omega) = L_0(\omega) - L_0(\omega) K L(\omega), \quad (\text{C.24})$$

where $L(\omega)$, $L_0(\omega)$ and K are $2N \times 2N$ matrices, with $N = N_v N_c$ (where $N_{v/c}$ is the number of valence/conduction orbitals).

For later use, we also introduce notation for (block) column vectors (with rows ordered as before):

$$\begin{pmatrix} A \\ B \end{pmatrix} = \left(\begin{array}{c|c} (v, c) & A^{v,c} \\ \hline (c, v) & B^{v,c} \end{array} \right) \quad (\text{C.25})$$

And for row vectors (with columns ordered as before):

$$(A \ B) = \left(\begin{array}{cc|c} (v, c) & (c, v) \\ \hline A_{v,c} & B_{v,c} \end{array} \right) \quad (\text{C.26})$$

N Matrix

Continuing from Eq. C.24, we can rewrite the BSE as:

$$\begin{aligned} M(\omega) &= \mathbb{1}_{2N} + L_0(\omega) K \\ M(\omega) L(\omega) &= L_0(\omega) \end{aligned} \quad (\text{C.27})$$

Since $L_0(\omega)$ is invertible (see below), also $M(\omega)$ and $L(\omega)$ are (thus also $N(\omega)$, see below), and we get further:

$$L(\omega) = M^{-1}(\omega) L_0(\omega) \quad (\text{C.28})$$

Using that for matrices A and B , we have $(AB)^{-1} = B^{-1}A^{-1}$, we get:

$$L(\omega) = N^{-1}(\omega), \quad (\text{C.29})$$

with:

$$\begin{aligned} N(\omega) &= L_0^{-1}(\omega)M(\omega) \\ &= L_0^{-1}(\omega) [\mathbb{1}_{2N} + L_0(\omega)K] \\ &= L_0^{-1}(\omega) + K \end{aligned} \quad (\text{C.30})$$

Note that N is simply the inverse of L , $N(\omega) = L^{-1}(\omega)$. Thus, if we can determine and invert N , we find L .

Matrix Elements of N

To understand how to invert N , let us first examine L_0^{-1} and K in more detail. Using the notation Eq. C.23, we can see that L_0 is a diagonal matrix with diagonal elements given by Eq. C.18. It can thus trivially be inverted, with L_0^{-1} being a diagonal matrix with entries:

$$\begin{aligned} L_0^{-1}{}^{v,c}{}_{v,c}(\omega) &= -[\omega + (\varepsilon_c^{QP} - \varepsilon_v^{QP}) - i\eta] \\ L_0^{-1}{}^{c,v}{}_{c,v}(\omega) &= \omega - (\varepsilon_c^{QP} - \varepsilon_v^{QP}) + i\eta \end{aligned} \quad (\text{C.31})$$

For K , we use the decomposition Eq. 2.207 and the definition Eq. C.8 of the matrix elements, to find:

$$\begin{aligned} K_{k,l}^{i,j} &= -i \int d(x_3, x_4, x_5, x_6) K(x_3, x_5, x_4, x_6) \psi_{i,j}^*(x_3, x_4) \psi_{k,l}(x_6, x_5) \\ &= - \int d(x_3, x_4, x_5, x_6) \delta(x_3, x_4) \delta(x_5, x_6) v(x_3, x_6) \psi_{i,j}^*(x_3, x_4) \psi_{k,l}(x_6, x_5) \\ &\quad + \int d(x_3, x_4, x_5, x_6) \delta(x_3, x_6) \delta(x_4, x_5) W(x_3, x_4) \psi_{i,j}^*(x_3, x_4) \psi_{k,l}(x_6, x_5) \\ &= - \int d(x_3, x_4) v(x_3, x_4) \psi_{i,j}^*(x_3, x_3) \psi_{k,l}(x_4, x_4) \\ &\quad + \int d(x_3, x_4) W(x_3, x_4) \psi_{i,j}^*(x_3, x_4) \psi_{k,l}(x_3, x_4) \\ &= -V_{k,l}^{i,j} + W_{k,l}^{i,j}, \end{aligned} \quad (\text{C.32})$$

where we defined:

$$\begin{aligned} V_{k,l}^{i,j} &\equiv \int d(x_3, x_4) v(x_3, x_4) \psi_{i,j}^*(x_3, x_3) \psi_{k,l}(x_4, x_4) \\ W_{k,l}^{i,j} &\equiv \int d(x_3, x_4) W(x_3, x_4) \psi_{i,j}^*(x_3, x_4) \psi_{k,l}(x_3, x_4) \end{aligned} \quad (\text{C.33})$$

Putting everything together, N becomes (showing the four sectors individually):

$$\begin{aligned} N_{v',c'}^{v,c}(\omega) &= [L_0^{-1}(\omega)]_{v',c'}^{v,c} + K_{v',c'}^{v,c} \\ &= -[\omega + (\varepsilon_c^{QP} - \varepsilon_v^{QP}) - i\eta] \delta_v^v \delta_{c'}^c - V_{v',c'}^{v,c} + W_{v',c'}^{v,c} \\ N_{c',v'}^{v,c} &= -V_{c',v'}^{v,c} + W_{c',v'}^{v,c} \\ N_{v',c'}^{c,v} &= -V_{v',c'}^{c,v} + W_{v',c'}^{c,v} \\ N_{c',v'}^{c,v}(\omega) &= [\omega - (\varepsilon_c^{QP} - \varepsilon_v^{QP}) + i\eta] \delta_v^v \delta_{c'}^c - V_{c',v'}^{c,v} + W_{c',v'}^{c,v} \end{aligned} \quad (\text{C.34})$$

Properties of V and W

Using $v(x, y) = v(y, x)$ and $W(x, y) = W(y, x)$ (see Appendix C.2), we find:

$$\begin{aligned}
V_{k,l}^{i,j} &= \int d(x_3, x_4) v(x_3, x_4) \psi_{i,j}^*(x_3, x_3) \psi_{k,l}(x_4, x_4) \\
&= \int d(x_3, x_4) v(x_3, x_4) \psi_{i,j}^*(x_4, x_4) \psi_{k,l}(x_3, x_3) \\
&= \int d(x_3, x_4) v(x_3, x_4) \psi_{l,k}^*(x_3, x_3) \psi_{j,i}(x_4, x_4) \\
&= V_{j,i}^{l,k} \\
W_{k,l}^{i,j} &= \int d(x_3, x_4) W(x_3, x_4) \psi_{i,j}^*(x_3, x_4) \psi_{k,l}(x_3, x_4) \\
&= \int d(x_3, x_4) W(x_3, x_4) \psi_{i,j}^*(x_4, x_3) \psi_{k,l}(x_4, x_3) \\
&= \int d(x_3, x_4) W(x_3, x_4) \psi_{l,k}^*(x_3, x_4) \psi_{j,i}(x_3, x_4) \\
&= W_{j,i}^{l,k}
\end{aligned} \tag{C.35}$$

Using that $v(x, y)$ and $W(x, y)$ are real (see Appendix C.2), we additionally get:

$$\begin{aligned}
(V^*)_{k,l}^{i,j} &\equiv (V_{k,l}^{i,j})^* = \int d(x_3, x_4) v(x_3, x_4) \psi_{i,j}(x_3, x_3) \psi_{k,l}^*(x_4, x_4) \\
&= \int d(x_3, x_4) v(x_3, x_4) \psi_{j,i}^*(x_3, x_3) \psi_{l,k}(x_4, x_4) \\
&= V_{l,k}^{j,i} \\
(W^*)_{k,l}^{i,j} &\equiv (W_{k,l}^{i,j})^* = \int d(x_3, x_4) W(x_3, x_4) \psi_{i,j}(x_3, x_4) \psi_{k,l}^*(x_3, x_4) \\
&= \int d(x_3, x_4) W(x_3, x_4) \psi_{k,l}^*(x_3, x_4) \psi_{i,j}(x_3, x_4) \\
&= W_{i,j}^{k,l} \\
&= W_{l,k}^{j,i}
\end{aligned} \tag{C.36}$$

Resonant Matrix and Coupling Matrix

For later use, we now define the matrices R and C . In analogy to the notation Eq. C.23 used for L , K , etc., we define smaller matrices over combinations (v, c) and (v', c') only (upper-left block in Eq. C.23) as:

$$A = \left(\begin{array}{c|c} & (v', c') \\ \hline (v, c) & A_{v',c'}^{v,c} \end{array} \right) \tag{C.37}$$

Rows and columns are defined to be ordered in the same way as in (the upper-left block of) Eq. C.23. Using this notation, we define the *resonant matrix* R as:

$$R_{v',c'}^{v,c} = (\varepsilon_c^{QP} - \varepsilon_v^{QP}) \delta_{v'}^v \delta_{c'}^c + V_{c',v'}^{c,v} - W_{c',v'}^{c,v} \tag{C.38}$$

Note that R is an Hermitian matrix (using that QP energies are assumed to be real, that is, their imaginary parts are neglected):

$$\begin{aligned}
(R^*)_{v',c'}^{v,c} &\equiv (R_{v',c'}^{v,c})^* \\
&= (\varepsilon_c^{QP} - \varepsilon_v^{QP}) \delta_v^c \delta_{c'}^c + V_{v',c'}^{v,c} - W_{v',c'}^{v,c} \\
&= (\varepsilon_c^{QP} - \varepsilon_v^{QP}) \delta_v^c \delta_{c'}^c + V_{c,v}^{c',v'} - W_{c,v}^{c',v'} \\
&= R_{v,c}^{v',c'}
\end{aligned} \tag{C.39}$$

Similarly, we define the *coupling matrix* C via:

$$C_{v',c'}^{v,c} = V_{v',c'}^{c,v} - W_{v',c'}^{c,v} \tag{C.40}$$

Note that C is not Hermitian,

$$\begin{aligned}
(C^*)_{v',c'}^{v,c} &\equiv (C_{v',c'}^{v,c})^* \\
&= V_{c',v'}^{v,c} - W_{c',v'}^{v,c} \\
&\neq C_{v,c}^{v',c'} ,
\end{aligned} \tag{C.41}$$

but instead a complex symmetric matrix:

$$\begin{aligned}
C_{v',c'}^{v,c} &= V_{v',c'}^{c,v} - W_{v',c'}^{c,v} \\
&= V_{v,c}^{c',v'} - W_{v,c}^{c',v'} \\
&= C_{v,c}^{v',c'}
\end{aligned} \tag{C.42}$$

BSE Hamiltonian

Using R and C , we then write N as¹²¹:

$$N(\omega) = \begin{pmatrix} -(\omega - i\eta) \mathbb{1}_N - R^* & -C^* \\ -C & (\omega + i\eta) \mathbb{1}_N - R \end{pmatrix}, \tag{C.43}$$

or explicitly:

$$\begin{aligned}
[N(\omega)]_{v',c'}^{v,c} &= -[\omega + (\varepsilon_c^{QP} - \varepsilon_v^{QP}) - i\eta] \delta_v^c \delta_{c'}^c - V_{v',c'}^{v,c} + W_{v',c'}^{v,c} \\
&= -(\omega - i\eta) \delta_v^c \delta_{c'}^c - (R^*)_{v',c'}^{v,c} \\
[N(\omega)]_{c',v'}^{v,c} &= -V_{c',v'}^{v,c} + W_{c',v'}^{v,c} \\
&= -(C^*)_{v',c'}^{v,c} \\
[N(\omega)]_{v',c'}^{c,v} &= -V_{v',c'}^{c,v} + W_{v',c'}^{c,v} \\
&= -C_{v',c'}^{v,c} \\
[N(\omega)]_{c',v'}^{c,v} &= [\omega - (\varepsilon_c^{QP} - \varepsilon_v^{QP}) + i\eta] \delta_v^c \delta_{c'}^c - V_{c',v'}^{c,v} + W_{c',v'}^{c,v} \\
&= (\omega + i\eta) \delta_v^c \delta_{c'}^c - R_{v',c'}^{v,c}
\end{aligned} \tag{C.44}$$

We now define the *BSE Hamiltonian* (matrix) H as

$$H = \begin{pmatrix} R & C \\ -C^* & -R^* \end{pmatrix}, \tag{C.45}$$

¹²¹Note that this compact notation is only possible due to the way rows and columns are ordered in Eqs. C.23 and C.37.

or explicitly:

$$\begin{aligned}
H_{v',c'}^{v,c} &= R_{v',c'}^{v,c} \\
H_{c',v'}^{v,c} &= C_{v',c'}^{v,c} \\
H_{v',c'}^{c,v} &= -(C^*)_{v',c'}^{v,c} \\
H_{c',v'}^{c,v} &= -(R^*)_{v',c'}^{v,c}
\end{aligned} \tag{C.46}$$

Additionally, we define the infinitesimal matrix

$$H' = \begin{pmatrix} -i\eta \mathbb{1}_N & 0 \\ 0 & i\eta \mathbb{1}_N \end{pmatrix}, \tag{C.47}$$

or explicitly:

$$\begin{aligned}
H_{v',c'}^{v,c} &= -i\eta \delta_{v'}^v \delta_{c'}^c \\
H_{c',v'}^{v,c} &= 0 \\
H_{v',c'}^{c,v} &= 0 \\
H_{c',v'}^{c,v} &= i\eta \delta_{v'}^v \delta_{c'}^c
\end{aligned} \tag{C.48}$$

We then find:

$$\begin{aligned}
[N(\omega)]_{v',c'}^{v,c} &= -\omega \delta_{v'}^v \delta_{c'}^c + H_{c',v'}^{c,v} + H_{c',v'}^{c,v} \\
[N(\omega)]_{c',v'}^{v,c} &= H_{v',c'}^{c,v} \\
[N(\omega)]_{v',c'}^{c,v} &= -H_{c',v'}^{v,c} \\
[N(\omega)]_{c',v'}^{c,v} &= \omega \delta_{v'}^v \delta_{c'}^c - H_{v',c'}^{v,c} - H_{v',c'}^{v,c}
\end{aligned} \tag{C.49}$$

Thus (which can be easily checked using block-matrix multiplication):

$$N(\omega) = \begin{pmatrix} 0 & -\mathbb{1}_N \\ \mathbb{1}_N & 0 \end{pmatrix} [\omega \mathbb{1}_{2N} - (H + H')] \begin{pmatrix} 0 & \mathbb{1}_N \\ \mathbb{1}_N & 0 \end{pmatrix} \tag{C.50}$$

Explicitly:

$$N_b^a(\omega) = \sum_{d,e} \begin{pmatrix} 0 & -\mathbb{1}_N \\ \mathbb{1}_N & 0 \end{pmatrix}_d^a [\omega \mathbb{1}_{2N} - (H + H')]_e^d \begin{pmatrix} 0 & \mathbb{1}_N \\ \mathbb{1}_N & 0 \end{pmatrix}_b^e \tag{C.51}$$

For example¹²²:

$$\begin{aligned}
N_{v',c'}^{v,c}(\omega) &= \sum_{d,e} \begin{pmatrix} 0 & -\mathbb{1}_N \\ \mathbb{1}_N & 0 \end{pmatrix}_{d,e}^{v,c} [\omega \mathbb{1}_{2N} - (H + H')]_e^d \begin{pmatrix} 0 & \mathbb{1}_N \\ \mathbb{1}_N & 0 \end{pmatrix}_{v',c'}^e \\
&= \sum_{(c'',v''),e} -\delta_{v''}^v \delta_{c''}^c [\omega \mathbb{1}_{2N} - (H + H')]_e^{c'',v''} \begin{pmatrix} 0 & \mathbb{1}_N \\ \mathbb{1}_N & 0 \end{pmatrix}_{v',c'}^e \\
&= \sum_e -[\omega \mathbb{1}_{2N} - (H + H')]_e^{c,v} \begin{pmatrix} 0 & \mathbb{1}_N \\ \mathbb{1}_N & 0 \end{pmatrix}_{v',c'}^e \\
&= \sum_{(c'',v'')} -[\omega \mathbb{1}_{2N} - (H + H')]_{c'',v''}^{c,v} \delta_{v''}^{v'} \delta_{c''}^{c'} \\
&= -[\omega \mathbb{1}_{2N} - (H + H')]_{c',v'}^{c,v} \\
&= -\omega \delta_{v'}^v \delta_{c'}^c + H_{c',v'}^{c,v} + H_{c',v'}'^{c,v} \\
&= -\omega \delta_{v'}^v \delta_{c'}^c - (R^*)_{v',c'}^{v,c} + i\eta \delta_{v'}^v \delta_{c'}^c \\
&= -(\omega - i\eta) \delta_{v'}^v \delta_{c'}^c - (R^*)_{v',c'}^{v,c}
\end{aligned} \tag{C.52}$$

Using $(ABC)^{-1} = C^{-1}B^{-1}A^{-1}$ (and that $N(\omega)$ is invertible), we then find L :

$$L(\omega) = \begin{pmatrix} 0 & \mathbb{1}_N \\ \mathbb{1}_N & 0 \end{pmatrix} [\omega \mathbb{1}_{2N} - (H + H')]^{-1} \begin{pmatrix} 0 & \mathbb{1}_N \\ -\mathbb{1}_N & 0 \end{pmatrix} \tag{C.53}$$

We will now focus on H (and H'). Diagonalization of H will allow us to invert $\omega \mathbb{1}_{2N} - (H + H')$ and thus find $L(\omega)$. Note H (as H') is independent of ω , so we only need to diagonalize a single matrix to obtain $L(\omega)$ for any ω (within the approximations made throughout this derivation).

Spectrum of the BSE Hamiltonian

First, note that eigenvalues of H occur in pairs. To see what we mean by this, we begin with:

$$H^* = \begin{pmatrix} R^* & C^* \\ -C & -R \end{pmatrix} \tag{C.54}$$

Defining the matrix

$$\zeta = \begin{pmatrix} 0 & \mathbb{1}_N \\ \mathbb{1}_N & 0 \end{pmatrix}, \tag{C.55}$$

we find

$$\zeta = \zeta^{-1} \tag{C.56}$$

¹²²We utilize here the order of rows and columns used in Eq. C.23, which gives us $\begin{pmatrix} 0 & -\mathbb{1}_N \\ \mathbb{1}_N & 0 \end{pmatrix}_{v',c'}^{v,c} = 0$, $\begin{pmatrix} 0 & -\mathbb{1}_N \\ \mathbb{1}_N & 0 \end{pmatrix}_{c',v'}^{v,c} = -\delta_{v'}^v \delta_{c'}^c$, $\begin{pmatrix} 0 & -\mathbb{1}_N \\ \mathbb{1}_N & 0 \end{pmatrix}_{v',c'}^{c,v} = \delta_{v'}^v \delta_{c'}^c$ and $\begin{pmatrix} 0 & -\mathbb{1}_N \\ \mathbb{1}_N & 0 \end{pmatrix}_{c',v'}^{c,v} = 0$.

and

$$\zeta H^* \zeta = -H. \quad (\text{C.57})$$

Thus, if Ω_m and $\begin{pmatrix} X_m \\ Y_m \end{pmatrix}$ are an eigenvalue and corresponding right eigenvector¹²³ of H , then it is trivial to show that $-\Omega_m^*$ is also an eigenvalue and $\begin{pmatrix} Y_m^* \\ X_m^* \end{pmatrix}$ is the corresponding right eigenvector! That is, if

$$H \begin{pmatrix} X_m \\ Y_m \end{pmatrix} = \Omega_m \begin{pmatrix} X_m \\ Y_m \end{pmatrix}, \quad (\text{C.58})$$

then

$$H \begin{pmatrix} Y_m^* \\ X_m^* \end{pmatrix} = -\Omega_m^* \begin{pmatrix} Y_m^* \\ X_m^* \end{pmatrix}. \quad (\text{C.59})$$

Additionally, complex eigenvalues in fact occur in quadruples. To see, this, we use the complex symmetry $C = C^T$ and the Hermiticity $R = R^\dagger$ to find:

$$H^\dagger = \begin{pmatrix} R & -C \\ C^* & -R^* \end{pmatrix} \quad (\text{C.60})$$

Defining

$$\gamma \equiv \begin{pmatrix} \mathbb{1}_N & 0 \\ 0 & -\mathbb{1}_N \end{pmatrix} = \gamma^{-1}, \quad (\text{C.61})$$

we find:

$$H = \gamma^{-1} H^\dagger \gamma \quad (\text{C.62})$$

Thus, H is pseudo-Hermitian (compare Ref. [202]) and we find as a result – which is again trivial to show – that if Ω_m is an eigenvalue with right eigenvector $\begin{pmatrix} X_m \\ Y_m \end{pmatrix}$, then Ω_m^* is also an eigenvalue, with left eigenvector $(X_m^\dagger \quad -Y_m^\dagger)$! That is, if

$$H \begin{pmatrix} X_m \\ Y_m \end{pmatrix} = \Omega_m \begin{pmatrix} X_m \\ Y_m \end{pmatrix}, \quad (\text{C.63})$$

then

$$(X_m^\dagger \quad -Y_m^\dagger) H = \Omega_m^* (X_m^\dagger \quad -Y_m^\dagger), \quad (\text{C.64})$$

or, equivalently:

$$H^\dagger \begin{pmatrix} X_m \\ -Y_m \end{pmatrix} = \Omega_m \begin{pmatrix} X_m \\ -Y_m \end{pmatrix} \quad (\text{C.65})$$

¹²³Where $\begin{pmatrix} X_m \\ Y_m \end{pmatrix}$ denotes a column vector in the block notation of Eq. C.25.

To summarize, the eigenvalues of H thus appear in purely real and/or purely imaginary pairs $\{\Omega_m, -\Omega_m\}$ and/or in complex quadruples $\{\Omega_m, -\Omega_m, \Omega_m^*, -\Omega_m^*\}$ [203]. Importantly, for most physical systems, the spectrum of H is purely real [203, 204] (see below), which we will assume from now on. For a real eigenvalue Ω_m , we then find for the left and right eigenvectors at $\pm\Omega_m$ (in the last line, the overall sign was chosen in accordance with the next step):

$$\begin{aligned} H \begin{pmatrix} X_m \\ Y_m \end{pmatrix} &= \Omega_m \begin{pmatrix} X_m \\ Y_m \end{pmatrix} \\ (X_m^\dagger \quad -Y_m^\dagger) H &= \Omega_m (X_m^\dagger \quad -Y_m^\dagger) \\ H \begin{pmatrix} Y_m^* \\ X_m^* \end{pmatrix} &= -\Omega_m \begin{pmatrix} Y_m^* \\ X_m^* \end{pmatrix} \\ (-Y_m^T \quad X_m^T) H &= -\Omega_m (-Y_m^T \quad X_m^T) \end{aligned} \quad (\text{C.66})$$

Eigendecomposition of the BSE Hamiltonian

Note that the matrix γH is trivially Hermitian based on Eqs. C.62 and C.61. Assuming additionally, that γH is positive definite, which it is for most physical systems, H 's spectrum becomes real (which was already used above) and H becomes diagonalizable [204, 205]. It can then be written as (compare Theorem 1 in Ref. [204] and express the matrix-multiplication as shown below via column- and row-vectors):

$$H = \sum_{m=1}^{2N} \Omega_m R_m L_m^\dagger, \quad (\text{C.67})$$

with positive¹²⁴ eigenvalues and eigenvectors

$$\begin{aligned} \Omega_1 &\geq \Omega_2 \geq \dots \geq \Omega_N > 0 \\ R_m &= \begin{pmatrix} X_m \\ Y_m \end{pmatrix}, \quad m = 1 \dots N \\ L_m^\dagger &= (X_m^\dagger \quad -Y_m^\dagger), \quad m = 1 \dots N, \end{aligned} \quad (\text{C.68})$$

negative eigenvalues and eigenvectors

$$\begin{aligned} \Omega_{N+m} &= -\Omega_m < 0, \quad m = 1 \dots N \\ R_{N+m} &= \begin{pmatrix} Y_m^* \\ X_m^* \end{pmatrix}, \quad m = 1 \dots N \\ L_{N+m}^\dagger &= (-Y_m^T \quad X_m^T), \quad m = 1 \dots N, \end{aligned} \quad (\text{C.69})$$

and the orthonormalization

$$L_i^\dagger R_j = \delta_{i,j}, \quad (\text{C.70})$$

which further leads to:

$$L_m^\dagger R_m = L_{N+m}^\dagger R_{N+m} = \sum_{(v,c)} |X_m^{v,c}|^2 - \sum_{(v,c)} |Y_m^{v,c}|^2 = 1, \quad m = 1 \dots N \quad (\text{C.71})$$

¹²⁴Note that the eigenvalues are strictly positive, which is in line with the ground-state contribution being eliminated in L (compared to G_2) – compare comments around Eq. 2.192.

Importantly for later, unity (i.e. the identity matrix) can be written as:

$$\mathbb{1}_{2N} = \sum_{m=1}^{2N} R_m L_m^\dagger \quad (\text{C.72})$$

Infinitesimal Shifts

We now include the infinitesimal matrix of Eq. C.47 ($\eta > 0$, infinitesimal),

$$H' = \begin{pmatrix} -i\eta \mathbb{1}_N & 0 \\ 0 & i\eta \mathbb{1}_N \end{pmatrix}, \quad (\text{C.73})$$

as a perturbation by correcting BSE eigenvalues in first-order perturbation theory while leaving eigenvectors unchanged¹²⁵. As we will see, this will result in the infinitesimal imaginary shifts already known from Eq. 2.192.

Let us first treat the case of a nondegenerate eigenvalue Ω_m . The first-order correction to the eigenvalue is then given by [206]:

$$\Delta\Omega_m = L_m^\dagger \begin{pmatrix} -i\eta \mathbb{1}_N & 0 \\ 0 & i\eta \mathbb{1}_N \end{pmatrix} R_m \quad (\text{C.74})$$

If $\Omega_m > 0$, i.e. $1 \leq m \leq N$, we find:

$$\begin{aligned} \Delta\Omega_m &= (X_m^\dagger \quad -Y_m^\dagger) \begin{pmatrix} -i\eta \mathbb{1}_N & 0 \\ 0 & i\eta \mathbb{1}_N \end{pmatrix} \begin{pmatrix} X_m \\ Y_m \end{pmatrix} \\ &= -i\eta \sum_{(v,c)} |X_m^{v,c}|^2 + |Y_m^{v,c}|^2 \end{aligned} \quad (\text{C.75})$$

For the case of a negative eigenvalue $\Omega_{N+m} < 0$ ($1 \leq m \leq N$) we conversely find:

$$\begin{aligned} \Delta\Omega_m &= (-Y_m^T \quad X_m^T) \begin{pmatrix} -i\eta \mathbb{1}_N & 0 \\ 0 & i\eta \mathbb{1}_N \end{pmatrix} \begin{pmatrix} Y_m^* \\ X_m^* \end{pmatrix} \\ &= i\eta \sum_{(v,c)} |X_m^{v,c}|^2 + |Y_m^{v,c}|^2 \end{aligned} \quad (\text{C.76})$$

In the degenerate case, we can follow the approach presented in Ref. [38] (which is shown there for the Hermitian case, but should conceptually transfer to the non-Hermitian situation presented here), where one needs to determine the *good* linear combinations of the degenerate eigenvectors. Whatever the good linear combinations are – we do not need to know them for the argument presented here – the corresponding change in the eigenvalue will be of the form $-i\delta^+$ ($\delta^+ > 0$, infinitesimal) for positive eigenvalues and $i\delta^+$ for negative eigenvalues (To see this, just create a linear combination of right eigenvectors and – via complex conjugated coefficients – the corresponding conjugate-transposed left eigenvector (with proper normalization), which can both simply be written via the corresponding linear combinations of $\{X_m\}$ and $\{Y_m\}$, and use Eq. C.74.).

Thus, we have found that all positive eigenvalues are shifted infinitesimally into the lower complex half and all negative eigenvalues are shifted infinitesimally into the upper complex half (compare Eq. 2.192). We will re-use η below to signify an infinitesimal positive shift.

¹²⁵We only correct eigenvalues, since adding an (albeit infinitesimal) imaginary part (see below) to an otherwise real eigenvalue is a relevant change, while corrections to the eigenvectors would only – via complex, infinitesimal coefficients – mix the already generally complex eigenvectors.

L expressed in BSE eigenvectors

Remember now, that our initial goal was to calculate L , for which we found in Eq. C.53:

$$L(\omega) = \begin{pmatrix} 0 & \mathbb{1}_N \\ \mathbb{1}_N & 0 \end{pmatrix} [\omega \mathbb{1}_{2N} - (H + H')]^{-1} \begin{pmatrix} 0 & \mathbb{1}_N \\ -\mathbb{1}_N & 0 \end{pmatrix} \quad (\text{C.77})$$

We have diagonalized $H + H'$ by first diagonalizing H and then including the second matrix perturbatively, thus giving us:

$$H + H' = \sum_{m=1}^N (\Omega_m - i\eta) R_m L_m^\dagger + \sum_{m=N+1}^{2N} (\Omega_m + i\eta) R_m L_m^\dagger \quad (\text{C.78})$$

Using Eq. C.72, we find:

$$\omega \mathbb{1}_{2N} - (H + H') = \sum_{m=1}^N (\omega - \Omega_m + i\eta) R_m L_m^\dagger + \sum_{m=N+1}^{2N} (\omega - \Omega_m - i\eta) R_m L_m^\dagger \quad (\text{C.79})$$

Based on the orthonormality Eq. C.70, we find the inverse as:

$$[\omega \mathbb{1}_{2N} - (H + H')]^{-1} = \sum_{m=1}^N \frac{1}{\omega - \Omega_m + i\eta} R_m L_m^\dagger + \sum_{m=N+1}^{2N} \frac{1}{\omega - \Omega_m - i\eta} R_m L_m^\dagger \quad (\text{C.80})$$

Inserting the structure of the eigenvalues and corresponding left and right eigenvectors, this becomes:

$$\begin{aligned} [\omega \mathbb{1}_{2N} - (H + H')]^{-1} &= \sum_{m=1}^N \frac{1}{\omega - \Omega_m + i\eta} \begin{pmatrix} X_m \\ Y_m \end{pmatrix} (X_m^\dagger \quad -Y_m^\dagger) \\ &\quad + \sum_{m=1}^N \frac{1}{\omega + \Omega_m - i\eta} \begin{pmatrix} Y_m^* \\ X_m^* \end{pmatrix} (-Y_m^T \quad X_m^T) \end{aligned} \quad (\text{C.81})$$

Finally, we get L :

$$\begin{aligned} L(\omega) &= \begin{pmatrix} 0 & \mathbb{1}_N \\ \mathbb{1}_N & 0 \end{pmatrix} [\omega \mathbb{1}_{2N} - (H + H')]^{-1} \begin{pmatrix} 0 & \mathbb{1}_N \\ -\mathbb{1}_N & 0 \end{pmatrix} \\ &= \sum_{m=1}^N \frac{1}{\omega - \Omega_m + i\eta} \begin{pmatrix} Y_m \\ X_m \end{pmatrix} (Y_m^\dagger \quad X_m^\dagger) - \sum_{m=1}^N \frac{1}{\omega + \Omega_m - i\eta} \begin{pmatrix} X_m^* \\ Y_m^* \end{pmatrix} (X_m^T \quad Y_m^T) \end{aligned} \quad (\text{C.82})$$

Or, in coordinates:

$$\begin{aligned} L_b^a(\omega) &= \sum_{m=1}^N \frac{1}{\omega - \Omega_m + i\eta} \begin{pmatrix} Y_m \\ X_m \end{pmatrix}^a (Y_m^\dagger \quad X_m^\dagger)_b \\ &\quad - \sum_{m=1}^N \frac{1}{\omega + \Omega_m - i\eta} \begin{pmatrix} X_m^* \\ Y_m^* \end{pmatrix}^a (X_m^T \quad Y_m^T)_b, \end{aligned} \quad (\text{C.83})$$

where a and b both run independently over all pairs (v, c) and (c, v) .

L in Position-Spin Representation

We now express L in terms of positions and spins again by using Eq. C.5:

$$L(x_1, x_2, x_{1'}, x_{2'}, \omega) = i \sum_{(i,j),(k,l)} L_{k,l}^{i,j}(\omega) \psi_{i,j}(x_1, x_{1'}) \psi_{k,l}^*(x_{2'}, x_2) \quad (\text{C.84})$$

As mentioned before, this can be written as:

$$L(x_1, x_2, x_{1'}, x_{2'}, \omega) = i \sum_{a,b} L_b^a(\omega) \psi_a(x_1, x_{1'}) \psi_b^*(x_{2'}, x_2), \quad (\text{C.85})$$

where a and b both run over all pairs (v, c) and (c, v) . Here, $L_b^a(\omega)$ is then the element in row a and column b of the matrix $L(\omega)$, as defined via Eq. C.23. Inserting Eq. C.83, we get:

$$\begin{aligned} L(x_1, x_2, x_{1'}, x_{2'}, \omega) = & i \sum_{m=1}^N \frac{1}{\omega - \Omega_m + i\eta} \left[\sum_a \begin{pmatrix} Y_m \\ X_m \end{pmatrix}^a \psi_a(x_1, x_{1'}) \right] \\ & \left[\sum_b \begin{pmatrix} Y_m^\dagger & X_m^\dagger \end{pmatrix}_b \psi_b^*(x_{2'}, x_2) \right] \\ & - i \sum_{m=1}^N \frac{1}{\omega + \Omega_m - i\eta} \left[\sum_a \begin{pmatrix} X_m^* \\ Y_m^* \end{pmatrix}^a \psi_a(x_1, x_{1'}) \right] \\ & \left[\sum_b \begin{pmatrix} X_m^T & Y_m^T \end{pmatrix}_b \psi_b^*(x_{2'}, x_2) \right] \end{aligned} \quad (\text{C.86})$$

And further (using Eqs. C.25 and C.26):

$$\begin{aligned} L(x_1, x_2, x_{1'}, x_{2'}, \omega) = & i \sum_{m=1}^N \frac{1}{\omega - \Omega_m + i\eta} \left[\sum_{(v,c)} X_m^{v,c} \psi_{c,v}(x_1, x_{1'}) + Y_m^{v,c} \psi_{v,c}(x_1, x_{1'}) \right] \\ & \left[\sum_{(v,c)} X_m^{*v,c} \psi_{c,v}^*(x_{2'}, x_2) + Y_m^{*v,c} \psi_{v,c}^*(x_{2'}, x_2) \right] \\ & - i \sum_{m=1}^N \frac{1}{\omega + \Omega_m - i\eta} \left[\sum_{(v,c)} X_m^{*v,c} \psi_{v,c}(x_1, x_{1'}) + Y_m^{*v,c} \psi_{c,v}(x_1, x_{1'}) \right] \\ & \left[\sum_{(v,c)} X_m^{v,c} \psi_{v,c}^*(x_{2'}, x_2) + Y_m^{v,c} \psi_{c,v}^*(x_{2'}, x_2) \right] \end{aligned} \quad (\text{C.87})$$

With the definition

$$\begin{aligned} \chi_m(x, y) & \equiv \sum_{(v,c)} X_m^{v,c} \psi_{c,v}(x, y) + Y_m^{v,c} \psi_{v,c}(x, y) \\ & = \sum_{(v,c)} X_m^{v,c} \phi_c(x) \phi_v^*(y) + Y_m^{v,c} \phi_v(x) \phi_c^*(y) \\ \chi_m^*(x, y) & = \sum_{(v,c)} X_m^{*v,c} \psi_{c,v}^*(x, y) + Y_m^{*v,c} \psi_{v,c}^*(x, y) \\ & = \sum_{(v,c)} X_m^{*v,c} \phi_c^*(x) \phi_v(y) + Y_m^{*v,c} \phi_v^*(x) \phi_c(y), \end{aligned} \quad (\text{C.88})$$

we finally find:

$$L(x_1, x_2, x_{1'}, x_{2'}, \omega) = i \sum_{m=1}^N \frac{\chi_m(x_1, x_{1'}) \chi_m^*(x_{2'}, x_2)}{\omega - \Omega_m + i\eta} - i \sum_{m=1}^N \frac{\chi_m(x_2, x_{2'}) \chi_m^*(x_{1'}, x_1)}{\omega + \Omega_m - i\eta} \quad (\text{C.89})$$

Thus, we find that we can construct L from the positive eigenvalues and corresponding right eigenvectors of the BSE Hamiltonian. For reference, this eigenvalue equation, that is, the Bethe-Salpeter equation, is given here in index-form. We start from:

$$\sum_b H_b^a \begin{pmatrix} X_m \\ Y_m \end{pmatrix}^b = \sum_b \begin{pmatrix} R & C \\ -C^* & -R^* \end{pmatrix}_b^a \begin{pmatrix} X_m \\ Y_m \end{pmatrix}^b = \Omega_m \begin{pmatrix} X_m \\ Y_m \end{pmatrix}^a \quad (\text{C.90})$$

This splits into two equations,

$$\begin{aligned} \sum_b \begin{pmatrix} R & C \\ -C^* & -R^* \end{pmatrix}_b^{v,c} \begin{pmatrix} X_m \\ Y_m \end{pmatrix}^b &= \Omega_m \begin{pmatrix} X_m \\ Y_m \end{pmatrix}^{v,c} \\ \sum_b \begin{pmatrix} R & C \\ -C^* & -R^* \end{pmatrix}_b^{c,v} \begin{pmatrix} X_m \\ Y_m \end{pmatrix}^b &= \Omega_m \begin{pmatrix} X_m \\ Y_m \end{pmatrix}^{c,v}, \end{aligned} \quad (\text{C.91})$$

which can be further evaluated to read (compare Eq. C.46):

$$\begin{aligned} \sum_{(v',c')} R_{v',c'}^{v,c} X_m^{v',c'} + C_{v',c'}^{v,c} Y_m^{v',c'} &= \Omega_m X_m^{v,c} \\ \sum_{(v',c')} -C_{v',c'}^{*v,c} X_m^{v',c'} - R_{v',c'}^{*v,c} Y_m^{v',c'} &= \Omega_m Y_m^{v,c} \end{aligned} \quad (\text{C.92})$$

Using the definitions of R and C , this becomes:

$$\begin{aligned} (\varepsilon_c^{QP} - \varepsilon_v^{QP}) X_m^{v,c} + \sum_{(v',c')} [V_{c',v'}^{c,v} - W_{c',v'}^{c,v}] X_m^{v',c'} + [V_{v',c'}^{c,v} - W_{v',c'}^{c,v}] Y_m^{v',c'} &= \Omega_m X_m^{v,c} \\ (\varepsilon_c^{QP} - \varepsilon_v^{QP}) Y_m^{v,c} + \sum_{(v',c')} [V_{c',v'}^{v,c} - W_{c',v'}^{v,c}] X_m^{v',c'} + [V_{v',c'}^{v,c} - W_{v',c'}^{v,c}] Y_m^{v',c'} &= -\Omega_m Y_m^{v,c}, \end{aligned} \quad (\text{C.93})$$

which has to be solved for positive energies $\Omega_m > 0$. For comparison, see for example Eqs. (12)-(14) and (18) in Ref. [36]¹²⁶ or Eqs. (19), (20) and (24)-(31) in Ref. [118].

¹²⁶Note that in Ref. [36] there is likely a typo in Eq. (14), where the second line should read $\psi_{v'}(\mathbf{x}_6) \psi_{c'}^*(\mathbf{x}_5)$, so with swapped complex conjugation. This becomes obvious when inspecting the conjugation patterns in Eqs. (8), (9) and (11) in combination with the BSE, Eq. (7). In contrast, Eq. (13) has the correct conjugation pattern (with $\mathbf{x}_4$ and $\mathbf{x}_6$ being the argument of an “unconjugated” orbital and $\mathbf{x}_3$ and $\mathbf{x}_5$ being the argument of a complex-conjugated orbital).

C.1.2 Tamm-Dancoff Approximation

The *Tamm-Dancoff approximation* (TDA) is a widely used approximation in solid-state physics and quantum chemistry and has been shown to invoke only small errors in optical spectra¹²⁷ of many physical systems, in particular bulk semiconductors and metals [204] as well as organic molecules [202]. The basis of the TDA is the observation that for many physical systems, the coupling matrix C is found to be small¹²⁸ (compare e.g. Ref. [36]) relative to R , which motivates setting $C = 0$. When applying the TDA, that is, when setting $C = 0$, the BSE Hamiltonian then becomes:

$$H = \begin{pmatrix} R & 0 \\ 0 & -R^* \end{pmatrix} \quad (\text{C.94})$$

Note that the BSE Hamiltonian is now fully Hermitian, since R is Hermitian! As mentioned before using γ from Eq. C.61, $\gamma H = \begin{pmatrix} R & 0 \\ 0 & R^* \end{pmatrix}$ is positive definite for most physical systems. Under this assumption R is positive definite and $-R^*$ is negative definite. Since H is block diagonal, its eigenvalues and eigenvectors can be obtained from the eigenvalues and eigenvectors of the two blocks R and $-R^*$. Thus, its positive eigenvalues are the eigenvalues of R . The eigendecomposition of H then becomes (compare Eq. C.67 and equations below it):

$$H = \sum_{m=1}^{2N} \Omega_m R_m L_m^\dagger, \quad (\text{C.95})$$

with positive eigenvalues and eigenvectors

$$\begin{aligned} \Omega_1 &\geq \Omega_2 \geq \dots \geq \Omega_N > 0 \\ R_m &= \begin{pmatrix} X_m \\ 0 \end{pmatrix}, \quad m = 1 \dots N \\ L_m^\dagger &= (X_m^\dagger \quad 0), \quad m = 1 \dots N \end{aligned} \quad (\text{C.96})$$

and negative eigenvalues and eigenvectors

$$\begin{aligned} \Omega_{N+m} &= -\Omega_m < 0, \quad m = 1 \dots N \\ R_{N+m} &= \begin{pmatrix} 0 \\ X_m^* \end{pmatrix}, \quad m = 1 \dots N \\ L_{N+m}^\dagger &= (0 \quad X_m^T), \quad m = 1 \dots N, \end{aligned} \quad (\text{C.97})$$

where Ω_m ($m = 1 \dots N$) and X_m are the m -th eigenvalue and right eigenvector of R :

$$R X_m = \Omega_m X_m \quad (\text{C.98})$$

¹²⁷Although the error is often small, it is interesting to mention that the TDA has been shown to always overestimate all eigenvalues of the BSE Hamiltonian [205].

¹²⁸See for example Ref. [207] on the breakdown of this assumption.

The two-particle correlation function then reads:

$$L(x_1, x_2, x_{1'}, x_{2'}, \omega) = i \sum_{m=1}^N \frac{\chi_m(x_1, x_{1'}) \chi_m^*(x_{2'}, x_2)}{\omega - \Omega_m + i\eta} - i \sum_{m=1}^N \frac{\chi_m(x_2, x_{2'}) \chi_m^*(x_{1'}, x_1)}{\omega + \Omega_m - i\eta}, \quad (\text{C.99})$$

with:

$$\chi_m(x, y) = \sum_{(v,c)} X_m^{v,c} \phi_c(x) \phi_v^*(y) \quad (\text{C.100})$$

and the necessary quantities are obtained by diagonalizing R :

$$(\varepsilon_c^{QP} - \varepsilon_v^{QP}) X_m^{v,c} + \sum_{(v',c')} [V_{c',v'}^{c,v} - W_{c',v'}^{c,v}] X_m^{v',c'} = \Omega_m X_m^{v,c}, \quad (\text{C.101})$$

where all eigenvalues $\{\Omega_m\}$ are positive (see above). We call this eigenvalue equation the *BSE in TDA*.

To conclude, note that we often perform exciton photoemission simulations (see Sec. 3.3.10) based on BSE calculations in the TDA. For the exPOT formalism, the quantity of interest is the $((v, c)$ -part of the) *BSE eigenvector*¹²⁹, X_m . While the references cited in the beginning of this section are mainly concerned with the excitation energies $\{\Omega_m\}$, it is natural to assume the BSE eigenvectors to only slightly change under application of the TDA, provided C is small. This has been explicitly verified for a gas-phase 6T molecule, see Sec. 5.6.

C.1.3 Gas-Phase Systems

For gas-phase systems like isolated molecules or molecular clusters, the above equations can be directly applied, with v and c denoting respectively the discrete valence and conduction orbitals. The valence- and conduction indices in the two-particle basis functions are then independent (compare the discussion below Eq. C.112) and can thus be summed over individually, such that the BSE becomes (compare Eq. C.93):

$$\begin{aligned} (\varepsilon_c^{QP} - \varepsilon_v^{QP}) X_m^{v,c} + \sum_{v',c'} [V_{c',v'}^{c,v} - W_{c',v'}^{c,v}] X_m^{v',c'} + [V_{v',c'}^{c,v} - W_{v',c'}^{c,v}] Y_m^{v',c'} &= \Omega_m X_m^{v,c} \\ (\varepsilon_c^{QP} - \varepsilon_v^{QP}) Y_m^{v,c} + \sum_{v',c'} [V_{c',v'}^{v,c} - W_{c',v'}^{v,c}] X_m^{v',c'} + [V_{v',c'}^{v,c} - W_{v',c'}^{v,c}] Y_m^{v',c'} &= -\Omega_m Y_m^{v,c} \end{aligned} \quad (\text{C.102})$$

And L is expressed as in Eq. C.89, using:

$$\chi_m(x, y) = \sum_{v,c} X_m^{v,c} \phi_c(x) \phi_v^*(y) + Y_m^{v,c} \phi_v(x) \phi_c^*(y) \quad (\text{C.103})$$

¹²⁹See text around Eq. 3.50 for details.

In TDA, this becomes

$$(\varepsilon_c^{QP} - \varepsilon_v^{QP})X_m^{v,c} + \sum_{v',c'} [V_{c',v'}^{c,v} - W_{c',v'}^{c,v}] X_m^{v',c'} = \Omega_m X_m^{v,c} \quad (\text{C.104})$$

and

$$\chi_m(x, y) = \sum_{v,c} X_m^{v,c} \phi_c(x) \phi_v^*(y). \quad (\text{C.105})$$

C.1.4 Periodic Systems

Two-Particle Bloch Orbitals

For periodic systems, the one-particle orbitals are Bloch orbitals $\{\phi_{i,\mathbf{q}}\}$, where i runs over valence- and conduction bands and $\mathbf{q}$ over the Brillouin zone (BZ). Instead of directly working with an infinitely-sized surface (the type of periodic system we are concerned with in this text), we follow the path of Appendix B.1 and first perform the derivation for a macroscopically-sized but finite surface, whose bound states (compare Footnote 117) are then (approximately) Bloch-like in the interior (and in the vacuum above the interior) of the surface, deviate from this Bloch-like form in the small region around the lateral sides of the surface and vanish in the vacuum beyond the lateral ends (and of course above and below the surface, since they are *bound* states, see Appendix A.1.1). We denote the surface area of the finite surface as $A = N_1 N_2 A_c$, where A_c is the area of the surface unit cell and N_1 and N_2 are respectively the number of repetitions of the unit cell (= number of Bloch momenta) forming the finite surface. The Bloch momenta of the bound states are then given by the discrete grid¹³⁰ Eq. A.8, which contains in total $N_1 N_2$ allowed Bloch momenta (which lie, as usual, in the Brillouin zone). Given that we use a finite number of valence- and conduction bands in our expansions (compare Footnote 117), we thus again work with a finite number of orbitals and thus with finitely sized matrices and vectors. In the end, the thermodynamic limit may be performed/approached (see below).

Working now with the finite, macroscopic surface and approximating its bound states to fully vanish beyond the lateral ends of the finite surface while being Bloch orbitals on the inside (thus neglecting edge-effects, which become less and less relevant the larger the surface becomes), the orthonormalization of the bound states can be written as:

$$\begin{aligned} \int dx \phi_{n,\mathbf{q}}^*(x) \phi_{n',\mathbf{q}'}(x) &\approx \sum_{s=\uparrow,\downarrow} \int_A d^2 r_{\parallel} \int_{\mathbb{R}} dz \phi_{n,\mathbf{q}}^*(x) \phi_{n',\mathbf{q}'}(x) \\ &= \delta_{n,n'} \delta_{\mathbf{q},\mathbf{q}'} \end{aligned} \quad (\text{C.106})$$

Note that this corresponds to the normalization of Eq. B.3. Note also, that integrals containing such Bloch-like functions can thus be restricted from all space to the area of the surface. In the following we routinely use that the bound states approximately satisfy commonly known properties of Bloch functions, e.g. Eq. C.110

¹³⁰ We end up with this Brillouin-zone sampling by imposing periodic boundary conditions on the bound states, which is argued by the fact that their behavior near the lateral edges is irrelevant anyway. See also the text below Eq. A.11 for details.

which holds true on the whole finite surface except for the small area near the lateral ends. Lastly, note that since we are interested in periodic surfaces, the Bloch momenta $\{\mathbf{q}\}$, the exciton momenta $\{\mathbf{Q}\}$ (see Sec. 2.4.4) as well as the translations $\{\mathbf{R}\}$ and reciprocal lattice vectors $\{\mathbf{G}\}$ are in-plane quantities (0 in z direction). The derivation can however also be used for 3d-periodic systems when appropriately adapting the orthonormalization of the bound states shown above.

The two-particle orbitals are then given by $\{\psi_{i,\mathbf{q}_i,j,\mathbf{q}_j}\}$, with:

$$\psi_{i,\mathbf{q}_i,j,\mathbf{q}_j}(x, y) = \phi_{i,\mathbf{q}_i}(x) \phi_{j,\mathbf{q}_j}^*(y) \quad (\text{C.107})$$

As shown above, the specific form of L_0 will allow us to drop combinations of two valence or two conduction orbitals, so we will only need the valence-conduction orbitals $\{\psi_{v,\mathbf{q}_v,c,\mathbf{q}_c}\}$ and $\{\psi_{c,\mathbf{q}_c,v,\mathbf{q}_v}\}$. Note that v and c are now band indices, while they were the complete valence/conduction index (so, implicitly including Bloch momentum) in the generic derivation given above.

We can rewrite this basis by using the periodicity of Bloch orbitals:

$$\phi_{\mathbf{q}+\mathbf{G}}(x) = \phi_{\mathbf{q}}(x), \quad (\text{C.108})$$

where $\mathbf{G}$ is any reciprocal lattice vector. This then allows us to write¹³¹ our two-particle valence-conduction orbitals as $\{\psi_{v,\mathbf{q},c,\mathbf{Q}}\}$ and $\{\psi_{c,\mathbf{Q},v,\mathbf{q}}\}$, with:

$$\begin{aligned} \psi_{v,\mathbf{q},c,\mathbf{Q}}(x, y) &= \phi_{v,\mathbf{q}}(x) \phi_{c,\mathbf{q}+\mathbf{Q}}^*(y) \\ \psi_{c,\mathbf{Q},v,\mathbf{q}}(x, y) &= \phi_{c,\mathbf{q}+\mathbf{Q}}(x) \phi_{v,\mathbf{q}}^*(y), \end{aligned} \quad (\text{C.109})$$

with $\mathbf{Q}$ restricted to BZ (and lying on the same discrete grid as the $\{\mathbf{q}\}$) and where we renamed $\mathbf{q}_v$ to $\mathbf{q}$. For later use, note that, for a lattice vector $\mathbf{R}$, we have:

$$\begin{aligned} \psi_{v,\mathbf{q},c,\mathbf{Q}}(\mathbf{r}_x + \mathbf{R}, s_x, \mathbf{r}_y + \mathbf{R}, s_y) &= \phi_{v,\mathbf{q}}(\mathbf{r}_x + \mathbf{R}, s_x) \phi_{c,\mathbf{q}+\mathbf{Q}}^*(\mathbf{r}_y + \mathbf{R}, s_y) \\ &= e^{i\mathbf{q}\cdot\mathbf{R}} \phi_{v,\mathbf{q}}(\mathbf{r}_x, s_x) e^{-i(\mathbf{q}+\mathbf{Q})\cdot\mathbf{R}} \phi_{c,\mathbf{q}+\mathbf{Q}}^*(\mathbf{r}_y, s_y) \\ &= e^{-i\mathbf{Q}\cdot\mathbf{R}} \psi_{v,\mathbf{q},c,\mathbf{Q}}(\mathbf{r}_x, s_x, \mathbf{r}_y, s_y) \\ \psi_{c,\mathbf{Q},v,\mathbf{q}}(\mathbf{r}_x + \mathbf{R}, s_x, \mathbf{r}_y + \mathbf{R}, s_y) &= e^{i\mathbf{Q}\cdot\mathbf{R}} \psi_{c,\mathbf{Q},v,\mathbf{q}}(\mathbf{r}_x, s_x, \mathbf{r}_y, s_y) \end{aligned} \quad (\text{C.110})$$

Note that, leaving the two-valence and two-conduction orbitals unchanged, all properties needed from the two-particle orbitals are still given. That is, they (talking about all four sectors, so including the two-valence and two-conduction orbitals) were still constructed from all combinations of one-particle orbitals and are thus still a complete and orthonormal (see below) two-particle set, i.e. a two-particle basis. Secondly, they are still orthonormal (the four sectors are trivially orthogonal to one another), where we in particular find:

$$\begin{aligned} \int d(x, y) \psi_{v,\mathbf{q},c,\mathbf{Q}}(x, y) \psi_{v',\mathbf{q}',c',\mathbf{Q}'}^*(x, y) &= \\ &= \int d(x, y) \phi_{v,\mathbf{q}}(x) \phi_{c,\mathbf{q}+\mathbf{Q}}^*(y) \phi_{v',\mathbf{q}'}^*(x) \phi_{c',\mathbf{q}'+\mathbf{Q}'}(y) \\ &= \delta_{v,v'} \delta_{\mathbf{q},\mathbf{q}'} \delta_{c,c'} \delta_{\mathbf{Q},\mathbf{Q}'} \end{aligned} \quad (\text{C.111})$$

¹³¹Introducing compact notation $\psi_{v,\mathbf{q},c,\mathbf{Q}}$ for the orbital $\psi_{v,\mathbf{q},c,\mathbf{q}+\mathbf{Q}}$ and similarly $\psi_{c,\mathbf{Q},v,\mathbf{q}}$ for $\psi_{c,\mathbf{q}+\mathbf{Q},v,\mathbf{q}}$.

and similarly for $\psi_{c,\mathbf{Q},v,\mathbf{q}}$. Thirdly, they still satisfy Eq. C.4, which for the valence-conduction orbitals becomes:

$$\begin{aligned}\psi_{v,\mathbf{q},c,\mathbf{Q}}(x,y) &= \phi_{v,\mathbf{q}}(x)\phi_{c,\mathbf{q}+\mathbf{Q}}^*(y) \\ &= (\phi_{c,\mathbf{q}+\mathbf{Q}}(y)\phi_{v,\mathbf{q}}^*(x))^* \\ &= \psi_{c,\mathbf{Q},v,\mathbf{q}}^*(y,x)\end{aligned}\tag{C.112}$$

And finally, the valence-conduction orbitals are still constructed in a way such that for every orbital $\psi_{v,\mathbf{q},c,\mathbf{Q}}$ in the *vc-sector*, there is an element $\psi_{c,\mathbf{Q},v,\mathbf{q}}$ in the *cv-sector*, thus allowing for the compact notation Eq. C.23 and the ensuing efficient treatment of the BSE in terms of matrices. Thus, the derivation shown above can be directly applied using this basis set. Note however, that in the valence-conduction orbitals, the Bloch momentum of the conduction orbital depends on that of the valence orbital, which is a result of the symmetry operation Eq. C.108 we used above. Written this way, we can thus not independently sum over valence and conduction indices, but have to sum over the pairs $((v,\mathbf{q}), (c,\mathbf{Q}))$ and $((c,\mathbf{Q}), (v,\mathbf{q}))$. This was already accounted for in the derivation above, see for example Eq. C.11.

Resonant Matrix

We continue by explicitly constructing the resonant matrix, which will turn out to be blockwise diagonal in Bloch representation (expansion in Bloch KS orbitals). To see this, let us first take a closer look at L_0 , which becomes for periodic (but finite) systems (compare Eq. C.17):

$$\begin{aligned}L_0(x_1, x_2, x_{1'}, x_{2'}, \omega) &= i \sum_{v,\mathbf{q}_v,c,\mathbf{q}_c} \frac{\phi_{c,\mathbf{q}_c}(x_1)\phi_{v,\mathbf{q}_v}^*(x_{1'})\phi_{c,\mathbf{q}_c}^*(x_{2'})\phi_{v,\mathbf{q}_v}(x_2)}{\omega - (\varepsilon_{c,\mathbf{q}_c}^{QP} - \varepsilon_{v,\mathbf{q}_v}^{QP}) + i\eta} \\ &\quad - \frac{\phi_{v,\mathbf{q}_v}(x_1)\phi_{c,\mathbf{q}_c}^*(x_{1'})\phi_{v,\mathbf{q}_v}^*(x_{2'})\phi_{c,\mathbf{q}_c}(x_2)}{\omega + (\varepsilon_{c,\mathbf{q}_c}^{QP} - \varepsilon_{v,\mathbf{q}_v}^{QP}) - i\eta}\end{aligned}\tag{C.113}$$

Note that we here implicitly assumed that our system is gapped (semiconductor or insulator), such that all bands are either fully occupied or completely empty. This is the type of system we perform calculations for in this text, see Chapters 4 and 5. Using Eq. C.108 this can be written as:

$$\begin{aligned}L_0(x_1, x_2, x_{1'}, x_{2'}, \omega) &= i \sum_{v,\mathbf{q},c,\mathbf{Q}} \frac{\phi_{c,\mathbf{q}+\mathbf{Q}}(x_1)\phi_{v,\mathbf{q}}^*(x_{1'})\phi_{c,\mathbf{q}+\mathbf{Q}}^*(x_{2'})\phi_{v,\mathbf{q}}(x_2)}{\omega - (\varepsilon_{c,\mathbf{q}+\mathbf{Q}}^{QP} - \varepsilon_{v,\mathbf{q}}^{QP}) + i\eta} \\ &\quad - \frac{\phi_{v,\mathbf{q}}(x_1)\phi_{c,\mathbf{q}+\mathbf{Q}}^*(x_{1'})\phi_{v,\mathbf{q}}^*(x_{2'})\phi_{c,\mathbf{q}+\mathbf{Q}}(x_2)}{\omega + (\varepsilon_{c,\mathbf{q}+\mathbf{Q}}^{QP} - \varepsilon_{v,\mathbf{q}}^{QP}) - i\eta} \\ &= i \sum_{v,\mathbf{q},c,\mathbf{Q}} \frac{\psi_{c,\mathbf{Q},v,\mathbf{q}}(x_1, x_{1'})\psi_{c,\mathbf{Q},v,\mathbf{q}}^*(x_{2'}, x_2)}{\omega - (\varepsilon_{c,\mathbf{q}+\mathbf{Q}}^{QP} - \varepsilon_{v,\mathbf{q}}^{QP}) + i\eta} \\ &\quad - \frac{\psi_{v,\mathbf{q},c,\mathbf{Q}}(x_1, x_{1'})\psi_{v,\mathbf{q},c,\mathbf{Q}}^*(x_{2'}, x_2)}{\omega + (\varepsilon_{c,\mathbf{q}+\mathbf{Q}}^{QP} - \varepsilon_{v,\mathbf{q}}^{QP}) - i\eta},\end{aligned}\tag{C.114}$$

where $\varepsilon_{c,\mathbf{q}+\mathbf{Q}}$ is given for momenta outside BZ via:

$$\varepsilon_{c,\mathbf{q}+\mathbf{Q}} = \varepsilon_{c,\mathbf{q}+\mathbf{Q} \bmod \mathbf{G}}\tag{C.115}$$

As expected, L_0 is still a diagonal matrix with diagonal elements given by:

$$\begin{aligned} L_{0\ v,\mathbf{q},c,\mathbf{Q}}^{v,\mathbf{q},c,\mathbf{Q}} &= \frac{-1}{\omega + (\varepsilon_{c,\mathbf{q}+\mathbf{Q}}^{QP} - \varepsilon_{v,\mathbf{q}}^{QP}) - i\eta} \\ L_{0\ c,\mathbf{Q},v,\mathbf{q}}^{c,\mathbf{Q},v,\mathbf{q}} &= \frac{1}{\omega - (\varepsilon_{c,\mathbf{q}+\mathbf{Q}}^{QP} - \varepsilon_{v,\mathbf{q}}^{QP}) + i\eta} \end{aligned} \quad (\text{C.116})$$

Next, let us look at V which reads in this basis:

$$\begin{aligned} V_{v',\mathbf{q}',c',\mathbf{Q}'}^{v,\mathbf{q},c,\mathbf{Q}} &= \int d(x_3, x_4) v(x_3, x_4) \psi_{v,\mathbf{q},c,\mathbf{Q}}^*(x_3, x_3) \psi_{v',\mathbf{q}',c',\mathbf{Q}'}(x_4, x_4) \\ V_{c',\mathbf{Q}',v',\mathbf{q}'}^{v,\mathbf{q},c,\mathbf{Q}} &= \int d(x_3, x_4) v(x_3, x_4) \psi_{v,\mathbf{q},c,\mathbf{Q}}^*(x_3, x_3) \psi_{c',\mathbf{Q}',v',\mathbf{q}'}(x_4, x_4) \\ V_{v',\mathbf{q}',c',\mathbf{Q}'}^{c,\mathbf{Q},v,\mathbf{q}} &= \int d(x_3, x_4) v(x_3, x_4) \psi_{c,\mathbf{Q},v,\mathbf{q}}^*(x_3, x_3) \psi_{v',\mathbf{q}',c',\mathbf{Q}'}(x_4, x_4) \\ V_{c',\mathbf{Q}',v',\mathbf{q}'}^{c,\mathbf{Q},v,\mathbf{q}} &= \int d(x_3, x_4) v(x_3, x_4) \psi_{c,\mathbf{Q},v,\mathbf{q}}^*(x_3, x_3) \psi_{c',\mathbf{Q}',v',\mathbf{q}'}(x_4, x_4) \end{aligned} \quad (\text{C.117})$$

Shifting integration variables by an arbitrary lattice vector $\mathbf{R}$ and using $v(\mathbf{r}_3 + \mathbf{R}, s_3, \mathbf{r}_4 + \mathbf{R}, s_4) = v(\mathbf{r}_3, s_3, \mathbf{r}_4, s_4)$ and using Eq. C.110 we find:

$$\begin{aligned} (1 - e^{i(\mathbf{Q}-\mathbf{Q}')\cdot\mathbf{R}}) V_{v',\mathbf{q}',c',\mathbf{Q}'}^{v,\mathbf{q},c,\mathbf{Q}} &= 0 \\ (1 - e^{i(\mathbf{Q}+\mathbf{Q}')\cdot\mathbf{R}}) V_{c',\mathbf{Q}',v',\mathbf{q}'}^{v,\mathbf{q},c,\mathbf{Q}} &= 0 \\ (1 - e^{i(-\mathbf{Q}-\mathbf{Q}')\cdot\mathbf{R}}) V_{v',\mathbf{q}',c',\mathbf{Q}'}^{c,\mathbf{Q},v,\mathbf{q}} &= 0 \\ (1 - e^{i(\mathbf{Q}'-\mathbf{Q})\cdot\mathbf{R}}) V_{c',\mathbf{Q}',v',\mathbf{q}'}^{c,\mathbf{Q},v,\mathbf{q}} &= 0 \end{aligned} \quad (\text{C.118})$$

Focusing on the first and last line, we can see that the prefactor vanishes for an arbitrary $\mathbf{R}$ (of the finite surface, take for example $\mathbf{R} = \mathbf{a}_1$ and $\mathbf{R} = \mathbf{a}_2$), if and only if:

$$\mathbf{Q} - \mathbf{Q}' = \mathbf{G} \quad (\text{C.119})$$

for some reciprocal lattice vector $\mathbf{G}$. Since $\mathbf{Q}$ and $\mathbf{Q}'$ are both restricted to BZ, this gives us:

$$\mathbf{Q} = \mathbf{Q}' + \mathbf{G} \rightarrow \mathbf{Q} = \mathbf{Q}' \quad (\text{C.120})$$

Thus, unless $\mathbf{Q} = \mathbf{Q}'$, the matrix element of V must vanish and we can write:

$$\begin{aligned} V_{v',\mathbf{q}',c',\mathbf{Q}'}^{v,\mathbf{q},c,\mathbf{Q}} &= V_{v',\mathbf{q}',c',\mathbf{Q}}^{v,\mathbf{q},c,\mathbf{Q}} \delta_{\mathbf{Q}'}^{\mathbf{Q}} \\ V_{c',\mathbf{Q}',v',\mathbf{q}'}^{c,\mathbf{Q},v,\mathbf{q}} &= V_{c',\mathbf{Q},v',\mathbf{q}'}^{c,\mathbf{Q},v,\mathbf{q}} \delta_{\mathbf{Q}'}^{\mathbf{Q}} \end{aligned} \quad (\text{C.121})$$

Similarly, for W we find:

$$\begin{aligned} W_{v',\mathbf{q}',c',\mathbf{Q}'}^{v,\mathbf{q},c,\mathbf{Q}} &= \int d(x_3, x_4) W(x_3, x_4) \psi_{v,\mathbf{q},c,\mathbf{Q}}^*(x_3, x_4) \psi_{v',\mathbf{q}',c',\mathbf{Q}'}(x_3, x_4) \\ W_{c',\mathbf{Q}',v',\mathbf{q}'}^{v,\mathbf{q},c,\mathbf{Q}} &= \int d(x_3, x_4) W(x_3, x_4) \psi_{v,\mathbf{q},c,\mathbf{Q}}^*(x_3, x_4) \psi_{c',\mathbf{Q}',v',\mathbf{q}'}(x_3, x_4) \\ W_{v',\mathbf{q}',c',\mathbf{Q}'}^{c,\mathbf{Q},v,\mathbf{q}} &= \int d(x_3, x_4) W(x_3, x_4) \psi_{c,\mathbf{Q},v,\mathbf{q}}^*(x_3, x_4) \psi_{v',\mathbf{q}',c',\mathbf{Q}'}(x_3, x_4) \\ W_{c',\mathbf{Q}',v',\mathbf{q}'}^{c,\mathbf{Q},v,\mathbf{q}} &= \int d(x_3, x_4) W(x_3, x_4) \psi_{c,\mathbf{Q},v,\mathbf{q}}^*(x_3, x_4) \psi_{c',\mathbf{Q}',v',\mathbf{q}'}(x_3, x_4) \end{aligned} \quad (\text{C.122})$$

And thus, using lattice-periodicity¹³² of W :

$$\begin{aligned}
(1 - e^{i(\mathbf{Q}-\mathbf{Q}')\cdot\mathbf{R}}) W_{v',\mathbf{q}',c',\mathbf{Q}'}^{v,\mathbf{q},c,\mathbf{Q}} &= 0 \\
(1 - e^{i(\mathbf{Q}+\mathbf{Q}')\cdot\mathbf{R}}) W_{c',\mathbf{Q}',v',\mathbf{q}'}^{v,\mathbf{q},c,\mathbf{Q}} &= 0 \\
(1 - e^{i(-\mathbf{Q}-\mathbf{Q}')\cdot\mathbf{R}}) W_{v',\mathbf{q}',c',\mathbf{Q}'}^{c,\mathbf{Q},v,\mathbf{q}} &= 0 \\
(1 - e^{i(\mathbf{Q}'-\mathbf{Q})\cdot\mathbf{R}}) W_{c',\mathbf{Q}',v',\mathbf{q}'}^{c,\mathbf{Q},v,\mathbf{q}} &= 0
\end{aligned} \tag{C.123}$$

Using the same argument as before, we find:

$$\begin{aligned}
W_{v',\mathbf{q}',c',\mathbf{Q}'}^{v,\mathbf{q},c,\mathbf{Q}} &= W_{v',\mathbf{q}',c',\mathbf{Q}}^{v,\mathbf{q},c,\mathbf{Q}} \delta_{\mathbf{Q}'}^{\mathbf{Q}} \\
W_{c',\mathbf{Q}',v',\mathbf{q}'}^{c,\mathbf{Q},v,\mathbf{q}} &= W_{c',\mathbf{Q},v',\mathbf{q}'}^{c,\mathbf{Q},v,\mathbf{q}} \delta_{\mathbf{Q}'}^{\mathbf{Q}}
\end{aligned} \tag{C.124}$$

For the resonant matrix we then find:

$$\begin{aligned}
R_{v',\mathbf{q}',c',\mathbf{Q}'}^{v,\mathbf{q},c,\mathbf{Q}} &= (\varepsilon_{c,\mathbf{q}+\mathbf{Q}}^{QP} - \varepsilon_{v,\mathbf{q}}^{QP}) \delta_{v'}^v \delta_{c'}^c \delta_{\mathbf{q}'}^{\mathbf{q}} \delta_{\mathbf{Q}'}^{\mathbf{Q}} + V_{c',\mathbf{Q}',v',\mathbf{q}'}^{c,\mathbf{Q},v,\mathbf{q}} - W_{c',\mathbf{Q}',v',\mathbf{q}'}^{c,\mathbf{Q},v,\mathbf{q}} \\
&= (\varepsilon_{c,\mathbf{q}+\mathbf{Q}}^{QP} - \varepsilon_{v,\mathbf{q}}^{QP}) \delta_{v'}^v \delta_{c'}^c \delta_{\mathbf{q}'}^{\mathbf{q}} \delta_{\mathbf{Q}'}^{\mathbf{Q}} + V_{c',\mathbf{Q},v',\mathbf{q}'}^{c,\mathbf{Q},v,\mathbf{q}} \delta_{\mathbf{Q}'}^{\mathbf{Q}} - W_{c',\mathbf{Q},v',\mathbf{q}'}^{c,\mathbf{Q},v,\mathbf{q}} \delta_{\mathbf{Q}'}^{\mathbf{Q}} \\
&= \left[(\varepsilon_{c,\mathbf{q}+\mathbf{Q}}^{QP} - \varepsilon_{v,\mathbf{q}}^{QP}) \delta_{v'}^v \delta_{c'}^c \delta_{\mathbf{q}'}^{\mathbf{q}} + V_{c',\mathbf{Q},v',\mathbf{q}'}^{c,\mathbf{Q},v,\mathbf{q}} - W_{c',\mathbf{Q},v',\mathbf{q}'}^{c,\mathbf{Q},v,\mathbf{q}} \right] \delta_{\mathbf{Q}'}^{\mathbf{Q}}
\end{aligned} \tag{C.125}$$

If we arrange rows (and columns) by using $\mathbf{Q}$ as the outermost loop (when flattening $v, \mathbf{q}, c, \mathbf{Q}$ into a single index) – which we are free to do, see comments below Eq. C.23 – we thus see that R becomes a block diagonal matrix¹³³, with one block per $\mathbf{Q}$.

BSE in TDA

For simplicity, and since all periodic calculations performed in the main text use it, we continue in the Tamm-Dancoff approximation¹³⁴ (TDA, see Sec. C.1.2). All that is left to do then is to diagonalize R . And since R is block diagonal in $\mathbf{Q}$, each $\mathbf{Q}$ can be treated individually, each giving us $N = N_v N_c N_q$ (positive, see Sec. C.1.2) eigenvalues and corresponding eigenvectors of R . It is then common practice to label eigenvalues and eigenvectors by $\mathbf{Q}$ (and m , which enumerates solutions for a given $\mathbf{Q}$) and the BSE in TDA becomes (compare Eq. C.101) – for each $\mathbf{Q}$ – an eigenvalue problem for a matrix of size $N \times N$, with $N = N_v N_c N_q$ (compare Eqs. (34), (35) and (48) in Ref. [36]):

$$(\varepsilon_{c,\mathbf{q}+\mathbf{Q}}^{QP} - \varepsilon_{v,\mathbf{q}}^{QP}) X_{m,\mathbf{Q}}^{v,c,\mathbf{q}} + \sum_{v',c',\mathbf{q}'} \left[V_{c',\mathbf{Q},v',\mathbf{q}'}^{c,\mathbf{Q},v,\mathbf{q}} - W_{c',\mathbf{Q},v',\mathbf{q}'}^{c,\mathbf{Q},v,\mathbf{q}} \right] X_{m,\mathbf{Q}}^{v',c',\mathbf{q}'} = \Omega_{m,\mathbf{Q}} X_{m,\mathbf{Q}}^{v,c,\mathbf{q}} \tag{C.126}$$

¹³²Which becomes obvious from the relation Eq. C.133 of W to the reducible polarizability χ , as defined in Eq. C.131. See also Appendix B in Ref. [208]. Of course, on the finite surface W is only approximately lattice-periodic, but becomes exactly lattice-periodic in the thermodynamic limit.

¹³³See also Appendix B in Ref. [208].

¹³⁴A treatment of periodic systems beyond the TDA can for example be found in Ref. [118].

And L becomes:

$$L(x_1, x_2, x_{1'}, x_{2'}, \omega) = i \sum_{m=1}^N \sum_{\mathbf{Q}}^{\text{BZ}} \frac{\chi_{m,\mathbf{Q}}(x_1, x_{1'}) \chi_{m,\mathbf{Q}}^*(x_{2'}, x_2)}{\omega - \Omega_{m,\mathbf{Q}} + i\eta} - i \sum_{m=1}^N \sum_{\mathbf{Q}}^{\text{BZ}} \frac{\chi_{m,\mathbf{Q}}(x_2, x_{2'}) \chi_{m,\mathbf{Q}}^*(x_{1'}, x_1)}{\omega + \Omega_{m,\mathbf{Q}} - i\eta}, \quad (\text{C.127})$$

with¹³⁵:

$$\chi_{m,\mathbf{Q}}(x, y) = \sum_{v,c,\mathbf{q}} X_{m,\mathbf{Q}}^{v,c,\mathbf{q}} \phi_{c,\mathbf{q}+\mathbf{Q}}(x) \phi_{v,\mathbf{q}}^*(y) \quad (\text{C.128})$$

To summarize, instead of directly diagonalizing the full BSE Hamiltonian, which is in the current situation a matrix of size $2N \times 2N$, with $N = N_v N_c N_{\mathbf{q}}^2$, translational symmetry and the TDA allows us to independently diagonalize $N_{\mathbf{Q}} = N_{\mathbf{q}}$ smaller matrices, each of size $N \times N$, with $N = N_v N_c N_{\mathbf{q}}$.

Lastly, note that when taking the thermodynamic limit (where we typically orthonormalize the Bloch functions according to Eq. B.11) sums over Bloch momenta turn into BZ integrals, as can be seen in Eq. (48) of Ref. [36]. As explained there in the context of Eq. (49)¹³⁶, the BSE as it is written in Eq. C.126 can then be understood as resulting from discretization of the BZ integrals (compare also the BSE in Ref. [104]), with the grid of Eq. A.8 forming one possibility for such a discretization (compare also Appendix B.3). Instead of performing the thermodynamic limit only to then discretize the resulting equations again, we can thus simply work with the formalism derived here and increase the sampling¹³⁷ of the Brillouin zone (make it finer) until we reach convergence in the quantities we want to calculate. This corresponds to the discretized version of the BSE used in BERKELEYGW [36, 95, 104] which we use for periodic calculations. Further computational details can for example be found in Ref. [104].

C.2 Screened Coulomb Interaction

In this section we derive properties of the screened Coulomb interaction W needed in other parts of this text.

¹³⁵Note that v , c and $\mathbf{q}$ are independent and can thus be summed over independently. Compare the discussion below Eq. C.112.

¹³⁶Here we replace the two remaining integrals over the part of the BZ shown there by the volume squared of that part (here: area) multiplied by the integrand evaluated at $\mathbf{k}'_i$, which results in a factor of V in front of the matrix element. This factor appears precisely when using the normalization Eq. B.19 instead of the normalization Eq. B.3 thus explaining the difference between Eq. (49) there and our Eq. C.126.

¹³⁷Where Γ -centered sampling corresponds to the use of periodic boundary conditions, see Footnote 130, while shifted (but still regular and rectilinear – in coordinates of the $\{\mathbf{b}_i\}$) grids correspond to the use of twisted boundary conditions, see Footnote 116 – with which the derivation shown here is equally compatible.

Relation to Reducible Polarizability

The screened Coulomb interaction W is defined in Eq. 2.157 as

$$W(1, 2) \equiv \int d(3) \varepsilon^{-1}(1, 3) v(3, 2), \quad (\text{C.129})$$

with the inverse dielectric function (as in Sec. 2.3.4 we omit writing $|\varphi=0$ next to each functional derivative for readability):

$$\varepsilon^{-1}(1, 2) \equiv \frac{\delta V(1)}{\delta \varphi(2)} \quad (\text{C.130})$$

Defining the *reducible polarizability* [82]

$$\chi(1, 2) \equiv \frac{\delta n(1)}{\delta \varphi(2)}, \quad (\text{C.131})$$

we get [82]

$$\varepsilon^{-1}(1, 2) = \delta(1, 2) + \int d(3) v(1, 3) \chi(3, 2), \quad (\text{C.132})$$

and thus [19]:

$$\begin{aligned} W(1, 2) &= \int d(3) \delta(1, 3) v(3, 2) + \int d(3, 4) v(1, 4) \chi(4, 3) v(3, 2) \\ &= v(1, 2) + \int d(3, 4) v(1, 4) \chi(4, 3) v(3, 2) \\ &= v(1, 2) + \int d(3, 4) v(1, 3) \chi(3, 4) v(4, 2) \end{aligned} \quad (\text{C.133})$$

Using that the bare Coulomb interaction is instantaneous, see Eq. 2.7, we get further:

$$\begin{aligned} W((x_1, t_1), (x_2, t_2)) &= v(x_1, x_2) \delta(t_1 - t_2) \\ &+ \int d(x_3, x_4) v(x_1, x_3) \chi((x_3, t_1), (x_4, t_2)) v(x_4, x_2) \end{aligned} \quad (\text{C.134})$$

Based on time-translational invariance this can be written as:

$$\begin{aligned} W(x_1, x_2, t_1 - t_2) &= v(x_1, x_2) \delta(t_1 - t_2) \\ &+ \int d(x_3, x_4) v(x_1, x_3) \chi(x_3, x_4, t_1 - t_2) v(x_4, x_2) \end{aligned} \quad (\text{C.135})$$

Finally, Fourier-transforming with respect to $t_1 - t_2$, we find (see Eq. A.60):

$$W(x_1, x_2, \omega) = v(x_1, x_2) + \int d(x_3, x_4) v(x_1, x_3) \chi(x_3, x_4, \omega) v(x_4, x_2) \quad (\text{C.136})$$

For reference, note that we can also find from Eq. C.129, from the fact that v is instantaneous and from time-translational invariance, that:

$$W(x_1, x_2, \omega) = \int dx_3 \varepsilon^{-1}(x_1, x_3, \omega) v(x_3, x_2) \quad (\text{C.137})$$

Expansion in Excited States

The reducible polarizability χ is related to the two-particle correlation function¹³⁸ L via [19]:

$$\chi(1, 2) = -iL(1, 2, 1^+, 2^+) \quad (\text{C.138})$$

This is precisely the time-ordering that was used for the derivation of Eq. 2.192 and we thus find:

$$\begin{aligned} \chi(x_1, x_2, \omega) &= -iL(x_1, x_2, x_1, x_2, \omega) \\ &= \sum_{S=1} \frac{\chi_S(x_1, x_1)\chi_S^*(x_2, x_2)}{\omega - \Omega_S + i\eta} - \frac{\chi_S^*(x_1, x_1)\chi_S(x_2, x_2)}{\omega + \Omega_S - i\eta} \end{aligned} \quad (\text{C.139})$$

For W we then find:

$$\begin{aligned} W(x_1, x_2, \omega) &= v(x_1, x_2) + \sum_{S=1} \int d(x_3, x_4) v(x_1, x_3) v(x_4, x_2) \\ &\quad \left[\frac{\chi_S(x_3, x_3)\chi_S^*(x_4, x_4)}{\omega - \Omega_S + i\eta} - \frac{\chi_S^*(x_3, x_3)\chi_S(x_4, x_4)}{\omega + \Omega_S - i\eta} \right] \end{aligned} \quad (\text{C.140})$$

Defining

$$w_S(y) = \int d(x) v(x, y) \chi_S(x, x) \quad (\text{C.141})$$

and using that the bare Coulomb interaction is real and symmetric, see Eq. 2.7, we get:

$$W(x_1, x_2, \omega) = v(x_1, x_2) + \sum_{S=1} \frac{w_S(x_1)w_S^*(x_2)}{\omega - \Omega_S + i\eta} - \frac{w_S^*(x_1)w_S(x_2)}{\omega + \Omega_S - i\eta} \quad (\text{C.142})$$

Properties of W in the Static Approximation

At $\omega = 0$ we find:

$$W(x_1, x_2, 0) = v(x_1, x_2) + \sum_{S=1} \frac{w_S(x_1)w_S^*(x_2) + w_S^*(x_1)w_S(x_2)}{-\Omega_S + i\eta} \quad (\text{C.143})$$

Since¹³⁹ $\Omega_S > 0$, we can safely let $\eta \rightarrow 0$:

$$W(x_1, x_2, 0) = v(x_1, x_2) - \sum_{S=1} \frac{w_S(x_1)w_S^*(x_2) + w_S^*(x_1)w_S(x_2)}{\Omega_S} \quad (\text{C.144})$$

And further:

$$\begin{aligned} W(x_1, x_2, 0) &= v(x_1, x_2) - 2 \sum_{S=1} \frac{\Re[w_S(x_1)w_S^*(x_2)]}{\Omega_S} \\ &= v(x_1, x_2) - 2 \sum_{S=1} \frac{\Re[w_S^*(x_1)w_S(x_2)]}{\Omega_S} \end{aligned} \quad (\text{C.145})$$

¹³⁸Note that, remembering Eq. C.131, this shows the close relation between the BSE and linear response!

¹³⁹In contrast to the Lehmann representation of G_2 (see Eq. 2.187), the Lehmann representation of L , Eq. 2.192, only contains excited states, see also the text below Eq. 2.191. Thus, Ω_S is strictly positive here.

Thus, we find that $W(x_1, x_2, 0)$ is real

$$W(x_1, x_2, 0) = W^*(x_1, x_2, 0) \quad (\text{C.146})$$

and symmetric

$$W(x_1, x_2, 0) = W(x_2, x_1, 0). \quad (\text{C.147})$$

D Photoemission Orbital Tomography

D.1 Equivalence of Dyson-Orbital Expressions

Here we show the equivalence of our Dyson-orbital definition of Eq. 3.23 and the formulation used in Ref. [132] by expanding both expressions in the one-particle ONB $\{\phi_j\}$ and showing that their linear coefficients are equal.

Second-Quantization Dyson Orbital

We start from the definition Eq. 3.23:

$$d_{i,f}(x) = \langle x | d_{i,f} \rangle = \langle N-1, f | \hat{\Psi}(x) | N, i \rangle \quad (\text{D.1})$$

Projecting onto ϕ_j we find (using Eq. 2.119):

$$\int dx \phi_j^*(x) d_{i,f}(x) = \langle N-1, f | \hat{a}_j | N, i \rangle \quad (\text{D.2})$$

Let us now expand the initial state in single Slater determinants (compare Appendix A.1.2):

$$\begin{aligned} |N, i\rangle &= \sum_D c_D |\phi_{D(1)}, \phi_{D(2)}, \dots, \phi_{D(N)}\rangle \\ &= \sum_D c_D |n_1^{(D)}, n_2^{(D)}, \dots\rangle \end{aligned} \quad (\text{D.3})$$

Using Eq. A.30 we finally get:

$$\begin{aligned} \int dx \phi_j^*(x) d_{i,f}(x) &= \sum_D c_D \langle N-1, f | \hat{a}_j | n_1^{(D)}, n_2^{(D)}, \dots \rangle \\ &= \sum_D c_D \delta_{1, n_j^{(D)}} (-1)^{\sum_{l=1}^{j-1} n_l^{(D)}} \dots \\ &\quad \langle N-1, f | n_1^{(D)}, n_2^{(D)}, \dots, n_j^{(D)} - 1, \dots \rangle \end{aligned} \quad (\text{D.4})$$

First-Quantization Dyson Orbital

We start from the expression given in Ref. [132]:

$$d_{i,f}(x) = \sqrt{N} \int d\{x_2, \dots, x_N\} \Psi_f^{(N-1)*}(\{x_2, \dots, x_N\}) \Psi_i^{(N)}(\{x, x_2, \dots, x_N\}) \quad (\text{D.5})$$

Projecting onto ϕ_j , expanding the initial state in Slater determinants and using Eq. 2.56 we find:

$$\begin{aligned}
\int dx \phi_j^*(x) d_{i,f}(x) &= \sqrt{N} \int d\{x_2, \dots, x_N\} \Psi_f^{(N-1)*}(\{x_2, \dots, x_N\}) \\
&\quad \int dx \phi_j^*(x) \Psi_i^{(N)}(\{x, x_2, \dots, x_N\}) \\
&= \sum_D c_D \sqrt{N} \int d\{x_2, \dots, x_N\} \Psi_f^{(N-1)*}(\{x_2, \dots, x_N\}) \\
&\quad \frac{1}{\sqrt{N!}} \int dx \phi_j^*(x) \left\langle \{x, x_2, \dots, x_N\} | n_1^{(D)}, n_2^{(D)}, \dots \right\rangle \quad (D.6)
\end{aligned}$$

We now focus on the integral over x and use the expression for the overlap of two antisymmetrized product states to find [42]:

$$\begin{aligned}
\int dx \phi_j^*(x) \left\langle \{x, x_2, \dots, x_N\} | n_1^{(D)}, n_2^{(D)}, \dots \right\rangle &= \\
&= \int dx \phi_j^*(x) \sum_{\Pi} (-1)^{|\Pi|} \prod_{i=2}^N \phi_{\Pi(i)}(x_i) \phi_{\Pi(1)}(x) \\
&= \sum_{\Pi} (-1)^{|\Pi|} \prod_{i=2}^N \phi_{\Pi(i)}(x_i) \int dx \phi_j^*(x) \phi_{\Pi(1)}(x) \quad (D.7)
\end{aligned}$$

From the orthonormality of the orbitals we find that only determinants that contain ϕ_j and permutations that put it at first place can contribute:

$$\int dx \phi_j^*(x) \left\langle \{x, x_2, \dots, x_N\} | n_1^{(D)}, n_2^{(D)}, \dots \right\rangle = \delta_{1, n_j^{(D)}} \sum_{\Pi} (-1)^{|\Pi|} \delta_{j, \Pi(1)} \prod_{i=2}^N \phi_{\Pi(i)}(x_i) \quad (D.8)$$

Finally, we note that these surviving permutations are simply obtained by first moving ϕ_j to first place, which may give us an overall minus sign, depending on its initial position, and then performing all permutations of the remaining $N - 1$ orbitals at the back:

$$\begin{aligned}
\int dx \phi_j^*(x) \left\langle \{x, x_2, \dots, x_N\} | n_1^{(D)}, n_2^{(D)}, \dots \right\rangle &= \\
&= \delta_{1, n_j^{(D)}} (-1)^{\sum_{l=1}^{j-1} n_l^{(D)}} \left\langle \{x_2, \dots, x_N\} | n_1^{(D)}, n_2^{(D)}, \dots, n_j^{(D)} - 1, \dots \right\rangle \quad (D.9)
\end{aligned}$$

Inserting this into Eq. D.6 we find (using Eqs. 2.56 and 2.47):

$$\begin{aligned}
\int dx \phi_j^*(x) d_{i,f}(x) &= \\
&= \sum_D c_D \int d\{x_2, \dots, x_N\} \Psi_f^{(N-1)*}(\{x_2, \dots, x_N\}) \frac{1}{\sqrt{(N-1)!}} \\
&\quad \delta_{1,n_j^{(D)}} (-1)^{\sum_{l=1}^{j-1} n_l^{(D)}} \left\langle \{x_2, \dots, x_N\} | n_1^{(D)}, n_2^{(D)}, \dots, n_j^{(D)} - 1, \dots \right\rangle \\
&= \sum_D c_D \delta_{1,n_j^{(D)}} (-1)^{\sum_{l=1}^{j-1} n_l^{(D)}} \int d\{x_2, \dots, x_N\} \Psi_f^{(N-1)*}(\{x_2, \dots, x_N\}) \\
&\quad \frac{1}{\sqrt{(N-1)!}} \left\langle \{x_2, \dots, x_N\} | n_1^{(D)}, n_2^{(D)}, \dots, n_j^{(D)} - 1, \dots \right\rangle \\
&= \sum_D c_D \delta_{1,n_j^{(D)}} (-1)^{\sum_{l=1}^{j-1} n_l^{(D)}} \left\langle \Psi_f^{(N-1)} | n_1^{(D)}, n_2^{(D)}, \dots, n_j^{(D)} - 1, \dots \right\rangle \quad (D.10)
\end{aligned}$$

Summary

Comparison shows that the expansion coefficients in the one-electron basis are identical and we thus find:

$$\begin{aligned}
d_{i,f}(x) &= \langle x | d_{i,f} \rangle = \langle N-1, f | \hat{\Psi}(x) | N, i \rangle \\
&= \sqrt{N} \int d\{x_2, \dots, x_N\} \Psi_f^{(N-1)*}(\{x_2, \dots, x_N\}) \Psi_i^{(N)}(\{x, x_2, \dots, x_N\}) \quad (D.11)
\end{aligned}$$

Lastly, note that Eq. D.5 is denoted by $d(x_1)$ in Ref. [132] and the authors there continue the text with $d(x_N)$ as their chosen Dyson orbitals. The two expressions however differ at most by an overall sign, which drops out when calculating transition rates, compare Eq. 3.24.

D.2 Photoemission Matrix Element of Periodic Systems

The aim of this section is to show that relative photoemission intensities stay well-defined when approaching the thermodynamic limit. For simplicity, we perform the derivation excluding spin. Inclusion is however trivially done by having lattice-periodic functions u be spin-dependent and summing over spin in the matrix elements $h^{(\text{int})}$.

D.2.1 Crystal-Momentum Conservation

We begin this section by deriving crystal-momentum conservation for a macroscopic but finite surface. As usual, we denote the area of the surface unit-cell A_c such that the area of the macroscopic surface becomes $A = N_1 N_2 A_c$, where N_1, N_2 are the number of in-plane repetitions of the surface unit cell. As argued in Sec. A.1.1, the bound Kohn-Sham (KS) orbitals of such a system are then, in the

interior region of the surface, to good approximation Bloch orbitals $\{\varphi_{n,\mathbf{q}}\}$ with Bloch momenta given by the Γ -centered grid of Eq. A.8:

$$\varphi_{n,\mathbf{q}}(\mathbf{r}) = e^{i\mathbf{q}\cdot\mathbf{r}_{\parallel}} u_{n,\mathbf{q}}(\mathbf{r}) \quad (\text{D.12})$$

They only differ from the Bloch-like nature in the small region around the lateral sides of the surface, and, of course, beyond the lateral sides, where they can be expected to quickly vanish in the vacuum. Normalization of these orbitals over all space leads to the normalization Eq. B.3 for their lattice-periodic parts:

$$\begin{aligned} \int_{\mathbb{R}^3} d^3r |\varphi_{n,\mathbf{q}}|^2 &\approx \int_A d^2r_{\parallel} \int_{\mathbb{R}} dz |\varphi_{n,\mathbf{q}}|^2 \\ &\approx \int_A d^2r_{\parallel} \int_{\mathbb{R}} dz |u_{n,\mathbf{q}}(\mathbf{r})|^2 \\ &= 1 \end{aligned} \quad (\text{D.13})$$

We restrict ourselves in the following to photoelectron states that are in-plane Bloch-states (compare Sec. 3.3.4):

$$\gamma(\mathbf{r}) = e^{i\mathbf{q}_{\gamma}\cdot\mathbf{r}_{\parallel}} u_{\gamma}(\mathbf{r}) \quad (\text{D.14})$$

We assume u_{γ} to be normalized according to Eq. B.19, such that a plane wave (which is the final state we will work with in practice) $\gamma(\mathbf{r}) = (2\pi)^{-3/2} e^{i\mathbf{k}\cdot\mathbf{r}}$ is Dirac-delta normalized, see Eq. A.51 (compare Appendix D.3).

Ground-State POT

We start with ground-state POT, where we use Eq. 3.40 as our starting point, where the photoemission intensity is given by the discrete sum over Bloch momenta and valence bands:

$$I_{0\rightarrow\gamma} \propto \sum_{\mathbf{q}}^{\text{BZ}} \sum_v \left| h_{\gamma,\varphi_{v,\mathbf{q}}}^{(\text{int})} \right|^2 \delta(\omega + \varepsilon_{v,\mathbf{q}} - E_{\text{kin}}) \quad (\text{D.15})$$

We now demand the final states to satisfy periodic boundary conditions at the sides of the finite area, such that their (in-plane) Bloch momenta are restricted to the same Γ -centered grid of Eq. A.8 as the bound orbitals. We will get back to this restriction later. Now, the photoemission matrix element of Eq. D.15 reads (compare Eq. 3.19):

$$\begin{aligned} h_{\gamma,\varphi_{v,\mathbf{q}}}^{(\text{int})} &= \langle \gamma | \mathbf{A} \cdot \hat{\mathbf{p}} | \varphi_{v,\mathbf{q}} \rangle \\ &= -i \int_{\mathbb{R}^3} d^3r \gamma^*(\mathbf{r}) \mathbf{A} \cdot \nabla \varphi_{v,\mathbf{q}}(\mathbf{r}) \\ &= -i \int_{\mathbb{R}^3} d^3r \varphi_{v,\mathbf{q}}(\mathbf{r}) \mathbf{A} \cdot \nabla \gamma^*(\mathbf{r}), \end{aligned} \quad (\text{D.16})$$

where we partially integrated to get to the last line and used the fact that surface terms vanish since the bound states of the finite surface vanish at infinity. Since the bound orbitals quickly vanish in the lateral directions outside the finite surface, it becomes:

$$h_{\gamma,\varphi_{v,\mathbf{q}}}^{(\text{int})} \approx -i \int_A d^2r_{\parallel} \int_{\mathbb{R}} dz \varphi_{v,\mathbf{q}}(\mathbf{r}) \mathbf{A} \cdot \nabla \gamma^*(\mathbf{r}) \quad (\text{D.17})$$

Since the area around the lateral sides only makes up a small part of the surface, we can further write:

$$h_{\gamma, \varphi_{v, \mathbf{q}}}^{(\text{int})} \approx -i \int_A d^2 r_{\parallel} \int_{\mathbb{R}} dz e^{i \mathbf{q} \cdot \mathbf{r}_{\parallel}} u_{v, \mathbf{q}}(\mathbf{r}) \mathbf{A} \cdot \nabla \gamma^*(\mathbf{r}) \quad (\text{D.18})$$

Since the error we make due to these approximations becomes less and less relevant (generally small relevant to the total matrix element), the larger the surface gets (irrelevant in thermodynamic limit, see below), we use from now on the “=” sign again. Inserting also the Bloch-form of the photoelectron wave function and using the product rule, we find:

$$h_{\gamma, \varphi_{v, \mathbf{q}}}^{(\text{int})} = -i \int_A d^2 r_{\parallel} \int_{\mathbb{R}} dz e^{i(\mathbf{q} - \mathbf{q}_{\gamma}) \cdot \mathbf{r}_{\parallel}} u_{v, \mathbf{q}}(\mathbf{r}) [\mathbf{A} \cdot \nabla - i \mathbf{A} \cdot \mathbf{q}_{\gamma}] u_{\gamma}^*(\mathbf{r}) \quad (\text{D.19})$$

By expanding the cell-periodic functions in plane waves, see Eq. A.58, we get:

$$h_{\gamma, \varphi_{v, \mathbf{q}}}^{(\text{int})} = -i \sum_{\mathbf{G}, \mathbf{G}'} \int_A d^2 r_{\parallel} e^{i(\mathbf{q} - \mathbf{q}_{\gamma} + \mathbf{G}' - \mathbf{G}) \cdot \mathbf{r}_{\parallel}} \dots \int_{\mathbb{R}} dz c_{v, \mathbf{q}}(\mathbf{G}', z) [\mathbf{A} \cdot \nabla - i \mathbf{A} \cdot (\mathbf{q}_{\gamma} + \mathbf{G})] c_{\gamma}^*(\mathbf{G}, z) \quad (\text{D.20})$$

Since $\mathbf{q}$ and $\mathbf{q}_{\gamma}$ are Bloch momenta from the Γ -centered grid corresponding to the finite surface's area A , we find:

$$h_{\gamma, \varphi_{v, \mathbf{q}}}^{(\text{int})} = -i \delta_{\mathbf{q}, \mathbf{q}_{\gamma}} A \sum_{\mathbf{G}} \int_{\mathbb{R}} dz c_{v, \mathbf{q}}(\mathbf{G}, z) [\mathbf{A} \cdot \nabla - i \mathbf{A} \cdot (\mathbf{q}_{\gamma} + \mathbf{G})] c_{\gamma}^*(\mathbf{G}, z) \quad (\text{D.21})$$

Using additionally

$$\begin{aligned} \int_{A_c} d^2 r_{\parallel} \int_{\mathbb{R}} dz u_{v, \mathbf{q}}(\mathbf{r}) [\mathbf{A} \cdot \nabla - i \mathbf{A} \cdot \mathbf{q}_{\gamma}] u_{\gamma}^*(\mathbf{r}) &= \\ &= \sum_{\mathbf{G}, \mathbf{G}'} \int_{A_c} d^2 r_{\parallel} \int_{\mathbb{R}} dz e^{i(\mathbf{G}' - \mathbf{G}) \cdot \mathbf{r}_{\parallel}} c_{v, \mathbf{q}}(\mathbf{G}', z) [\mathbf{A} \cdot \nabla - i \mathbf{A} \cdot (\mathbf{q}_{\gamma} + \mathbf{G})] c_{\gamma}^*(\mathbf{G}, z) \\ &= A_c \sum_{\mathbf{G}} \int_{\mathbb{R}} dz c_{v, \mathbf{q}}(\mathbf{G}, z), [\mathbf{A} \cdot \nabla - i \mathbf{A} \cdot (\mathbf{q}_{\gamma} + \mathbf{G})] c_{\gamma}^*(\mathbf{G}, z), \end{aligned} \quad (\text{D.22})$$

we find:

$$h_{\gamma, \varphi_{v, \mathbf{q}}}^{(\text{int})} = -i N_1 N_2 \delta_{\mathbf{q}, \mathbf{q}_{\gamma}} \int_{A_c} d^2 r_{\parallel} \int_{\mathbb{R}} dz u_{v, \mathbf{q}}(\mathbf{r}) [\mathbf{A} \cdot \nabla - i \mathbf{A} \cdot \mathbf{q}_{\gamma}] u_{\gamma}^*(\mathbf{r}) \quad (\text{D.23})$$

We thus see that *crystal momentum is conserved in photoemission*, which is an important result and will help us tremendously when implementing our photoemission formalism.

exPOT

Let us now turn to the exPOT formalism, where we use Eq. 3.60 as our starting point:

$$I_{(m, \mathbf{Q}) \rightarrow \gamma} \propto \sum_{\mathbf{q}} \sum_{v}^{\text{BZ}} \left| h_{\gamma, d(m, \mathbf{Q}), (v, \mathbf{q})}^{(\text{int})} \right|^2 \delta(\omega + \Omega^{(m, \mathbf{Q})} + \varepsilon_{v, \mathbf{q}} - E_{\text{kin}}) \quad (\text{D.24})$$

The Dyson orbitals in exPOT are given by Eq. 3.58 (with $f = v$):

$$\begin{aligned} d_{(m,\mathbf{Q}),(v,\mathbf{q})}(\mathbf{r}) &= \sum_c X_{v,c,\mathbf{q}}^{(m,\mathbf{Q})} \varphi_{c,\mathbf{q}+\mathbf{Q}}(\mathbf{r}) \\ &= \sum_c X_{v,c,\mathbf{q}}^{(m,\mathbf{Q})} \varphi_{c,\mathbf{q}+\mathbf{Q} \bmod \mathbf{G}}(\mathbf{r}), \end{aligned} \quad (\text{D.25})$$

where we used Eq. C.108. They are thus also Bloch functions (composed of Bloch-like bound states) and their lattice-periodic functions are then written as:

$$u_{v,\mathbf{q}}^{(m,\mathbf{Q})}(\mathbf{r}) = \sum_c X_{v,c,\mathbf{q}}^{(m,\mathbf{Q})} u_{c,\mathbf{q}+\mathbf{Q} \bmod \mathbf{G}}(\mathbf{r}) \quad (\text{D.26})$$

Following the above derivation we then we find crystal-momentum conservation in analogy to Eq. D.23 as:

$$\begin{aligned} h_{\gamma,d_{(m,\mathbf{Q}),(v,\mathbf{q})}}^{(\text{int})} &= \\ &= -iN_1N_2\delta_{\mathbf{q}+\mathbf{Q} \bmod \mathbf{G},\mathbf{q}_\gamma} \int_{A_c} d^2r_{\parallel} \int_{\mathbb{R}} dz u_{v,\mathbf{q}}^{(m,\mathbf{Q})}(\mathbf{r}) [\mathbf{A} \cdot \nabla - i\mathbf{A} \cdot \mathbf{q}_\gamma] u_{\gamma}^*(\mathbf{r}) \\ &= -iN_1N_2\delta_{\mathbf{q},\mathbf{q}_\gamma-\mathbf{Q} \bmod \mathbf{G}} \int_{A_c} d^2r_{\parallel} \int_{\mathbb{R}} dz u_{v,\mathbf{q}}^{(m,\mathbf{Q})}(\mathbf{r}) [\mathbf{A} \cdot \nabla - i\mathbf{A} \cdot \mathbf{q}_\gamma] u_{\gamma}^*(\mathbf{r}) \end{aligned} \quad (\text{D.27})$$

D.2.2 Thermodynamic Limit and Renormalization

Ground-State POT

We now again continue with ground-state POT to analyze how our equations behave in the thermodynamic limit. First, note that $u_{v,\mathbf{q}}$ is normalized according to Eq. B.3. Thus, with growing system size N_1 and N_2 , the integral in Eq. D.23 would shrink as $\sim \frac{1}{\sqrt{N_1N_2}}$. Let us now change the normalization to Eq. B.19. Comparison with the old normalization Eq. B.3 shows that we must include a factor of $\sqrt{\frac{(2\pi)^2}{A_cN_1N_2}}$.

Using $u_{v,\mathbf{q}} = \sqrt{\frac{(2\pi)^2}{A_cN_1N_2}} \tilde{u}_{v,\mathbf{q}}$ we get:

$$h_{\gamma,\varphi_{v,\mathbf{q}}}^{(\text{int})} = -i2\pi \sqrt{\frac{N_1N_2}{A_c}} \delta_{\mathbf{q},\mathbf{q}_\gamma} \int_{A_c} d^2r_{\parallel} \int_{\mathbb{R}} dz \tilde{u}_{v,\mathbf{q}}(\mathbf{r}) [\mathbf{A} \cdot \nabla - i\mathbf{A} \cdot \mathbf{q}_\gamma] u_{\gamma}^*(\mathbf{r}) \quad (\text{D.28})$$

Note that, we generally assume the bound states to be restricted to a finite z interval $[0, L]$ while being practically zero outside of it (see Appendix A.1.1). Thus, $\tilde{u}_{v,\mathbf{q}_\gamma}$ is restricted to this integral (vanishes outside), such that we can write:

$$h_{\gamma,\varphi_{v,\mathbf{q}}}^{(\text{int})} = -i2\pi \sqrt{\frac{N_1N_2}{A_c}} \delta_{\mathbf{q},\mathbf{q}_\gamma} \int_{A_c} d^2r_{\parallel} \int_0^L dz \tilde{u}_{v,\mathbf{q}}(\mathbf{r}) [\mathbf{A} \cdot \nabla - i\mathbf{A} \cdot \mathbf{q}_\gamma] u_{\gamma}^*(\mathbf{r}) \quad (\text{D.29})$$

Finally, we can re-insert the matrix element into the photoemission intensity Eq. D.15. The Kronecker delta eliminates the sum over the Brillouin zone and

we absorb the constant prefactor $\left[2\pi\sqrt{\frac{N_1 N_2}{A_c}}\right]^2$ into the proportionality (we calculate *relative* intensities) such that we find:

$$I_{0\rightarrow\gamma} \propto \sum_v \left| \tilde{h}_{\gamma,\varphi_{v,\mathbf{q}_\gamma}}^{(\text{int})} \right|^2 \delta(\omega + \varepsilon_{v,\mathbf{q}_\gamma} - E_{\text{kin}}), \quad (\text{D.30})$$

with the *renormalized* matrix element:

$$\tilde{h}_{\gamma,\varphi_{v,\mathbf{q}}}^{(\text{int})} = \delta_{\mathbf{q},\mathbf{q}_\gamma} \int_{A_c} d^2 r_{\parallel} \int_0^L dz \tilde{u}_{v,\mathbf{q}}(\mathbf{r}) [\mathbf{A} \cdot \nabla - i\mathbf{A} \cdot \mathbf{q}_\gamma] u_\gamma^*(\mathbf{r}) \quad (\text{D.31})$$

Approaching now the thermodynamic limit, we can see that the renormalized matrix elements and the (relative) photoemission intensities stay well-defined, that is, they do not diverge! Further, since we used the normalization Eq. B.19 – which is independent of the system size – the expression also does not vanish in the thermodynamic limit.

In addition, our approximation for the bound states – that they are Bloch functions – becomes exact in this limit and the edge effects in the photoemission integral – which we neglected above, see Eqs. D.17 and D.18 – become irrelevant¹⁴⁰. And finally, the periodic boundary conditions we forced on the photoelectron state become irrelevant in the thermodynamic limit. That is, the grid of allowed photoelectron Bloch momenta becomes arbitrarily dense (the same holds for the bound orbitals). At one specific photoelectron state, the formula for calculating the intensity at that specific photoelectron state however remains unchanged and well-defined. Note also, that in practice we can choose to normalize the surface-unit-cell periodic functions to any (finite) value over A_c (as long as we normalize them consistently the same, of course) since the normalization drops out anyway when calculating relative intensities.

To summarize, we can approach an infinite surface by making our finite surface arbitrarily large. In the process, the grid of allowed Bloch momenta becomes arbitrarily dense (like the rational numbers $\mathbb{Q}$ are dense in $\mathbb{R}$) and relative photoemission intensities stay well-defined, justifying the use of our photoemission formalism in combination with an arbitrarily large surface (model system) with a Brillouin zone sampling that approaches continuity.

exPOT

We can again perform similar steps in the exPOT formalism. Following the same derivation and introducing

$$\tilde{u}_{v,\mathbf{q}}^{(m,\mathbf{Q})}(\mathbf{r}) = \sum_c X_{v,c,\mathbf{q}}^{(m,\mathbf{Q})} \tilde{u}_{c,\mathbf{q}+\mathbf{Q} \bmod \mathbf{G}}(\mathbf{r}), \quad (\text{D.32})$$

¹⁴⁰The infinite surface has no ends; more formally: the edge area becomes vanishingly small compared to the interior, such that the integral there is vanishingly small compared to the interior. If, in a special case, there exists a photoelectron state where the integral in the interior vanishes while the integral on the edge does not, then the resulting matrix element is still vanishingly small compared to the photoemission intensities of other photoelectron states with nonzero interior integral. And since we calculate relative intensities, the intensity of the prior is then still vanishingly small.

we then ultimately find:

$$I_{(m,\mathbf{Q}) \rightarrow \gamma} \propto \sum_v \left| \tilde{h}_{\gamma, d(m,\mathbf{Q}), (v, \mathbf{q}_\gamma - \mathbf{Q} \bmod \mathbf{G})}^{(\text{int})} \right|^2 \delta(\omega + \Omega^{(m,\mathbf{Q})} + \varepsilon_{v, \mathbf{q}_\gamma - \mathbf{Q} \bmod \mathbf{G}} - E_{\text{kin}}), \quad (\text{D.33})$$

with the renormalized matrix element:

$$\begin{aligned} \tilde{h}_{\gamma, d(m,\mathbf{Q}), (v, \mathbf{q}_\gamma - \mathbf{Q} \bmod \mathbf{G})}^{(\text{int})} &= \\ &= \delta_{\mathbf{q}, \mathbf{q}_\gamma - \mathbf{Q} \bmod \mathbf{G}} \int_{A_c} d^2 r_{\parallel} \int_0^L dz \tilde{u}_{v, \mathbf{q}}^{(m, \mathbf{Q})}(\mathbf{r}) [\mathbf{A} \cdot \nabla - i \mathbf{A} \cdot \mathbf{q}_\gamma] u_\gamma^*(\mathbf{r}) \end{aligned} \quad (\text{D.34})$$

For reference, note explicitly that:

$$\tilde{u}_{v, \mathbf{q}_\gamma - \mathbf{Q} \bmod \mathbf{G}}^{(m, \mathbf{Q})}(\mathbf{r}) = \sum_c X_{v, c, \mathbf{q}_\gamma - \mathbf{Q} \bmod \mathbf{G}}^{(m, \mathbf{Q})} \tilde{u}_{c, \mathbf{q}_\gamma}(\mathbf{r}) \quad (\text{D.35})$$

Having followed the above steps, note that the renormalized matrix element will with the current normalization go to zero when approaching the thermodynamic limit, which is a consequence of the fact that the Bethe-Salpeter equation (BSE) eigenvector is generally normalized via (compare Eq. C.71):

$$\sum_{v, c} \sum_{\mathbf{q}}^{\text{BZ}} |X_{v, c, \mathbf{q}}^{(m, \mathbf{Q})}|^2 = 1, \quad (\text{D.36})$$

such that we can generally expect $\tilde{u}_{v, \mathbf{q}}^{(m, \mathbf{Q})} \sim \frac{1}{\sqrt{N_1 N_2}}$ with growing system size N_1 , N_2 (number of Bloch momenta in BZ equals number of unit-cell repetitions, see Eq. A.8). In practice this is not a concern, since we never actually approach the thermodynamic limit, compare the discussion at the end of Appendix C.1.4. If we were concerned with this, this problem could however easily be mitigated, by normalizing the BSE eigenvectors such that individual values do not go to zero (e.g. multiply them by $\sqrt{N_1 N_2}$) and absorbing the resulting factor into the proportionality constant such that it again is irrelevant for relative photoemission intensities.

D.2.3 Renormalized Matrix Elements and Discrete Fourier Transform

The aim of this section is to further evaluate the renormalized photoemission matrix elements of ground-state POT, Eq. D.31 and exPOT, Eq. D.34, which may generally be written as:

$$\tilde{h}_{\gamma, d}^{(\text{int})} = \int_{A_c} d^2 r_{\parallel} \int_0^L dz u_d(\mathbf{r}) [\mathbf{A} \cdot \nabla - i \mathbf{A} \cdot \mathbf{q}_\gamma] u_\gamma^*(\mathbf{r}) \quad (\text{D.37})$$

with in-plane unit-cell-periodic functions u_d and u_γ . In ground-state POT we simply have

$$u_d(\mathbf{r}) = \tilde{u}_{v, \mathbf{q}_\gamma}(\mathbf{r}), \quad (\text{D.38})$$

while in exPOT we have (see Eq. D.35):

$$\begin{aligned} u_d(\mathbf{r}) &= \tilde{u}_{v, \mathbf{q}_\gamma - \mathbf{Q} \bmod \mathbf{G}}^{(m, \mathbf{Q})}(\mathbf{r}) \\ &= \sum_c X_{v, c, \mathbf{q}_\gamma - \mathbf{Q} \bmod \mathbf{G}}^{(m, \mathbf{Q})} \tilde{u}_{c, \mathbf{q}_\gamma}(\mathbf{r}) \end{aligned} \quad (\text{D.39})$$

Now, remember that $[0, L]$ is the z interval that the bound orbitals are located in (assumed practically zero outside this interval). In practice, this finite interval in z direction is determined by the used *repeated slab unit cell* and the bound states are calculated in this approach (see comments on periodic boundary conditions and vanishing boundary conditions throughout Appendix A.1.1 for details, e.g. the paragraph around Eq. A.9). The integral then runs over the volume of the slab and we write u_d inside this volume as (slab-periodic; again, see paragraph around Eq. A.9; see also Appendix A.4.1)

$$u_d(\mathbf{r}) = \sum_{\mathbf{G}} c_d(\mathbf{G}) e^{i\mathbf{G} \cdot \mathbf{r}}, \quad (\text{D.40})$$

with ($\mathbf{b}_i$ is the i -th reciprocal cell vector of the slab):

$$\{\mathbf{G}\} = \left\{ \sum_{i=1}^3 n_i \mathbf{b}_i \mid n_i = \dots - 2, -1, 0, 1, 2, \dots \right\} \quad (\text{D.41})$$

Note that, while we argued here based on the repeated-slab calculations we perform in practice, such an expansion of u_d inside the interval $[0, L]$ is generally possible and not restricted to such calculations.

Inserting this expansion into photoemission matrix element we get:

$$\tilde{h}_{\gamma, d}^{(\text{int})} = \sum_{\mathbf{G}} c_d(\mathbf{G}) \int_{A_c} d^2 r_{\parallel} \int_0^L dz e^{i\mathbf{G} \cdot \mathbf{r}} [\mathbf{A} \cdot \nabla - i\mathbf{A} \cdot \mathbf{q}_\gamma] u_\gamma^*(\mathbf{r}) \quad (\text{D.42})$$

While we use this expression in the main text for the plane-wave final states, it holds for all in-plane-Bloch photoemission states, for example for the damped plane-wave state of Ref. [35].

D.3 Fermi's Golden Rule

The aim of this section is to give precise meaning to the transition rate density of Eq. 3.15 and to give additional details of the practical calculation of photoemission intensity distributions. For simplicity, we omit the photoelectron-spin in the derivation. Its inclusion is however trivial for systems/treatments with pure spin-up/down photoelectron final states, with transition rates and intensities simply acquiring an additional dependence on s ($s = \uparrow / \downarrow$) by using photoelectron states $\gamma_{\mathbf{k}, s}$ in place of $\gamma_{\mathbf{k}}$.

D.3.1 Transitions to the Continuous Spectrum

As detailed in Sec. 3.3.3, we model the N -electron states after photoemission as an antisymmetrized product states each consisting of an $N - 1$ -electron eigenstate

$|N - 1, f\rangle$ (energy $E(N - 1, f)$) and a one-electron scattering/photoelectron state $|\gamma\rangle$ (energy E_{kin}):

$$\begin{aligned} |N, (f, \gamma)\rangle &\approx \frac{1}{\sqrt{N!}} \hat{\mathcal{A}}(|\gamma\rangle \otimes |N - 1, f\rangle) \\ E(N, f) &\approx E(N - 1, f) + E_{\text{kin}} \end{aligned} \quad (\text{D.43})$$

The prefactor originates from Eq. A.23 and guarantees us that these product states are properly orthonormalized, provided that the $N - 1$ -electron states are orthogonal and normalized to 1 (bound states) and the photoelectron states are orthogonal and Dirac-delta normalized (scattering states, see Appendix A.1.1). This can be seen by expressing the $N - 1$ -electron states as a linear combination of Slater determinants (antisymmetrized product states based on some set of orthonormal orbitals, compare Appendix A.1.2),

$$|N - 1, f\rangle = \sum_D c_D^{(f)} |\phi_{D(1)}, \phi_{D(2)}, \dots, \phi_{D(N-1)}\rangle, \quad (\text{D.44})$$

such that we get:

$$\begin{aligned} \langle N, (f, \gamma) | N, (f', \gamma') \rangle &= \\ &= \frac{1}{N!} \hat{\mathcal{A}}(\langle \gamma | \otimes \langle N - 1, f |) \hat{\mathcal{A}}(|\gamma'\rangle \otimes |N - 1, f'\rangle) \\ &= \frac{1}{N!} \sum_{D, D'} c_D^{(f)*} c_{D'}^{(f')} \hat{\mathcal{A}}(\langle \gamma | \otimes \langle \phi_{D(1)}, \phi_{D(2)}, \dots, \phi_{D(N-1)} |) \dots \\ &\quad \hat{\mathcal{A}}(|\gamma'\rangle \otimes |\phi_{D'(1)}, \phi_{D'(2)}, \dots, \phi_{D'(N-1)}\rangle) \\ &= \sum_{D, D'} c_D^{(f)*} c_{D'}^{(f')} \langle \gamma, \phi_{D(1)}, \phi_{D(2)}, \dots, \phi_{D(N-1)} | \gamma', \phi_{D'(1)}, \phi_{D'(2)}, \dots, \phi_{D'(N-1)} \rangle \\ &= \sum_{D, D'} c_D^{(f)*} c_{D'}^{(f')} \sum_{\Pi} (-1)^{|\Pi|} \langle \gamma | \psi_{\Pi(1)} \rangle \langle \phi_{D(1)} | \psi_{\Pi(2)} \rangle \dots \langle \phi_{D(N-1)} | \psi_{\Pi(N)} \rangle, \end{aligned} \quad (\text{D.45})$$

where ψ_i is the i -th element of the ordered set $\{\gamma', \phi_{D'(1)}, \phi_{D'(2)}, \dots, \phi_{D'(N-1)}\}$ and the step to the last line can be found in Ref. [42]. We now assume that the photoelectron states are orthogonal to all orbitals used in the $N - 1$ -electron final states¹⁴¹. Under this assumption, only permutations can survive that leave γ' at first place. The remaining permutations are precisely the ones we would find when only calculating the overlap between $|N - 1, f\rangle$ and $|N - 1, f'\rangle$ and they have the same number of transpositions as those that would occur there. We thus find:

$$\langle N, (f, \gamma) | N, (f', \gamma') \rangle = \langle \gamma | \gamma' \rangle \langle N - 1, f | N - 1, f' \rangle \quad (\text{D.46})$$

As detailed in Sec. 3.3.4, we generally index the photoelectron states by their photoelectron momentum $\mathbf{k}$, such that their orthonormalization reads $\langle \gamma_{\mathbf{k}} | \gamma_{\mathbf{k}'} \rangle = \delta(\mathbf{k} - \mathbf{k}')$.

¹⁴¹In line with Sec. 3.3.5 this assumption becomes exact when using scattering KS states as our photoelectron states and bound KS states for the construction of the $N - 1$ -electron final states while it is not generally true for a PWFS. In practice, we assume that the resulting inconsistent normalization of the N -electron (sudden-approximation-)final states can be ignored. See also comments below for a discussion of normalization-issues in practice.

Note that we will in practice approximate the $N - 1$ -electron final states by *quasiparticle* (QP) states, see Sec. 3.3.9. We interpret these as approximate eigenstates with well-defined energies to justify using them in Fermi's golden rule. Note further, that these states are generally not orthonormal! Note however, that under the assumption of a normalized single Slater determinant ground state (which we routinely assume in Sec. 3.3), we can explicitly write these states in the form of Eq. 2.174 and they are then automatically orthonormal, as explained below Eq. 2.176. If the ground state is an unnormalized single Slater determinant, then these QP states are still orthogonal and are all normalized to the same value. Normalization to the same value is in fact all we need, since this norm drops out anyway when calculating relative photoemission intensities (see below). We thus generally assume in practice that the ground state is close-enough to a single Slater determinant, or, more generally, that our QP final states (be they Eq. 2.174 or the more general Eq. 2.172) are approximately normalized¹⁴² equally (such that no final state is artificially preferred in Fermi's golden rule, which becomes particularly important when summing over the final states to get the photoemission intensity, see below). In the following derivation, we will however assume that they are fully orthonormal eigenstates of the Hamiltonian, with these comments in mind.

Similar comments can be made about the initial state. In ground-state POT, the initial state is the ground state, while in exciton POT we usually work with the exciton states Eq. 2.226 (or Eq. 2.232). Note that the latter generally assume a single Slater determinant ground state, in line with the comments made above about the final states. As explained below Eq. 2.226, these states are normalized if the ground state is normalized (and the BSE eigenvector is normalized). If we are only interested in the photoemission intensity distribution relative to some specific initial state – which is usually the case – the initial state's normalization is in fact irrelevant again, since it drops out in relative intensities. Only if intensities for different initial states were to be compared would this normalization become relevant. See also comments below Eq. 3.30. In the following, we will however again assume the initial state to be normalized.

Provided that the N -electron initial state is normalized, $\langle N, i | N, i \rangle = 1$, we can then follow Ref. [126] to find the *transition rate density* from the initial state $|N, i\rangle$ to the final state Eq. D.43 under the perturbation Eq. 3.8 as (neglecting again the emission part):

$$W_{i \rightarrow f, \gamma} = 2\pi \left| \langle N, (f, \gamma) | \hat{H}_{\text{int}} | N, i \rangle \right|^2 \delta(\omega + E(N, i) - E(N - 1, f) - E_{\text{kin}}) \quad (\text{D.47})$$

That is, $W_{i \rightarrow f, \gamma}$ gives us – at large times – the probability (density) per unit time for a transition from the initial to the (one specific) final state to occur¹⁴³.

Importantly, since the final state is a continuum state and our experiments do not have perfect resolution, we can never meaningfully measure the transition rate

¹⁴²Note that assuming/demanding them to be normalized is of course a sane approach. After all they replace the exact $N - 1$ -electron eigenstates in the one-particle Green's function, whose normalization was essential in the derivation of the Lehmann representation, see for example the expansion made in Eq. 2.130.

¹⁴³Note that it is a *probability mass function* with respect to the discrete $N - 1$ -electron final states! This is why we can pick out one specific $|N - 1, f\rangle$ when calculating transition rates (see below), while the scattering-state must be integrated over. Compare the discussion involving spin and position in Sec. 2.2.1.

to such a single final state, but get instead the rate for the transition to a *group of final states*. As detailed in Sec. 3.3.4, we can generally index our photoelectron states by the photoelectron momentum $\mathbf{k}$ which is related to their energy via $E_{\text{kin}} = \frac{k^2}{2}$. We can thus also index them by the direction $\mathbf{k}/k$ and the kinetic energy E_{kin} . In photoemission experiments the photoemission intensity is then generally obtained for a finite interval δE_{kin} in the kinetic energy and a finite domain of photoelectron directions which can be expressed as a solid-angle $\delta\Omega$. The transition rate to a set of final states with the $N-1$ -electron in the state $|N-1, f\rangle$, the photoelectron momentum in the interval δE_{kin} around the value E_{kin} and the solid angle $\delta\Omega$ around $\mathbf{k}/k$ is then given by [126]:

$$W_{i \rightarrow f, (\delta E_{\text{kin}}, \delta\Omega)} = \int_{\delta E_{\text{kin}}} d\tilde{E}_{\text{kin}} \int_{\delta\Omega} d\tilde{\Omega} \rho(\tilde{E}_{\text{kin}}) W_{i \rightarrow f, \gamma=(\tilde{E}_{\text{kin}}, \tilde{\mathbf{k}}/\tilde{k})}, \quad (\text{D.48})$$

where ρ is the density of scattering states and is given by:

$$\rho(E_{\text{kin}}) = \sqrt{2E_{\text{kin}}} \quad (\text{D.49})$$

Neglecting (for now) energy uncertainties for simplicity, the N -electron initial and $N-1$ -electron final states as well as the probe energy ω determine the photoelectron kinetic energy at which a transition can occur. If this energy is not in δE_{kin} , then $W_{i \rightarrow f, (\delta E_{\text{kin}}, \delta\Omega)}$ vanishes. On the other hand, if it is in the interval, then we can use the Dirac delta. In total, we thus find:

$$\begin{aligned} W_{i \rightarrow f, (\delta E_{\text{kin}}, \delta\Omega)} &= \\ &= 2\pi\rho(\omega + E(N, i) - E(N-1, f)) \int_{\delta\Omega} d\tilde{\Omega} \left| \langle N, (f, \tilde{\gamma}) | \hat{H}_{\text{int}} | N, i \rangle \right|^2 \\ &\quad \mathbf{1}(\omega + E(N, i) - E(N-1, f) \in \delta E_{\text{kin}}) \\ &\quad \tilde{\gamma} = (\omega + E(N, i) - E(N-1, f), \tilde{\mathbf{k}}/\tilde{k}), \end{aligned} \quad (\text{D.50})$$

where the indicator function $\mathbf{1}$ equals 1 if its argument is true and 0 else. Assuming the energy-window δE_{kin} to be small enough such that quantities are approximately constant in it, we can also express the above via the middle-point E_{kin} of the energy window:

$$\begin{aligned} W_{i \rightarrow f, (\delta E_{\text{kin}}, \delta\Omega)} &= 2\pi\rho(E_{\text{kin}}) \int_{\delta\Omega} d\tilde{\Omega} \left| \langle N, (f, \tilde{\gamma}) | \hat{H}_{\text{int}} | N, i \rangle \right|^2 \\ &\quad \mathbf{1}(\omega + E(N, i) - E(N-1, f) \in \delta E_{\text{kin}}) \\ &\quad \tilde{\gamma} = (E_{\text{kin}}, \tilde{\mathbf{k}}/\tilde{k}) \end{aligned} \quad (\text{D.51})$$

The kinetic energy E_{kin} describes a hemisphere in the configuration space $\{\mathbf{k}\}$ of photoelectron momenta (enforcing as usual $k_z > 0$) and the solid angle $\delta\Omega$ defines an area on this sphere. Suppose now that the solid angle $\delta\Omega$ is small and positioned (for the hemisphere at E_{kin}) around the in-plane momenta k_x and k_y (which define a point on the hemisphere). Under the assumption that the matrix element is approximately constant on the small solid angle we find:

$$\begin{aligned} W_{i \rightarrow f, (\delta E_{\text{kin}}, \delta\Omega)} &= 2\pi\rho(E_{\text{kin}})\delta\Omega \left| \langle N, (f, \gamma_{\mathbf{k}}) | \hat{H}_{\text{int}} | N, i \rangle \right|^2 \\ &\quad \mathbf{1}(\omega + E(N, i) - E(N-1, f) \in \delta E_{\text{kin}}), \\ &\quad \mathbf{k} = (k_x, k_y, \sqrt{2E_{\text{kin}} - k_x^2 - k_y^2})^T \end{aligned} \quad (\text{D.52})$$

Finally, as detailed in Sec. 3.3.8, we arrive at the relative photoemission intensity by additionally summing over the $N - 1$ -electron final states and dropping constant prefactors:

$$I_{i \rightarrow \delta E_{\text{kin}}, \delta \Omega} \propto k \delta \Omega \sum_f \left| \langle N, (f, \gamma_{\mathbf{k}}) | \hat{H}_{\text{int}} | N, i \rangle \right|^2 \mathbf{1}(\omega + E(N, i) - E(N - 1, f) \in \delta E_{\text{kin}}), \quad (\text{D.53})$$

where we used Eq. D.49. On a sidenote, this equation is fully compatible with periodic systems and the treatment of Appendix D.2, where the sum over f becomes a sum over v and $\mathbf{q}$ and where the latter sum is eliminated by crystal-momentum conservation.

D.3.2 Momentum Maps and Band-Structure Plots

Our most common way of analyzing the photoemission distribution for a given N -electron initial state $|N, i\rangle$ is to plot the intensity distribution at a fixed photoelectron kinetic energy E_{kin} , or, more precisely, for a small interval δE_{kin} that includes this value. To do so, we usually define a square grid of in-plane momenta $\{(k_x, k_y)\}$, which can be thought of as being put on top of the hemisphere defined by E_{kin} . By convention, we assign the square around each grid point (k_x, k_y) to the grid point. This area is often called the $k_x - k_y$ bin. Each grid point (k_x, k_y) then represents a group of in-plane photoelectron momenta, namely the ones that lie in this square/bin. Next, we can assign the area $\delta A(k_x, k_y)$ on the hemisphere which lies below that square to the grid point (k_x, k_y) . Finally, this area $\delta A(k_x, k_y)$ defines a solid angle $\delta \Omega(k_x, k_y)$ which we thus identify with the grid point (k_x, k_y) . This solid angle must then be used in Eq. D.53 to calculate the transition rate to the photoelectron states with kinetic energy in δE_{kin} and in-plane photoelectron momenta in the $k_x - k_y$ bin. Of course, application of Eq. D.53 assumes that the used momentum grid is fine-enough such that the corresponding solid angles are small.

Let us now calculate $\delta \Omega(k_x, k_y)$. To do so, we first calculate the surface area $\delta A(k_x, k_y)$. For a hemisphere of radius $k = \sqrt{2E_{\text{kin}}}$, we find the point k_z on the hemisphere to lie at:

$$k_z(k_x, k_y) = \sqrt{(k^2 - k_x^2 - k_y^2)} \quad (\text{D.54})$$

As usual, the surface area element is then given by:

$$dA = \sqrt{1 + \left(\frac{\partial k_z}{\partial k_x}\right)^2 + \left(\frac{\partial k_z}{\partial k_y}\right)^2} dk_x dk_y \quad (\text{D.55})$$

We then find:

$$\delta A(k_x, k_y) = \int_{k_x-h/2}^{k_x+h/2} d\tilde{k}_x \int_{k_y-h/2}^{k_y+h/2} d\tilde{k}_y \frac{k}{\sqrt{k^2 - \tilde{k}_x^2 - \tilde{k}_y^2}} \theta(k^2 - \tilde{k}_x^2 - \tilde{k}_y^2), \quad (\text{D.56})$$

where we assumed that our grid-spacing h is the same in k_x and k_y direction. Note that the Heaviside function θ is only relevant for grid points near the equator (see

below), where it ensures that we only integrate over the $k_x - k_y$ region which lies above the sphere. We now assume that our grid-spacing is fine-enough such that the integrand is approximately constant in the square and we find:

$$\delta A(k_x, k_y) \approx h^2 \frac{k}{\sqrt{k^2 - k_x^2 - k_y^2}} \quad (\text{D.57})$$

Note that this approximation is problematic in the “outermost ring” of grid points, which lie along the equator of the sphere, since there, (i) part of the integrand should vanish for these points due to the Heaviside function and (ii) the integrand rapidly changes when approaching the equator, such that the position of the grid point relative to the equator heavily influences the resulting value when using Eq. D.57. Instead of explicitly treating these points we can however simply remove them from our plots, which is justified when using a fine-enough grid-spacing where they would have only contributed a vanishingly thin outer ring in the created momentum maps. Note also, that for grid points that lie beyond the equator, Eq. D.57 is of course ill-defined, and $\delta A(k_x, k_y)$ is instead – as demanded by the Heaviside function – set to 0. In the following we will simply write $\delta A(k_x, k_y)$ via Eq. D.57 and implicitly understand these two points.

The solid angle at (k_x, k_y) is then simply given by:

$$\delta \Omega(k_x, k_y) = \frac{\delta A(k_x, k_y)}{k^2} \approx h^2 \frac{1}{k \sqrt{k^2 - k_x^2 - k_y^2}} \quad (\text{D.58})$$

With this result we can now finally write the photoemission intensity for δE_{kin} and for the in-plane momentum bin $k_x - k_y$ as:

$$I_{i \rightarrow \delta E_{\text{kin}}, \delta \Omega} \propto \frac{1}{\sqrt{k^2 - k_x^2 - k_y^2}} \sum_f \left| \langle N, (f, \gamma_{\mathbf{k}}) | \hat{H}_{\text{int}} | N, i \rangle \right|^2 \mathbf{1}(\omega + E(N, i) - E(N - 1, f) \in \delta E_{\text{kin}}), \quad (\text{D.59})$$

where we dropped the constant h^2 prefactor. Lastly, remember that we want to simulate photoemission experiments, which is why we adapted our formalism to the finite resolution in energy- and in-plane-momentum-measurements, as detailed above Eq. D.48. While our formula for the photoemission intensity now gives us the intensity over a finite energy-window and in-plane momentum area, the used formalism and resulting values do not fully correspond to what is measured experimentally! Imagine, for example, that the “true kinetic energy” of a photoelectron lies at the edge of the interval δE_{kin} . Then, due to its finite accuracy, the detector may detect it as belonging to this interval (as does our current formalism), but may also, with a smaller probability, detect it as belonging to the neighboring interval, or, even one of the next neighbors. For example, in the experiments underlying Chapter 5, kinetic energies were experimentally obtained with a measurement uncertainty of ≈ 150 meV (standard deviation) [16]. To account for this (and at the same time also account for true energy uncertainties/broadening, for example at ultra-short pulse-durations, see Sec. 3.2) in our calculations, we replace the Dirac delta in Eq. D.47 by a Gaussian that is centered at $\omega + E(N, i) - E(N - 1, f)$ and has a standard deviation corresponding to the measurement error of the detector. Assuming the energy-interval δE_{kin} to be small we can evaluate the integrand at

E_{kin} and find The resulting photoemission intensity formula then reads:

$$I_{i \rightarrow \delta E_{\text{kin}}, \delta \Omega} \propto \frac{\delta E_{\text{kin}}}{\sqrt{k^2 - k_x^2 - k_y^2}} \sum_f \left| \langle N, (f, \gamma_{\mathbf{k}}) | \hat{H}_{\text{int}} | N, i \rangle \right|^2 \exp \left(- \frac{[E_{\text{kin}} - (\omega + E(N, i) - E(N - 1, f))]^2}{2\sigma_E^2} \right), \quad (\text{D.60})$$

where the Gaussian's prefactor is irrelevant for relative intensities. Note that the same argument can be made with respect to the in-plane momenta, which is why we often apply Gaussian filters onto calculated momentum maps (or band structures) calculated with Eq. D.60, where we use a standard deviation σ_k corresponding to the experimental k_x and k_y measurement uncertainty (which is usually the same in both directions). Note that this is essentially Eq. 3.32, however with additionally the $\mathbf{k}$ -dependent prefactor and a Gaussian in place of the Dirac delta.

Note that when plotting a single momentum map, the energy window δE_{kin} is irrelevant for the relative intensities – only a single value E_{kin} suffices. This is why we often simply speak of a momentum map *at kinetic energy* E_{kin} . If intensities are to be compared among multiple momentum maps, it is then implicitly assumed that they belong to equally-sized energy intervals. Similarly, when plotting photoemission band-structures (see below), we divide the kinetic-energy axis into equally sized intervals, such that the size δE_{kin} of each interval again drops out when plotting the relative intensities.

Note that there are different ways in which momentum maps can be plotted. If we want to plot the photoemission intensity per $k_x - k_y$ bin then we use Eq. D.60. This is shown in the central column of Fig. D.1 for the HOMO of an isolated (gas-phase) PTCDA molecule (thus, we remove the sum over f and only use $f = \text{HOMO}$ – this way, upon independent normalization of each momentum map, the Gaussian becomes irrelevant and can also be dropped). Conversely, it is also common to drop the $\frac{1}{\sqrt{k^2 - k_x^2 - k_y^2}}$ -prefactor when plotting momentum maps. For a single, individually normalized (for example to a maximum value of 1) momentum map this corresponds to dividing the photoemission intensity of each bin by the solid angle represented by the bin, or, equivalently (since k is constant on a single momentum map and since we normalize the map) by the surface-area on the hemisphere that corresponds to the bin. This can also be understood as first plotting the photoemission intensity distribution *on the hemisphere* and then looking at the hemisphere from atop (To see this, imagine the matrix-element $\left| \langle N, (f, \gamma_{\mathbf{k}}) | \hat{H}_{\text{int}} | N, i \rangle \right|^2$ is angle-independent. Then, the intensity is the same for each point (k_x, k_y) on the hemisphere and, when plotting the intensity on the hemisphere, it should have a single solid color. If we plot a momentum map without the prefactor, it will also be of a single – the same – solid color.). This way of plotting momentum maps is shown in the left column of Fig. D.1 and the prefactor $\frac{1}{\sqrt{k^2 - k_x^2 - k_y^2}}$ is shown in the right column. As can be seen, visual differences only occur when dominant photoemission features approach the equator, while the inner regions of the momentum maps look practically identical. The other theoretical momentum maps shown throughout this text are all calculated *without* the prefactor.

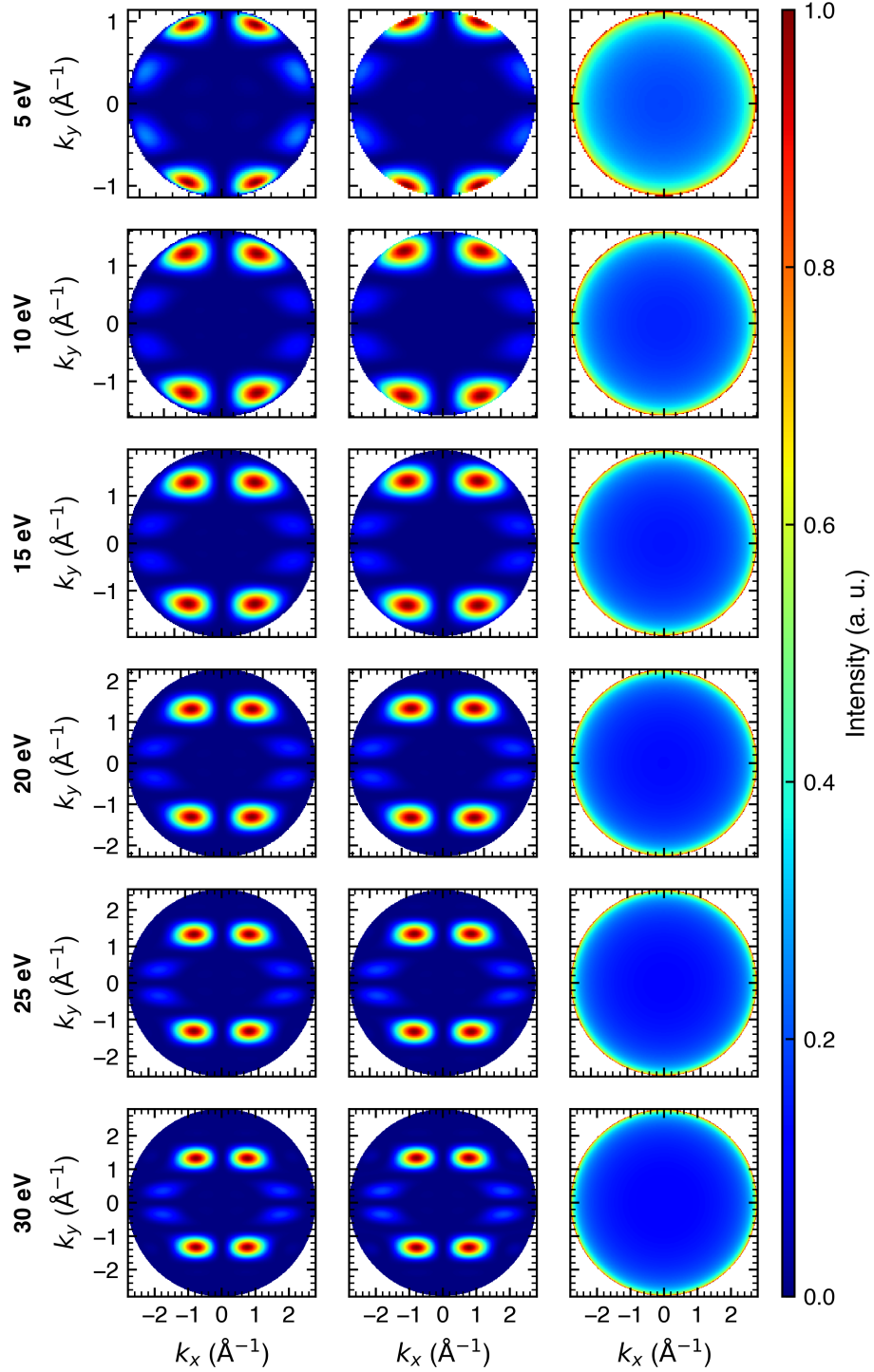


Figure D.1: Different ways of plotting momentum maps. Different rows show momentum maps of PTCDA's HOMO (gas-phase) at different kinetic energies (and without the $|\mathbf{A} \cdot \mathbf{k}|^2$ prefactor, compare Eq. 3.39). The left column shows photoemission intensity per $k_x - k_y$ bin, divided by the solid angle of the bin. The middle column shows photoemission intensity per $k_x - k_y$ bin. The right column shows the solid angle per bin. Multiplying the two outer columns results (up to normalization) in the central one. Each momentum map is individually normalized to a maximum value of 1.

While we restricted the above discussion to momentum maps, we can also use

Eq. D.60 for the creation of photoemission band-structure plots. In these plots, the kinetic energy typically spans the vertical axis and a path in the $k_x - k_y$ -plane spans the horizontal axis. We then subdivide the kinetic-energy interval of interest into small sub-intervals of equal size δE_{kin} . Similarly, we divide the in-plane momenta into bins of size h^2 , as explained above. Each point on the chosen momentum-path then falls into one of these bins. At each kinetic energy (the center of each sub-interval) we can then use Eq. D.60 to calculate the intensities for the relevant bins. Additionally, we may apply a Gaussian filter for the momenta – typically only in the path’s direction. As detailed below Eq. D.57, at each kinetic energy, we can simply set the intensity of bins that cross the equator at that kinetic energy to zero to avoid numerical complications. An example of such a band structure is shown in Fig. 4.4. See also Fig. D.2 which shows the prefactor $\frac{1}{\sqrt{k^2 - k_x^2 - k_y^2}}$ for different energy- and momentum-intervals.

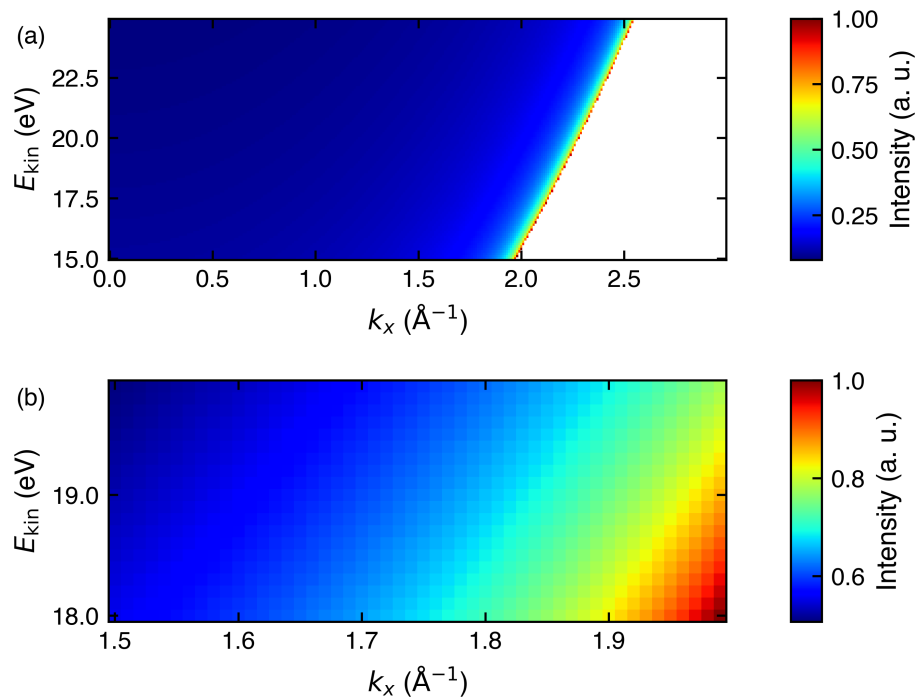


Figure D.2: Influence of the photoemission intensity prefactor $\frac{1}{\sqrt{k^2 - k_x^2 - k_y^2}}$ on band-structure plots. Panels (a) and (b) show two different E_{kin} - and k_x intervals at $k_y = 0$. The prefactor was individually normalized to a maximum value of 1 in each plot.

D.3.3 Large-Energy-Interval Integration

To improve statistics we often integrate experimental photoemission intensity data over large kinetic-energy windows, often on the order of ≈ 0.5 eV. To mimic such experimental data the same integration should be performed on the theory-side. Since we are integrating over such large kinetic-energy windows it is in this case not necessary to replace the Dirac delta by a Gaussian, which was only introduced above to make sure that theoretical momentum maps at a given kinetic energy and small kinetic-energy window include all photoelectrons that can appear at that energy in experiments. When instead working with a large energy-window

they are all included anyway in the integrated photoemission data¹⁴⁴. In a rather simple approach we can then divide the large interval ΔE_{kin} into N sub-intervals $\delta E_{\text{kin},i}$ and calculate the *energy-integrated* photoemission intensity for the $k_x - k_y$ bin from Eq. D.59 as:

$$I_{i \rightarrow \Delta E_{\text{kin}}, \delta \Omega} \propto \sum_{i=1}^N \frac{1}{\sqrt{k_i^2 - k_x^2 - k_y^2}} \sum_f \left| \langle N, (f, \gamma_{\mathbf{k}_i}) | \hat{H}_{\text{int}} | N, i \rangle \right|^2 \mathbf{1}(\omega + E(N, i) - E(N-1, f) \in \delta E_{\text{kin},i}), \quad (\text{D.61})$$

where $\mathbf{k}_i$ is determined by $E_{\text{kin},i}$, the central value of $\delta E_{\text{kin},i}$. This approach was used in practice for the 6T clusters, where we found that only the HOMO-like valence cluster-orbitals contribute to the considered excitons. That is, we calculated the absolute square of the photoemission matrix element for each valence cluster-orbital at its precise kinetic energy, as determined by Eq. 3.54 and then sum up (while neglecting in this case the $\frac{1}{\sqrt{k_i^2 - k_x^2 - k_y^2}}$ prefactor, which is justified by it being approximately the same for all of the valence cluster-orbitals and us choosing the representation that does not include this factor). This is how the cluster exPOT k-Maps shown in Fig. 5.5b,c and e have been created (where we additionally neglected the polarization prefactor). For completeness, note that for the monomer k-map, Fig. 5.5a, we have simply used the HOMO-derived k-map (dropping again the polarization factor).

In a simpler approximation we may also use Eq. D.59 directly, simply with ΔE_{kin} in place of δE_{kin} . This is justified as long as ΔE_{kin} is not too large, see text above Eq. D.51. As an example, this is fully justified for the system of a 6T monolayer and photoemission from the HOMO band, because the band was found to have a very small dispersion of less than 0.1 eV. The same approach was there also used for the LUMO (≈ 0.5 eV band dispersion) “IPA” k-map. Both momentum maps can be found in the right column of Fig. 5.2b (while including in that case the polarization prefactor). Additionally, the exciton momentum maps shown in Fig. 5.5d and 5.7a (using in both cases the HOMO-band) were also calculated in such a way (where we additionally neglected the polarization prefactor).

¹⁴⁴A Gaussian may however, as an improvement to the proposed formalism, still be used to better mimic the experimental uncertainties which ultimately lead to a smearing of features in energy-integrated momentum maps. Since we anyway use Gaussian filtering on top of momentum maps, this is however not strictly necessary to well-reproduce and predict experimental results.

E List of Publications

1. Siegfried Kaidisch, Amir Kleiner, Sivan Refaely-Abramson, Peter Puschnig, and Christian S. Kern. Photoemission tomography of excitons in 2D systems: momentum-space signatures of correlated electron-hole wave functions. *arXiv preprint arXiv:2511.14956v2*, 2025. URL <https://doi.org/10.48550/arXiv.2511.14956>.
2. Marcel Theilen, Siegfried Kaidisch, Monja Stettner, Sarah Zajusch, Eric Fackelman, Alexa Adamkiewicz, Robert Wallauer, Andreas Windischbacher, Christian S. Kern, Michael G. Ramsey, François C. Bocquet, Serguei Soubatch, F. Stefan Tautz, Ulrich Höfer, and Peter Puschnig. Observing the spatial and temporal evolution of exciton wave functions in organic semiconductors. *Physical Review X*, 2026. URL <https://doi.org/10.1103/3zmg-276c>.
3. Monja Stettner, Siegfried Kaidisch, Andrey V. Matetskiy, Eric Fackelman, Serguei Soubatch, Christian Kumpf, François C. Bocquet, Michael G. Ramsey, Peter Puschnig, and F. Stefan Tautz. Tracing the film structure of an organic semiconductor with photoemission orbital tomography. *arXiv preprint arXiv:2603.06204*, 2026. URL <https://doi.org/10.48550/arXiv.2603.06204>.
4. Ariyan Tavakoli, Stefan Lach, Frederik Pütz, Dominic Stephan, Anne Lüpke, Dominik Laible, Siegfried Kaidisch, Andreas Windischbacher, Eva Rentschler, Peter Puschnig, Hans-Christian Schneider, and Christiane Ziegler. Investigating the structural factors influencing the magnetic interaction between individual copper spins in the CuCu₄ metallocrown complex, from its bulk form to its adsorption on Au(111). *Advanced Materials Interfaces*, 13(4):e00906, 2026. URL <https://doi.org/10.1002/admi.202500906>.

Bibliography

- [1] Prashant V. Kamat. Quantum dot solar cells. semiconductor nanocrystals as light harvesters. *The Journal of Physical Chemistry C*, 112(48):18737–18753, 2008. URL <https://doi.org/10.1021/jp806791s>.
- [2] Gordon J. Hedley, Arvydas Ruseckas, and Ifor D. W. Samuel. Light harvesting for organic photovoltaics. *Chemical Reviews*, 117(2):796–837, 2017. URL <https://doi.org/10.1021/acs.chemrev.6b00215>.
- [3] Yifan Dong, Vasileios C. Nikolis, Felix Talnack, Yi-Chun Chin, Johannes Benduhn, Giacomo Londi, Jonas Kublitski, Xijia Zheng, Stefan C. B. Mannsfeld, Donato Spoltore, Luca Muccioli, Jing Li, Xavier Blase, David Beljonne, Ji-Seon Kim, Artem A. Bakulin, Gabriele D’Avino, James R. Durrant, and Koen Vandewal. Orientation dependent molecular electrostatics drives efficient charge generation in homojunction organic solar cells. *Nature Communications*, 11(1):4617, 2020. URL <https://doi.org/10.1038/s41467-020-18439-z>.
- [4] Thomas Mueller and Ermin Malic. Exciton physics and device application of two-dimensional transition metal dichalcogenide semiconductors. *npj 2D Materials and Applications*, 2(1):29, 2018. URL <https://doi.org/10.1038/s41699-018-0074-2>.
- [5] Jun Xiao, Mervin Zhao, Yuan Wang, and Xiang Zhang. Excitons in atomically thin 2D semiconductors and their applications. *Nanophotonics*, 6(6):1309–1328, 2017. URL <https://doi.org/10.1515/nanoph-2016-0160>.
- [6] Surendra B. Anantharaman, Kiyoun Jo, and Deep Jariwala. Exciton–photonics: from fundamental science to applications. *ACS Nano*, 15(8):12628–12654, 2021. URL <https://doi.org/10.1021/acsnano.1c02204>.
- [7] Julien Madéo, Michael K. L. Man, Chakradhar Sahoo, Marshall Campbell, Vivek Pareek, E. Laine Wong, Abdullah Al-Mahboob, Nicholas S. Chan, Arka Karmakar, Bala Murali Krishna Mariserla, Xiaoqin Li, Tony F. Heinz, Ting Cao, and Keshav M. Dani. Directly visualizing the momentum-forbidden dark excitons and their dynamics in atomically thin semiconductors. *Science*, 370(6521):1199–1204, 2020. URL <https://doi.org/10.1126/science.aba1029>.
- [8] Michael K. L. Man, Julien Madéo, Chakradhar Sahoo, Kaichen Xie, Marshall Campbell, Vivek Pareek, Arka Karmakar, E Laine Wong, Abdullah Al-Mahboob, Nicholas S. Chan, David R. Bacon, Xing Zhu, Mohamed

- M. M. Abdelrasoul, Xiaoqin Li, Tony F. Heinz, Felipe H. da Jornada, Ting Cao, and Keshav M. Dani. Experimental measurement of the intrinsic excitonic wave function. *Science Advances*, 7(17):eabg0192, 2021. URL <https://doi.org/10.1126/sciadv.abg0192>.
- [9] Shuo Dong, Michele Puppin, Tommaso Pincelli, Samuel Beaulieu, Dominik Christiansen, Hannes Hübener, Christopher Nicholson, Rui Xian, Maciej Dendzik, Yunpei Deng, Yoav Windsor, Malte Selig, Ermin Malic, Angel Rubio, Andreas Knorr, Martin Wolf, Laurenz Rettig, and Ralph Ernstorfer. Direct measurement of key exciton properties: Energy, dynamics, and spatial distribution of the wave function. *Natural Sciences*, 1(1):e10010, 2021. URL <https://doi.org/10.1002/ntls.10010>.
- [10] Robert Wallauer, Miriam Rath, Klaus Stallberg, Lasse Münster, Dominik Brandstetter, Xiaosheng Yang, Jens Gütde, Peter Puschnig, Serguei Soubatch, Christian Kumpf, Francois C. Bocquet, Frank Stefan Tautz, and Ulrich Höfer. Tracing orbital images on ultrafast time scales. *Science*, 371(6533):1056–1059, 2021. URL <https://doi.org/10.1126/science.abf3286>.
- [11] Robert Wallauer, Raul Perea-Causin, Lasse Münster, Sarah Zajusch, Samuel Brem, Jens Gütde, Katsumi Tanimura, Kai-Qiang Lin, Rupert Huber, Ermin Malic, and Ulrich Höfer. Momentum-resolved observation of exciton formation dynamics in monolayer WS₂. *Nano Letters*, 21(13):5867–5873, 2021. URL <https://doi.org/10.1021/acs.nanolett.1c01839>.
- [12] Wiebke Bennecke, Andreas Windischbacher, David Schmitt, Jan Philipp Bange, Ralf Hemm, Christian S. Kern, Gabriele D’Avino, Xavier Blase, Daniel Steil, Sabine Steil, Martin Aeschlimann, Benjamin Stadtmüller, Marcel Reutz, Peter Puschnig, G. S. Matthijs Jansen, and Stefan Mathias. Disentangling the multiorbital contributions of excitons by photoemission exciton tomography. *Nature Communications*, 15(1):1804, 2024. URL <https://doi.org/10.1038/s41467-024-45973-x>.
- [13] Marcel Reutz, G. S. Matthijs Jansen, and Stefan Mathias. Probing excitons with time-resolved momentum microscopy. *Advances in Physics: X*, 9(1):2378722, 2024. URL <https://doi.org/10.1080/23746149.2024.2378722>.
- [14] Wiebke Bennecke, Ignacio Gonzalez Oliva, Jan Philipp Bange, Paul Werner, David Schmitt, Marco Merboldt, Anna M. Seiler, Kenji Watanabe, Takashi Taniguchi, Daniel Steil, R. Thomas Weitz, Peter Puschnig, Claudia Draxl, G. S. Matthijs Jansen, Marcel Reutz, and Stefan Mathias. Hybrid Frenkel-Wannier excitons facilitate ultrafast energy transfer at a 2D-organic interface. *Nature Physics*, 21:1973–1980, 2025. URL <https://doi.org/10.1038/s41567-025-03075-5>.
- [15] Alexander Neef, Samuel Beaulieu, Sebastian Hammer, Shuo Dong, Julian Maklar, Tommaso Pincelli, R. Patrick Xian, Martin Wolf, Laurenz Rettig, and Jens et al. Pflaum. Orbital-resolved observation of singlet fission. *Nature*, 616(7956):275–279, 2023. URL <https://doi.org/10.1038/s41586-023-05814-1>.

- [16] Marcel Theilen, Siegfried Kaidisch, Monja Stettner, Sarah Zajusch, Eric Fackelman, Alexa Adamkiewicz, Robert Wallauer, Andreas Windischbacher, Christian S. Kern, Michael G. Ramsey, François C. Bocquet, Serguei Soubatch, F. Stefan Tautz, Ulrich Höfer, and Peter Puschnig. Observing the spatial and temporal evolution of exciton wave functions in organic semiconductors. *Physical Review X*, 2026. URL <https://doi.org/10.1103/3zmg-276c>.
- [17] Matthias Dauth and Stephan Kümmel. Predicting photoemission intensities and angular distributions with real-time density-functional theory. *Physical Review A*, 93(2):022502, 2016. URL <https://doi.org/10.1103/PhysRevA.93.022502>.
- [18] Umberto De Giovannini, Hannes Hübener, and Angel Rubio. A first-principles time-dependent density functional theory framework for spin and time-resolved angular-resolved photoelectron spectroscopy in periodic systems. *Journal of Chemical Theory and Computation*, 13(1):265–273, 2017. URL <https://doi.org/10.1021/acs.jctc.6b00897>.
- [19] Xavier Blase, Ivan Duchemin, Denis Jacquemin, and Pierre-François Loos. The Bethe–Salpeter equation formalism: From physics to chemistry. *The Journal of Physical Chemistry Letters*, 11(17):7371–7382, 2020. URL <https://doi.org/10.1021/acs.jpcllett.0c01875>.
- [20] Jim K. Freericks, Hulikal R. Krishnamurthy, and Thomas Pruschke. Theoretical description of time-resolved photoemission spectroscopy: Application to pump-probe experiments. *Physical Review Letters*, 102(13):136401, 2009. URL <https://doi.org/10.1103/PhysRevLett.102.136401>.
- [21] Enrico Perfetto, Davide Sangalli, Andrea Marini, and Gianluca Stefanucci. First-principles approach to excitons in time-resolved and angle-resolved photoemission spectra. *Physical Review B*, 94(24):245303, 2016. URL <https://doi.org/10.1103/PhysRevB.94.245303>.
- [22] Michael Schüler and Michael A. Sentef. Theory of subcycle time-resolved photoemission: Application to terahertz photodressing in graphene. *Journal of Electron Spectroscopy and Related Phenomena*, 253:147121, 2021. URL <https://doi.org/10.1016/j.elspec.2021.147121>.
- [23] Avinash Rustagi and Alexander F. Kemper. Photoemission signature of excitons. *Physical Review B*, 97(23):235310, 2018. URL <https://doi.org/10.1103/PhysRevB.97.235310>.
- [24] Davide Sangalli. Excitons and carriers in transient absorption and time-resolved ARPES spectroscopy: An ab initio approach. *Physical Review Materials*, 5(8):083803, 2021. URL <https://doi.org/10.1103/PhysRevMaterials.5.083803>.
- [25] Päivi Törmä. Essay: Where can quantum geometry lead us? *Physical Review Letters*, 131(24):240001, 2023. URL <https://doi.org/10.1103/PhysRevLett.131.240001>.

- [26] Mingu Kang, Sunje Kim, Yuting Qian, Paul M. Neves, Linda Ye, Junseo Jung, Denny Puntel, Federico Mazzola, Shiang Fang, Chris Jozwiak, Aaron Bostwick, Eli Rotenberg, Jun Fuji, Ivana Vobornik, Jae-Hoon Park, Joseph G. Checkelsky, Bohm-Jung Yang, and Riccardo Comin. Measurements of the quantum geometric tensor in solids. *Nature Physics*, 21(1):110–117, 2025. URL <https://doi.org/10.1038/s41567-024-02678-8>.
- [27] Soohyun Cho, Jin-Hong Park, Jisook Hong, Jongkeun Jung, Beom Seo Kim, Garam Han, Wonshik Kyung, Yeongkwan Kim, S.-K. Mo, J. D. Denlinger, Ji Hoon Shim, Jung Hoon Han, Changyoung Kim, and Seung Ryong Park. Experimental observation of hidden Berry curvature in inversion-symmetric bulk 2H-WSe₂. *Physical Review Letters*, 121(18):186401, 2018. URL <https://doi.org/10.1103/PhysRevLett.121.186401>.
- [28] Michael Schüler, Umberto De Giovannini, Hannes Hübener, Angel Rubio, Michael A. Sentef, and Philipp Werner. Local Berry curvature signatures in dichroic angle-resolved photoelectron spectroscopy from two-dimensional materials. *Science Advances*, 6(9):eaay2730, 2020. URL <https://doi.org/10.1126/sciadv.aay2730>.
- [29] M. Ünzelmann, H. Bentmann, T. Figgemeier, P. Eck, J. N. Neu, B. Geldiyev, F. Diekmann, S. Rohlf, J. Buck, M. Hoesch, M. Kalläne, K. Rossnagel, R. Thomale, T. Siegrist, G. Sangiovanni, D. Di Sante, and F. Reinert. Momentum-space signatures of Berry flux monopoles in the weyl semimetal TaAs. *Nature Communications*, 12(1):3650, 2021. URL <https://doi.org/10.1038/s41467-021-23727-3>.
- [30] Michael Schüler, Umberto De Giovannini, Hannes Hübener, Angel Rubio, Michael A. Sentef, Thomas P. Devereaux, and Philipp Werner. How circular dichroism in time- and angle-resolved photoemission can be used to spectroscopically detect transient topological states in graphene. *Physical Review X*, 10(4):041013, 2020. URL <https://doi.org/10.1103/PhysRevX.10.041013>.
- [31] I. Adawi. Theory of the surface photoelectric effect for one and two photons. *Physical Review*, 134(3A):A788–A798, 1964. URL <https://doi.org/10.1103/PhysRev.134.A788>.
- [32] P. J. Feibelman and D. E. Eastman. Photoemission spectroscopy - correspondence between quantum theory and experimental phenomenology. *Physical Review B*, 10(12):4932–4947, 1974. URL <https://doi.org/10.1103/PhysRevB.10.4932>.
- [33] Peter Puschnig, Stephen Berkebile, Alexander J. Fleming, Georg Koller, Konstantin Emtsev, Thomas Seyller, John D. Riley, Claudia Ambrosch-Draxl, Falko P. Netzer, and Michael G. Ramsey. Reconstruction of molecular orbital densities from photoemission data. *Science*, 326(5953):702–706, 2009. URL <https://doi.org/10.1126/science.1176105>.
- [34] Christian S. Kern, Andreas Windischbacher, and Peter Puschnig. Photoemission orbital tomography for excitons in organic molecules. *Physical Review*

- B*, 108(8):085132, 2023. URL <https://doi.org/10.1103/PhysRevB.108.085132>.
- [35] Daniel Lüftner, Simon Weiß, Xiaosheng Yang, Philipp Hurdax, Vitaliy Feyer, Alexander Gottwald, Georg Koller, Serguei Soubatch, Peter Puschnig, and Michael G. et al. Ramsey. Understanding the photoemission distribution of strongly interacting two-dimensional overlayers. *Physical Review B*, 96(12):125402, 2017. URL <https://doi.org/10.1103/PhysRevB.96.125402>.
- [36] Michael Rohlfing and Steven G. Louie. Electron-hole excitations and optical spectra from first principles. *Physical Review B*, 62(8):4927, 2000. URL <https://doi.org/10.1103/PhysRevB.62.4927>.
- [37] Xavier Gonze, Philippe Ghosez, and Rex W. Godby. Density-functional theory of polar insulators. *Physical Review Letters*, 78(2):294, 1997. URL <https://doi.org/10.1103/PhysRevLett.78.294>.
- [38] David J. Griffiths and Darrell F. Schroeter. *Introduction to Quantum Mechanics*. Cambridge University Press, 3rd edition, 2018.
- [39] J. J. Sakurai and Jim Napolitano. *Modern Quantum Mechanics*. Cambridge University Press, 3rd edition, 2020.
- [40] Walter Kohn. Nobel lecture: Electronic structure of matter—wave functions and density functionals. *Reviews of Modern Physics*, 71(5):1253–1266, 1999. URL <https://doi.org/10.1103/RevModPhys.71.1253>.
- [41] Frank H. Stillinger. *Energy landscapes, inherent structures, and condensed-matter phenomena*. Princeton University Press, 2016.
- [42] Richard P. Feynman. *Statistical mechanics: a set of lectures*. CRC press, 2018.
- [43] Wolfgang Domcke, Horst Koppel, and David R. Yarkony. *Conical intersections: electronic structure, dynamics & spectroscopy*, volume 15 of *Advanced series in physical chemistry*. World Scientific, 2004.
- [44] Brian K. Kendrick, C. Alden Mead, and Donald G. Truhlar. Properties of nonadiabatic couplings and the generalized born–oppenheimer approximation. *Chemical Physics*, 277(1):31–41, 2002. URL [https://doi.org/10.1016/S0301-0104\(02\)00281-1](https://doi.org/10.1016/S0301-0104(02)00281-1).
- [45] Volker Blum, Ryoji Asahi, Jochen Autschbach, Christoph Bannwarth, Gustav Bihlmayer, Stefan Blügel, Lori A. Burns, T. Daniel Crawford, William Dawson, Wibe Albert de Jong, Claudia Draxl, Claudia Filippi, Luigi Genovese, Paolo Giannozzi, Niranjana Govind, Sharon Hammes-Schiffer, Jeff R. Hammond, Benjamin Hourahine, Anubhav Jain, Yosuke Kanai, Paul R. C. Kent, Ask Hjorth Larsen, Susi Lehtola, Xiaosong Li, Roland Lindh, Satoshi Maeda, Nancy Makri, Jonathan Moussa, Takahito Nakajima, Jessica A. Nash, Micael J. T. Oliveira, Pansy D. Patel, Giovanni Pizzi, Geoffrey Pourtois, Benjamin P. Pritchard, Eran Rabani, Markus Reiher, Lucia Reining,

- Xinguo Ren, Mariana Rossi, H. Bernhard Schlegel, Nicola Seriani, Lyudmila V. Slipchenko, Alexander Thom, Edward F. Valeev, Benoit Van Troeye, Lucas Visscher, Vojtěch Vlček, Hans-Joachim Werner, David B. Williams-Young, and Theresa L. Windus. Roadmap on methods and software for electronic structure based simulations in chemistry and materials. *Electronic Structure*, 6(4):042501, 2024. URL <https://doi.org/10.1088/2516-1075/ad48ec>.
- [46] David S. Sholl and Janice A. Steckel. *Density functional theory: a practical introduction*. John Wiley & Sons, 2009.
- [47] Robert G. Parr and Yang Weitao. *Density-Functional Theory of Atoms and Molecules*. International Series of Monographs on Chemistry. Oxford University Press, 1989.
- [48] Reiner M. Dreizler and Eberhard K. U. Gross. *Density functional theory: an approach to the quantum many-body problem*. Springer-Verlag, 1990.
- [49] Carlos Fiolhais, Fernando Nogueira, and Miguel A. L. Marques. *A primer in density functional theory*. Springer-Verlag, 2003.
- [50] Ramamurti Shankar. *Principles of quantum mechanics*. Springer, 2nd edition, 1994.
- [51] Elliott H. Lieb. Density functionals for coulomb systems. *International Journal of Quantum Chemistry*, 24(3):243–277, 1983. URL <https://doi.org/10.1002/qua.560240302>.
- [52] Thomas L. Gilbert. Hohenberg-kohn theorem for nonlocal external potentials. *Physical Review B*, 12(6):2111, 1975. URL <https://doi.org/10.1103/PhysRevB.12.2111>.
- [53] Eberhard Engel and Reiner M. Dreizler. *Density functional theory: An advanced course*. Springer, 2011.
- [54] Pierre Hohenberg and Walter Kohn. Inhomogeneous electron gas. *Physical Review*, 136(3B):B864, 1964. URL <https://doi.org/10.1103/PhysRev.136.B864>.
- [55] Klaus Capelle, Carsten A. Ullrich, and Giovanni Vignale. Degenerate ground states and nonunique potentials: Breakdown and restoration of density functionals. *Physical Review A*, 76(1):012508, 2007. URL <https://doi.org/10.1103/PhysRevA.76.012508>.
- [56] Mel Levy. Universal variational functionals of electron densities, first-order density matrices, and natural spin-orbitals and solution of the v-representability problem. *Proceedings of the National Academy of Sciences*, 76(12):6062–6065, 1979. URL <https://doi.org/10.1073/pnas.76.12.6062>.
- [57] Walter Kohn and Lu Jeu Sham. Self-consistent equations including exchange and correlation effects. *Physical Review*, 140(4A):A1133, 1965. URL <https://doi.org/10.1103/PhysRev.140.A1133>.

- [58] Jorge M. Seminario. *Recent developments and applications of modern density functional theory*. Elsevier, 1996.
- [59] Richard M. Martin. *Electronic structure: basic theory and practical methods*. Cambridge university press, 2010.
- [60] Rhiannon A. Zarotiadis, Hugh G. A. Burton, and Alex J. W. Thom. Towards a holomorphic density functional theory. *Journal of Chemical Theory and Computation*, 16(12):7400–7412, 2020. URL <https://doi.org/10.1021/acs.jctc.0c00822>.
- [61] Alex J. W. Thom and Martin Head-Gordon. Locating multiple self-consistent field solutions: an approach inspired by metadynamics. *Physical Review Letters*, 101(19):193001, 2008. URL <https://doi.org/10.1103/PhysRevLett.101.193001>.
- [62] Rudolf Zeller. Spin-polarized DFT calculations and magnetism. *Jülich: John von Neumann Institute for Computing, NIC series*, 31:419–445, 2006. URL <http://hdl.handle.net/2128/4796>.
- [63] Narbe Mardirossian and Martin Head-Gordon. Thirty years of density functional theory in computational chemistry: an overview and extensive assessment of 200 density functionals. *Molecular Physics*, 115(19):2315–2372, 2017. URL <https://doi.org/10.1080/00268976.2017.1333644>.
- [64] John P. Perdew. Climbing the ladder of density functional approximations. *MRS Bulletin*, 38(9):743–750, 2013. URL <https://doi.org/10.1557/mrs.2013.178>.
- [65] Gianluca Regni, Lorenzo Baldinelli, and Giovanni Bistoni. A quantum chemical method for dissecting london dispersion energy into atomic building blocks. *ACS Central Science*, 11(6):890–898, 2025. URL <https://doi.org/10.1021/acscentsci.5c00356>.
- [66] John P. Perdew, Kieron Burke, and Matthias Ernzerhof. Generalized gradient approximation made simple. *Physical Review Letters*, 77(18):3865, 1996. URL <https://doi.org/10.1103/PhysRevLett.77.3865>.
- [67] A. Seidl, Andreas Görling, Peter Vogl, Jacek A. Majewski, and Mel Levy. Generalized kohn-sham schemes and the band-gap problem. *Physical Review B*, 53(7):3764, 1996. URL <https://doi.org/10.1103/PhysRevB.53.3764>.
- [68] Rachel Garrick, Amir Natan, Tim Gould, and Leeor Kronik. Exact generalized kohn-sham theory for hybrid functionals. *Physical Review X*, 10(2):021040, 2020. URL <https://doi.org/10.1103/PhysRevX.10.021040>.
- [69] Axel D. Becke. Density-functional thermochemistry. iii. the role of exact exchange. *The Journal of Chemical Physics*, 98(7):5648–5652, 1993. URL <https://doi.org/10.1063/1.464913>.

- [70] Philip J. Stephens, Frank J. Devlin, Cary F. Chabalowski, and Michael J. Frisch. Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields. *The Journal of Physical Chemistry*, 98(45):11623–11627, 1994. URL <https://doi.org/10.1021/j100096a001>.
- [71] Fatah Chiter, Van Bac Nguyen, Nathalie Tarrat, Magali Benoit, Hao Tang, and Corinne Lacaze-Dufaure. Effect of van der waals corrections on DFT-computed metallic surface properties. *Materials Research Express*, 3(4):046501, 2016. URL <https://doi.org/10.1088/2053-1591/3/4/046501>.
- [72] Jiří Klimeš and Angelos Michaelides. Perspective: Advances and challenges in treating van der waals dispersion forces in density functional theory. *The Journal of Chemical Physics*, 137(12):120901, 2012. URL <https://doi.org/10.1063/1.4754130>.
- [73] Stefan Grimme, Jens Antony, Stephan Ehrlich, and Helge Krieg. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *The Journal of Chemical Physics*, 132(15):154104, 2010. URL <https://doi.org/10.1063/1.3382344>.
- [74] Stefan Grimme, Stephan Ehrlich, and Lars Goerigk. Effect of the damping function in dispersion corrected density functional theory. *Journal of Computational Chemistry*, 32(7):1456–1465, 2011. URL <https://doi.org/10.1002/jcc.21759>.
- [75] Franz Schwabl. *Advanced quantum mechanics*. Springer, 3rd edition, 2005.
- [76] Arthur J. Layzer. Properties of the one-particle Green’s function for nonuniform many-fermion systems. *Physical Review*, 129(2):897, 1963. URL <https://doi.org/10.1103/PhysRev.129.897>.
- [77] Richard M. Martin, Lucia Reining, and David M. Ceperley. *Interacting electrons*. Cambridge University Press, 2016.
- [78] Paul C. Martin and Julian Schwinger. Theory of many-particle systems. i. *Physical Review*, 115(6):1342, 1959. URL <https://doi.org/10.1103/PhysRev.115.1342>.
- [79] Martin Brokate and Götz Kersting. *Measure and Integral*. Springer, 2015.
- [80] Satish Shirali. *A concise introduction to measure theory*. Springer, 2018.
- [81] Lars Hedin. New method for calculating the one-particle Green’s function with application to the electron-gas problem. *Physical Review*, 139(3A):A796, 1965. URL <https://doi.org/10.1103/PhysRev.139.A796>.
- [82] Dorothea Golze, Marc Dvorak, and Patrick Rinke. The GW compendium: A practical guide to theoretical photoemission spectroscopy. *Frontiers in Chemistry*, 7:377, 2019. URL <https://doi.org/10.3389/fchem.2019.00377>.
- [83] James J. Kelly. *Graduate mathematical physics*. WILEY-VCH Verlag GmbH & Co. KGaA, 2006.

- [84] C. O. Almbladh and L. Hedin. “*Beyond the one-electron model. Many-body effects in atoms, molecules, and solids*” in *Handbook on synchrotron radiation, Koch, EE (ed.), Vol. 1*. North-Holland Publ. Co., 1983.
- [85] Simone Di Marino, Mathieu Lewin, and Luca Nenna. Ground state energy is not always convex in the number of electrons. *The Journal of Physical Chemistry A*, 128(49):10697–10706, 2024. URL <https://doi.org/10.1021/acs.jpca.4c06345>.
- [86] Philippe Blanchard and Erwin Brüning. *Mathematical methods in Physics: Distributions, Hilbert space operators and variational methods*. Birkhäuser, 2003.
- [87] Giovanni Onida, Lucia Reining, and Angel Rubio. Electronic excitations: density-functional versus many-body Green’s-function approaches. *Reviews of Modern Physics*, 74(2):601, 2002. URL <https://doi.org/10.1103/RevModPhys.74.601>.
- [88] Behnam Farid. Dynamical correlation functions expressed in terms of many-particle ground-state wavefunction; the dynamical self-energy operator. *Philosophical Magazine B*, 82(14):1413–1610, 2002. URL <https://doi.org/10.1080/13642810208222682>.
- [89] Fabien Bruneval. *Exchange and Correlation in the Electronic Structure of Solids, from Silicon to Cuprous Oxide: GW Approximation and beyond*. École Polytechnique, Palaiseau (France), 2005. URL https://etsf.polytechnique.fr/sites/default/files/2024-07/bruneval_these_0.pdf.
- [90] Matteo Gatti. *Correlation effects in valence electron spectroscopy of transition metal oxides: many-body perturbation theory and alternative approaches*. École Polytechnique, Palaiseau (France), 2007. URL https://etsf.polytechnique.fr/sites/default/files/2024-07/Thesis_Gatti.pdf.
- [91] Norman H. March. *Farid, Behnam in Electron Correlations in the Solid State*. World Scientific Publishing Company, 1999.
- [92] Andrea Damascelli. Probing the electronic structure of complex systems by ARPES. *Physica Scripta*, 2004(T109):61–74, 2004. URL <https://doi.org/10.1238/Physica.Topical.109a00061>.
- [93] Peter Wölfle. Quasiparticles in condensed matter systems. *Reports on Progress in Physics*, 81(3):032501, 2018. URL <https://doi.org/10.1088/1361-6633/aa9bc4>.
- [94] Henry Ehrenreich and Frans Spaepen. *Aulbur, Wilfried G and Jönsson, L and Wilkins, John W in Solid state physics*. Academic Press, 2001.
- [95] Mark S. Hybertsen and Steven G. Louie. Electron correlation in semiconductors and insulators: Band gaps and quasiparticle energies. *Physical Review B*, 34(8):5390, 1986. URL <https://doi.org/10.1103/PhysRevB.34.5390>.

- [96] Christopher J. Cramer. *Essentials of computational chemistry: theories and models*. John Wiley & Sons, 2nd edition, 2004.
- [97] Behnam Farid. A Luttinger’s theorem revisited. *arXiv preprint cond-mat/0004476v1*, 2000. URL <https://doi.org/10.48550/arXiv.cond-mat/0004476>.
- [98] Tonica Valla, Alexei V. Fedorov, Peter D. Johnson, and S. L. Hulbert. Many-body effects in angle-resolved photoemission: quasiparticle energy and lifetime of a Mo(110) surface state. *Physical Review Letters*, 83(10):2085, 1999. URL <https://doi.org/10.1103/PhysRevLett.83.2085>.
- [99] Paul Cecil Martin. *Measurements and correlation functions*. CRC Press, 1968.
- [100] Mickaël Véril, Pina Romaniello, JA Berger, and Pierre-François Loos. Unphysical discontinuities in GW methods. *Journal of Chemical Theory and Computation*, 14(10):5220–5228, 2018. URL <https://doi.org/10.1021/acs.jctc.8b00745>.
- [101] Jiachen Li, Ye Jin, Patrick Rinke, Weitao Yang, and Dorothea Golze. Benchmark of GW methods for core-level binding energies. *Journal of Chemical Theory and Computation*, 18(12):7570–7585, 2022. URL <https://doi.org/10.1021/acs.jctc.2c00617>.
- [102] Xia Leng, Fan Jin, Min Wei, and Yuchen Ma. GW method and Bethe–Salpeter equation for calculating electronic excitations. *Wiley Interdisciplinary Reviews: Computational Molecular Science*, 6(5):532–550, 2016. URL <https://doi.org/10.1002/wcms.1265>.
- [103] T. Körzdörfer, Stephan Kümmel, Noa Marom, and Leeor Kronik. When to trust photoelectron spectra from kohn-sham eigenvalues: The case of organic semiconductors. *Physical Review B*, 79(20):201205, 2009. URL <https://doi.org/10.1103/PhysRevB.79.201205>.
- [104] Jack Deslippe, Georgy Samsonidze, David A. Strubbe, Manish Jain, Marvin L. Cohen, and Steven G. Louie. BerkeleyGW: A massively parallel computer package for the calculation of the quasiparticle and optical properties of materials and nanostructures. *Computer Physics Communications*, 183(6):1269–1289, 2012. URL <https://doi.org/10.1016/j.cpc.2011.12.006>.
- [105] Mark E. Casida. Time-dependent density functional response theory of molecular systems: Theory, computational methods, and functionals. In J.M. Seminario, editor, *Recent Developments and Applications of Modern Density Functional Theory*, volume 4 of *Theoretical and Computational Chemistry*, pages 391–439. Elsevier, 1996. URL [https://doi.org/10.1016/S1380-7323\(96\)80093-8](https://doi.org/10.1016/S1380-7323(96)80093-8).
- [106] Zeng-hui Yang and Carsten A. Ullrich. Direct calculation of exciton binding energies with time-dependent density-functional theory. *Physical Review B*, 87(19):195204, 2013. URL <https://doi.org/10.1103/PhysRevB.87.195204>.

- [107] Miguel A. L. Marques, Neepa T. Maitra, Fernando M. S. Nogueira, Eberhard K. U. Gross, and Angel Rubio. *Fundamentals of time-dependent density functional theory*, volume 837 of *Lecture Notes in Physics*. Springer, 2012.
- [108] Andreas Dreuw and Martin Head-Gordon. Failure of time-dependent density functional theory for long-range charge-transfer excited states: the zincbacteriochlorin- bacteriochlorin and bacteriochlorophyll- spheroidene complexes. *Journal of the American Chemical Society*, 126(12):4007–4016, 2004. URL <https://doi.org/10.1021/ja039556n>.
- [109] Giancarlo Strinati. Effects of dynamical screening on resonances at inner-shell thresholds in semiconductors. *Physical Review B*, 29(10):5718, 1984. URL <https://doi.org/10.1103/PhysRevB.29.5718>.
- [110] Antoine Marie, Pina Romaniello, Xavier Blase, and Pierre-François Loos. Anomalous propagators and the particle–particle channel: Bethe–Salpeter equation. *The Journal of Chemical Physics*, 162(13):134105, 2025. URL <https://doi.org/10.1063/5.0250155>.
- [111] Davide Sangalli, Pina Romaniello, Giovanni Onida, and Andrea Marini. Double excitations in correlated systems: A many–body approach. *The Journal of Chemical Physics*, 134(3):034115, 2011. URL <https://doi.org/10.1063/1.3518705>.
- [112] Andrea Marini and Rodolfo Del Sole. Dynamical excitonic effects in metals and semiconductors. *Physical Review Letters*, 91(17):176402, 2003. URL <https://doi.org/10.1103/PhysRevLett.91.176402>.
- [113] Steven M. Girvin and Kun Yang. *Modern condensed matter physics*. Cambridge University Press, 2019.
- [114] Daniel Erkensten. *Quantum Theory of Exciton-Exciton Interactions in Atomically Thin Semiconductors*. Chalmers, 2023. URL <https://research.chalmers.se/en/publication/538712>.
- [115] M. Combescot, O. Betbeder-Matibet, and R. Combescot. Exciton-exciton scattering: Composite boson versus elementary boson. *Physical Review B*, 75(17):174305, 2007. URL <https://doi.org/10.1103/PhysRevB.75.174305>.
- [116] Hartmut Haug, Stephen W. Koch, and Leonid V. Keldysh. *Quantum theory of the optical and electronic properties of semiconductors*. American Institute of Physics, 1994.
- [117] Leonid V. Butov. Exciton condensation in coupled quantum wells. *Solid State Communications*, 127(2):89–98, 2003. URL [https://doi.org/10.1016/S0038-1098\(03\)00312-0](https://doi.org/10.1016/S0038-1098(03)00312-0).
- [118] Tobias Sander, Emanuele Maggio, and Georg Kresse. Beyond the tamm-dancoff approximation for extended systems using exact diagonalization. *Physical Review B*, 92(4):045209, 2015. URL <https://doi.org/10.1103/PhysRevB.92.045209>.

- [119] Giancarlo Strinati. Application of the Green's functions method to the study of the optical properties of semiconductors. *La Rivista del Nuovo Cimento (1978-1999)*, 11(12):1–86, 1988. URL <https://doi.org/10.1007/BF02725962>.
- [120] Margherita Marsili, Alejandro Molina-Sánchez, Maurizia Palummo, Davide Sangalli, and Andrea Marini. Spinorial formulation of the GW-BSE equations and spin properties of excitons in two-dimensional transition metal dichalcogenides. *Physical Review B*, 103(15):155152, 2021. URL <https://doi.org/10.1103/PhysRevB.103.155152>.
- [121] Siegfried Kaidisch, Amir Kleiner, Sivan Refaely-Abramson, Peter Puschnig, and Christian S. Kern. Photoemission tomography of excitons in 2D systems: momentum-space signatures of correlated electron-hole wave functions. *arXiv preprint arXiv:2511.14956v2*, 2025. URL <https://doi.org/10.48550/arXiv.2511.14956>.
- [122] Alexa Adamkiewicz, Miriam Rath, Monja Stettner, Marcel Theilen, Lasse Munster, Sabine Wenzel, Mark Hutter, Serguei Soubatch, Christian Kumpf, and François C. et al. Bocquet. Coherent and incoherent excitation pathways in time-resolved photoemission orbital tomography of CuPc/Cu(001)-2O. *The Journal of Physical Chemistry C*, 127(41):20411–20418, 2023. URL <https://doi.org/10.1021/acs.jpcc.3c04859>.
- [123] Claude Cohen-Tannoudji, Jacques Dupont-Roc, and Gilbert Grynberg. *Atom-photon interactions: basic processes and applications*. John Wiley & Sons, 2024.
- [124] Josef Freudenstein, M. Borsch, Manuel Meierhofer, Dmytro Afanasiev, Christoph P. Schmid, Fabian Sandner, Marlene Liebich, Anna Girnghuber, Matthias Knorr, and M. et al. Kira. Attosecond clocking of correlations between bloch electrons. *Nature*, 610(7931):290–295, 2022. URL <https://doi.org/10.1038/s41586-022-05190-2>.
- [125] Jan R. Kuklinski and Shaul Mukamel. Optical properties of Wannier excitons in the linear and weakly nonlinear regime. *Physical Review B*, 42(5):2959, 1990. URL <https://doi.org/10.1103/PhysRevB.42.2959>.
- [126] Claude Cohen-Tannoudji, Bernard Diu, and Franck Laloë. *Quantum Mechanics Vol II Chapter XIII*. Wiley, 1977.
- [127] Ji Hoon Ryoo and Cheol-Hwan Park. Lippmann-Schwinger approach for accurate photoelectron wave functions and angle-resolved photoemission spectra from first principles. *Physical Review Letters*, 135(5):056403, 2025. URL <https://doi.org/10.1103/gwmm-6157>.
- [128] Gian Parusa, Sotirios Fragkos, Samuel Beaulieu, and Michael Schüler. Accurate and efficient simulation of photoemission spectroscopy via kohn-sham scattering states. *arXiv preprint arXiv:2601.12490*, 2026. URL <https://doi.org/10.48550/arXiv.2601.12490>.

- [129] John R. Taylor. *Scattering Theory: The Quantum Theory on Nonrelativistic Collisions*. John Wiley & Sons, 1972.
- [130] Mathias Schwendt. *A Lippmann-Schwinger approach to the photoelectron final state*. University of Graz, 2026. URL <https://unipub.uni-graz.at/urn:nbn:at:at-ubg:1-232180>.
- [131] Jürgen Braun, Ján Minár, and Hubert Ebert. Correlation, temperature and disorder: Recent developments in the one-step description of angle-resolved photoemission. *Physics Reports*, 740:1–34, 2018. URL <https://doi.org/10.1016/j.physrep.2018.02.007>.
- [132] Matthias Dauth, Michael Wießner, Vitaliy Feyer, Achim Schöll, Peter Puschnig, Friedrich Reinert, and Stephan Kümmel. Angle resolved photoemission from organic semiconductors: orbital imaging beyond the molecular orbital interpretation. *New Journal of Physics*, 16(10):103005, 2014. URL <https://doi.org/10.1088/1367-2630/16/10/103005>.
- [133] Peter Puschnig, Eva Maria Reinisch, Thomas Ules, Georg Koller, Sergey Soubatch, Markus Ostler, Lorenz Romaner, F. Stefan Tautz, Claudia Ambrosch-Draxl, and Michael G. Ramsey. Orbital tomography: Deconvoluting photoemission spectra of organic molecules. *Physical Review B*, 84:235427, 2011. URL <https://doi.org/10.1103/PhysRevB.84.235427>.
- [134] Daniel Lüftner, Thomas Ules, Eva Maria Reinisch, Georg Koller, Sergey Soubatch, F. Stefan Tautz, Michael G. Ramsey, and Peter Puschnig. Imaging the wave functions of adsorbed molecules. *Proceedings of the National Academy of Sciences*, 111(2):605–610, 2014. URL <https://doi.org/10.1073/pnas.1315716110>.
- [135] Anja Haags, Dominik Brandstetter, Xiaosheng Yang, Larissa Egger, Hans Kirschner, Alexander Gottwald, Mathias Richter, Georg Koller, François C. Bocquet, Christian Wagner, Michael G. Ramsey, Serguei Soubatch, Peter Puschnig, and F. Stefan Tautz. Tomographic identification of all molecular orbitals in a wide binding-energy range. *Physical Review B*, 111(16):165402, 2025. URL <https://doi.org/10.1103/PhysRevB.111.165402>.
- [136] Peter Puschnig and Daniel Lüftner. Simulation of angle-resolved photoemission spectra by approximating the final state by a plane wave: from graphene to polycyclic aromatic hydrocarbon molecules. *Journal of Electron Spectroscopy and Related Phenomena*, 200:193–208, 2015. URL <https://doi.org/10.1016/j.elspec.2015.06.003>.
- [137] Simon Moser. An experimentalist’s guide to the matrix element in angle resolved photoemission. *Journal of Electron Spectroscopy and Related Phenomena*, 214:29–52, 2017. URL <https://doi.org/10.1016/j.elspec.2016.11.007>.
- [138] Malte Selig, Gunnar Berghäuser, Marten Richter, Rudolf Bratschitsch, Andreas Knorr, and Ermin Malic. Dark and bright exciton formation, thermalization, and photoluminescence in monolayer transition metal dichalco-

- genides. *2D Materials*, 5(3):035017, 2018. URL <https://doi.org/10.1088/2053-1583/aabea3>.
- [139] Davide Sangalli, Enrico Perfetto, Gianluca Stefanucci, and Andrea Marini. An ab-initio approach to describe coherent and non-coherent exciton dynamics. *The European Physical Journal B*, 91(8):171, 2018. URL <https://doi.org/10.1140/epjb/e2018-90126-5>.
- [140] Andrea Marini, Enrico Perfetto, and Gianluca Stefanucci. Coherence and de-coherence in the time-resolved ARPES of realistic materials: An ab-initio perspective. *Journal of Electron Spectroscopy and Related Phenomena*, 257:147189, 2022. URL <https://doi.org/10.1016/j.elspec.2022.147189>.
- [141] John et al. Hunt. *Advanced guide to Python 3 programming*. Springer, 2nd edition, 2023.
- [142] Dominik Brandstetter, Xiaosheng Yang, Daniel Lüftner, F. Stefan Tautz, and Peter Puschnig. kmap.py: A Python program for simulation and data analysis in photoemission tomography. *Computer Physics Communications*, 263:107905, 2021. URL <https://doi.org/10.1016/j.cpc.2021.107905>.
- [143] Frank Neese. The ORCA program system. *WIREs Computational Molecular Science*, 2(1):73–78, 2012. URL <https://doi.org/10.1002/wcms.81>.
- [144] Frank Neese. Software update: the ORCA program system, version 5.0. *WIREs Computational Molecular Science*, 12(1):e1606, 2022. URL <https://doi.org/10.1002/wcms.1606>.
- [145] Denis Jacquemin, Ivan Duchemin, and Xavier Blase. Is the Bethe–Salpeter formalism accurate for excitation energies? Comparisons with TD-DFT, CASPT2, and EOM-CCSD. *The Journal of Physical Chemistry Letters*, 8(7):1524–1529, 2017. URL <https://doi.org/10.1021/acs.jpclett.7b00381>.
- [146] Georg Kresse and Jürgen Hafner. Ab initio molecular dynamics for liquid metals. *Physical Review B*, 47(1):558, 1993. URL <https://doi.org/10.1103/PhysRevB.47.558>.
- [147] Georg Kresse and Jürgen Hafner. Ab initio molecular-dynamics simulation of the liquid-metal–amorphous-semiconductor transition in germanium. *Physical Review B*, 49(20):14251, 1994. URL <https://doi.org/10.1103/PhysRevB.49.14251>.
- [148] Georg Kresse and Jürgen Furthmüller. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Computational Materials Science*, 6(1):15–50, 1996. URL [https://doi.org/10.1016/0927-0256\(96\)00008-0](https://doi.org/10.1016/0927-0256(96)00008-0).
- [149] Georg Kresse and J. Furthmüller. Software VASP, Vienna (1999). *Physical Review B*, 54(11):169, 1996. URL <https://doi.org/10.1103/PhysRevB.54.11169>.

- [150] Paolo Giannozzi, Stefano Baroni, Nicola Bonini, Matteo Calandra, Roberto Car, Carlo Cavazzoni, Davide Ceresoli, Guido L. Chiarotti, Matteo Cococcioni, Ismaila Dabo, Andrea Dal Corso, Stefano de Gironcoli, Stefano Fabris, Guido Fratesi, Ralph Gebauer, Uwe Gerstmann, Christos Gougoussis, Anton Kokalj, Michele Lazzeri, Layla Martin-Samos, Nicola Marzari, Francesco Mauri, Riccardo Mazzarello, Stefano Paolini, Alfredo Pasquarello, Lorenzo Paulatto, Carlo Sbraccia, Sandro Scandolo, Gabriele Scлаuzero, Ari P. Seitsonen, Alexander Smogunov, Paolo Umari, and Renata M. Wentzcovitch. Quantum ESPRESSO: a modular and open-source software project for quantum simulations of materials. *Journal of Physics: Condensed Matter*, 21:395502, 2009. URL <https://doi.org/10.1088/0953-8984/21/39/395502>.
- [151] P. Giannozzi, O. Andreussi, T. Brumme, O. Bunau, M. Buongiorno Nardelli, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, M. Cococcioni, N. Colonna, I. Carnimeo, A. Dal Corso, S. de Gironcoli, P. Delugas, R. A. DiStasio, A. Ferretti, A. Floris, G. Fratesi, G. Fugallo, R. Gebauer, U. Gerstmann, F. Giustino, T. Gorni, J. Jia, M. Kawamura, H.-Y. Ko, A. Kokalj, E. Küçükbenli, M. Lazzeri, M. Marsili, N. Marzari, F. Mauri, N. L. Nguyen, H.-V. Nguyen, A. Otero de-la Roza, L. Paulatto, S. Poncé, D. Rocca, R. Sabatini, B. Santra, M. Schlipf, A. P. Seitsonen, A. Smogunov, I. Timrov, T. Thonhauser, P. Umari, N. Vast, X. Wu, and S. Baroni. Advanced capabilities for materials modelling with Quantum ESPRESSO. *Journal of Physics: Condensed Matter*, 29(46):465901, 2017. URL <https://doi.org/10.1088/1361-648X/aa8f79>.
- [152] Paolo Giannozzi, Oscar Baseggio, Pietro Bonfà, Davide Brunato, Roberto Car, Ivan Carnimeo, Carlo Cavazzoni, Stefano de Gironcoli, Pietro Delugas, Fabrizio Ferrari Ruffino, Andrea Ferretti, Nicola Marzari, Iurii Timrov, Andrea Urru, and Stefano Baroni. Quantum ESPRESSO toward the exascale. *The Journal of Chemical Physics*, 152(15):154105, 2020. URL <https://doi.org/10.1063/5.0005082>.
- [153] Pauli Virtanen, Ralf Gommers, Travis E. Oliphant, Matt Haberland, Tyler Reddy, David Cournapeau, Evgeni Burovski, Pearu Peterson, Warren Weckesser, Jonathan Bright, Stéfan J. van der Walt, Matthew Brett, Joshua Wilson, K. Jarrod Millman, Nikolay Mayorov, Andrew R. J. Nelson, Eric Jones, Robert Kern, Eric Larson, C J Carey, İlhan Polat, Yu Feng, Eric W. Moore, Jake VanderPlas, Denis Laxalde, Josef Perktold, Robert Cimrman, Ian Henriksen, E. A. Quintero, Charles R. Harris, Anne M. Archibald, Antônio H. Ribeiro, Fabian Pedregosa, Paul van Mulbregt, and SciPy 1.0 Contributors. SciPy 1.0: Fundamental algorithms for scientific computing in Python. *Nature Methods*, 17:261–272, 2020. URL <https://doi.org/10.1038/s41592-019-0686-2>.
- [154] Davide Sangalli, Andrea Ferretti, Henrique Miranda, Claudio Attaccalite, Ivan Marri, Elena Cannuccia, Paolo Melo, Margherita Marsili, Fulvio Paleari, and Antimo et al. Marrazzo. Many-body perturbation theory calculations using the yambo code. *Journal of Physics: Condensed Matter*, 31(32):325902, 2019. URL <https://doi.org/10.1088/1361-648X/ab15d0>.

- [155] Andrea Marini, Conor Hogan, Myrta Grüning, and Daniele Varsano. Yambo: an ab initio tool for excited state calculations. *Computer Physics Communications*, 180(8):1392–1403, 2009. URL <https://doi.org/10.1016/j.cpc.2009.02.003>.
- [156] Dominik Brandstetter. Blentom, 2026. URL <https://github.com/brands-d/blentom>. GitHub repository, accessed 2026-08-15.
- [157] Alexander Kirchhoff, Thorsten Deilmann, Peter Krüger, and Michael Rohlfing. Electronic and optical properties of a hexagonal boron nitride monolayer in its pristine form and with point defects from first principles. *Physical Review B*, 106(4):045118, 2022. URL <https://doi.org/10.1103/PhysRevB.106.045118>.
- [158] Gregory H. Wannier. The structure of electronic excitation levels in insulating crystals. *Physical Review*, 52(3):191, 1937. URL <https://doi.org/10.1103/PhysRev.52.191>.
- [159] Thomas Galvani, Fulvio Paleari, Henrique P. C. Miranda, Alejandro Molina-Sánchez, Ludger Wirtz, Sylvain Latil, Hakim Amara, and François Ducastelle. Excitons in boron nitride single layer. *Physical Review B*, 94(12):125303, 2016. URL <https://doi.org/10.1103/PhysRevB.94.125303>.
- [160] Martin Weinelt, Michael Kutschera, Thomas Fauster, and Michael Rohlfing. Dynamics of exciton formation at the Si(100) c(4x2) surface. *Physical Review Letters*, 92(12):126801, 2004. URL <https://doi.org/10.1103/PhysRevLett.92.126801>.
- [161] Ouri Karni, Elyse Barré, Vivek Pareek, Johnathan D. Georgaras, Michael K. L. Man, Chakradhar Sahoo, David R. Bacon, Xing Zhu, Henrique B. Ribeiro, Aidan L. O’Beirne, Jenny Hu, Abdullah Al-Mahboob, Mohamed M. M. Abdelrasoul, Nicholas S. Chan, Arka Karmakar, Andrew J. Winchester, Bumho Kim, Kenji Watanabe, Takashi Taniguchi, Katayun Barmak, Julien Madéo, Felipe H. da Jornada, Tony F. Heinz, and Keshav M. Dani. Structure of the moiré exciton captured by imaging its electron and hole. *Nature*, 603(7900):247–252, 2022. URL <https://doi.org/10.1038/s41586-021-04360-y>.
- [162] Isabella Gierz, Jürgen Henk, Hartmut Höchst, Christian R. Ast, and Klaus Kern. Illuminating the dark corridor in graphene: Polarization dependence of angle-resolved photoemission spectroscopy on graphene. *Physical Review B*, 83(12):121408, 2011. URL <https://doi.org/10.1103/PhysRevB.83.121408>.
- [163] Eugene Krasovskii. Ab initio theory of photoemission from graphene. *Nanomaterials*, 11(5):1212, 2021. URL <https://doi.org/10.3390/nano11051212>.
- [164] Christian S. Kern, Anja Haags, Larissa Egger, Xiaosheng Yang, Hans Kirschner, Susanne Wolff, Thomas Seyller, Alexander Gottwald, Mathias Richter, Umberto De Giovannini, Angel Rubio, Michael G. Ramsey, François C. Bocquet, Serguei Soubatch, F. Stefan Tautz, Peter Puschnig, and

- Simon Moser. Simple extension of the plane-wave final state in photoemission: Bringing understanding to the photon-energy dependence of two-dimensional materials. *Physical Review Research*, 5(3):033075, 2023. URL <https://doi.org/10.1103/PhysRevResearch.5.033075>.
- [165] B. Adolph, V. I. Gavrilenko, K. Tenelsen, F. Bechstedt, and R. Del Sole. Nonlocality and many-body effects in the optical properties of semiconductors. *Physical Review B*, 53(15):9797, 1996. URL <https://doi.org/10.1103/PhysRevB.53.9797>.
- [166] Alejandro José Uría-Álvarez, Juan José Esteve-Paredes, M.A. García-Blázquez, and Juan José Palacios. Efficient computation of optical excitations in two-dimensional materials with the Xatu code. *Computer Physics Communications*, 295:109001, 2024. URL <https://doi.org/10.1016/j.cpc.2023.109001>.
- [167] Alexey Bosak, Jorge Serrano, Michael Krisch, Kenji Watanabe, Takashi Taniguchi, and Hisao Kanda. Elasticity of hexagonal boron nitride: Inelastic x-ray scattering measurements. *Physical Review B*, 73(4):041402, 2006. URL <https://doi.org/10.1103/PhysRevB.73.041402>.
- [168] Thibault Sohier, Matteo Calandra, and Francesco Mauri. Density functional perturbation theory for gated two-dimensional heterostructures: Theoretical developments and application to flexural phonons in graphene. *Physical Review B*, 96(7):075448, 2017. URL <https://doi.org/10.1103/PhysRevB.96.075448>.
- [169] Felipe H. da Jornada, Diana Y. Qiu, and Steven G. Louie. Nonuniform sampling schemes of the brillouin zone for many-electron perturbation-theory calculations in reduced dimensionality. *Physical Review B*, 95(3):035109, 2017. URL <https://doi.org/10.1103/PhysRevB.95.035109>.
- [170] Jack Deslippe, Georgy Samsonidze, Manish Jain, Marvin L. Cohen, and Steven G. Louie. Coulomb-hole summations and energies for GW calculations with limited number of empty orbitals: A modified static remainder approach. *Physical Review B*, 87(16):165124, 2013. URL <https://doi.org/10.1103/PhysRevB.87.165124>.
- [171] S.V. Frolov, Ch. Kloc, S. Berg, G.A. Thomas, and B. Batlogg. Transient spectroscopy of Frenkel excitons in α -hexathiophene single crystals. *Chemical Physics Letters*, 326(5):558–566, 2000. URL [https://doi.org/10.1016/S0009-2614\(00\)00823-X](https://doi.org/10.1016/S0009-2614(00)00823-X).
- [172] Fayçal Kouki, Peter Spearman, Pierre Valat, Gilles Horowitz, and Francis Garnier. Experimental determination of excitonic levels in α -oligothiophenes. *The Journal of Chemical Physics*, 113(1):385–391, 2000. URL <https://doi.org/10.1063/1.481804>.
- [173] E. Varene, L. Bogner, C. Bronner, and P. Tegeder. Ultrafast exciton population, relaxation, and decay dynamics in thin oligothiophene films. *Physical Review Letters*, 109(20):207601, 2012. URL <https://doi.org/10.1103/PhysRevLett.109.207601>.

- [174] Wibke Bronsch, Thorsten Wagner, Sebastian Baum, Malte Wansleben, Kristof Zielke, Ebrahim Ghanbari, Michael Györök, Andrea Navarro-Quezada, Peter Zeppenfeld, Martin Weinelt, and Cornelius Gahl. Interplay between morphology and electronic structure in α -sexithiophene films on Au(111). *The Journal of Physical Chemistry C*, 123(13):7931–7939, 2019. URL <https://doi.org/10.1021/acs.jpcc.8b07280>.
- [175] J.-W. van der Horst, P. A. Bobbert, M. A. J. Michels, G. Brocks, and P. J. Kelly. Ab initio calculation of the electronic and optical excitations in polythiophene: Effects of intra- and interchain screening. *Physical Review Letters*, 83:4413, 1999. URL <https://doi.org/10.1103/PhysRevLett.83.4413>.
- [176] Giovanni Bussi, Alice Ruini, Elisa Molinari, Marilia J. Caldas, Peter Puschnig, and Claudia Ambrosch-Draxl. Interchain interaction and davydov splitting in polythiophene crystals: An ab initio approach. *Applied Physics Letters*, 80(22):4118–4120, 2002. URL <https://doi.org/10.1063/1.1483905>.
- [177] Xia Leng, Huabing Yin, Dongmei Liang, and Yuchen Ma. Excitons and davydov splitting in sexithiophene from first-principles many-body Green’s function theory. *The Journal of Chemical Physics*, 143(11):114501, 2015. URL <https://doi.org/10.1063/1.4930975>.
- [178] Lidong Sun, Stephen Berkebile, Gunther Weidlinger, Mariella Denk, Richard Denk, Michael Hohage, Georg Koller, Falko P. Netzer, Michael G. Ramsey, and Peter Zeppenfeld. Layer resolved evolution of the optical properties of alpha-sexithiophene thin films. *Physical Chemistry Chemical Physics*, 14(39):13651–13655, 2012. URL <https://doi.org/10.1039/C2CP42270K>.
- [179] Stephen Berkebile, Georg Koller, Peter Puschnig, Claudia Ambrosch-Draxl, Falko P. Netzer, and Michael G. Ramsey. Angle-resolved photoemission of chain-like molecules: the electronic band structure of sexithiophene and sexiphenyl. *Applied Physics A*, 95:101–105, 2009. URL <https://doi.org/10.1007/s00339-008-5034-9>.
- [180] Monja Stettner, Siegfried Kaidisch, Andrey V. Matetskiy, Eric Fackelman, Serguei Soubatch, Christian Kumpf, François C. Bocquet, Michael G. Ramsey, Peter Puschnig, and F. Stefan Tautz. Tracing the film structure of an organic semiconductor with photoemission orbital tomography. *arXiv preprint arXiv:2603.06204*, 2026. URL <https://doi.org/10.48550/arXiv.2603.06204>.
- [181] Anna Köhler and Heinz Bässler. *Electronic Processes in Organic Semiconductors*. Wiley-VCH, 2015.
- [182] Tomojit Chowdhury, Aurélie Champagne, Patrick Knüppel, Zehra Naqvi, Ariana Ray, Mengyu Gao, David A. Muller, Nathan Guisinger, Kin Fai Mak, Jeffrey B. Neaton, and Jiwoong Park. Bright hybrid excitons in molecularly tunable bilayer crystals. *arXiv preprint arXiv:2502.13460*, 2025. URL <https://doi.org/10.48550/arXiv.2502.13460>.

- [183] G. Horowitz, B. Bachet, A. Yasser, P. Lang, F. Demanze, J.-L. Fave, and F. Garnier. Growth and characterization of sexithiophene single crystals. *Chemical Materials*, 7(7):1337, 1995. URL <https://doi.org/10.1021/cm00055a010>.
- [184] Koichi Momma and Fujio Izumi. VESTA3 for three-dimensional visualization of crystal, volumetric and morphology data. *Journal of Applied Crystallography*, 44(6):1272–1276, 2011. URL <https://doi.org/10.1107/S0021889811038970>.
- [185] RBJS Krishnan, J. Stephen Binkley, Rolf Seeger, and John A. Pople. Self-consistent molecular orbital methods. XX. a basis set for correlated wave functions. *The Journal of Chemical Physics*, 72(1):650–654, 1980. URL <https://doi.org/10.1063/1.438955>.
- [186] A. D. McLean and G. S. Chandler. Contracted Gaussian basis sets for molecular calculations. I. second row atoms, $Z=11-18$. *The Journal of Chemical Physics*, 72(10):5639–5648, 1980. URL <https://doi.org/10.1063/1.438980>.
- [187] Aaron R. Altman, Sudipta Kundu, and Felipe H. da Jornada. Mixed stochastic-deterministic approach for many-body perturbation theory calculations. *Physical Review Letters*, 132(8):086401, 2024. URL <https://doi.org/10.1103/PhysRevLett.132.086401>.
- [188] Elisabet Romero, Ramunas Augulis, Vladimir I. Novoderezhkin, Marco Ferretti, Jos Thieme, Donatas Zigmantas, and Rienk Van Grondelle. Quantum coherence in photosynthesis for efficient solar-energy conversion. *Nature Physics*, 10(9):676–682, 2014. URL <https://doi.org/10.1038/nphys3017>.
- [189] Koen Vandewal, Abay Gadisa, Wibren D. Oosterbaan, Sabine Bertho, Fateme Banishoeib, Ineke Van Severen, Laurence Lutsen, Thomas J. Cleij, Dirk Vanderzande, and Jean V. Manca. The relation between open-circuit voltage and the onset of photocurrent generation by charge-transfer absorption in polymer: fullerene bulk heterojunction solar cells. *Advanced Functional Materials*, 18(14):2064–2070, 2008. URL <https://doi.org/10.1002/adfm.200800056>.
- [190] Institute of Physics, University of Graz. PhysikMDB: Molecular orbital database, 2026. URL <https://physikmdb.uni-graz.at/>. Accessed: 2026-08-15.
- [191] Siegfried Kaidisch. RIIGID, 2026. URL <https://github.com/siegfriedkaidisch/RIIGID>. GitHub repository, accessed 2026-08-15.
- [192] Ariyan Tavakoli, Stefan Lach, Frederik Pütz, Dominic Stephan, Anne Lüpke, Dominik Laible, Siegfried Kaidisch, Andreas Windischbacher, Eva Rentschler, and Peter et al. Puschnig. Investigating the structural factors influencing the magnetic interaction between individual copper spins in the CuCu₄ metallacrown complex, from its bulk form to its adsorption on Au(111). *Advanced Materials Interfaces*, 13(4):e00906, 2026. URL <https://doi.org/10.1002/admi.202500906>.

- [193] Michael Reed and Barry Simon. *Methods of modern mathematical physics: Functional analysis*. Academic Press, revised and enlarged edition, 1980.
- [194] Sheldon Axler. *Linear algebra done right*. Springer, 4th edition, 2024.
- [195] Neil W. Ashcroft and N. David et al. Mermin. *Solid state physics*. Harcourt, 1976.
- [196] Axel Gross. *Theoretical surface science: a microscopic perspective*. Springer, 2nd edition, 2009.
- [197] Tilo Arens. *Mathematik*. Spektrum Akademischer Verlag, 2. aufl., 1. korr. nachdr. edition, 2012.
- [198] Rafael De la Madrid. The role of the rigged Hilbert space in quantum mechanics. *European Journal of Physics*, 26(2):287–312, 2005. URL <https://doi.org/10.1088/0143-0807/26/2/008>.
- [199] Walter Greiner and Joachim Reinhardt. *Field Quantization*. Springer, 1996.
- [200] Rodney Coleman. *Calculus on Normed Vector Spaces*. Universitext. Springer, 2012.
- [201] Mariano Giaquinta and Stefan Hildebrandt. *Calculus of Variations I*. Grundlehren der mathematischen Wissenschaften. Springer, corr. 2nd printing of 1st edition, 2004.
- [202] Mathias P. Ljungberg, Peter Koval, Francesco Ferrari, Dietrich Foerster, and Daniel Sanchez-Portal. Cubic-scaling iterative solution of the Bethe-Salpeter equation for finite systems. *Physical Review B*, 92(7):075422, 2015. URL <https://doi.org/10.1103/PhysRevB.92.075422>.
- [203] Fernando Alvarruiz, Blanca Mellado-Pinto, and Jose E. Roman. Variants of thick-restart Lanczos for the Bethe-Salpeter eigenvalue problem. *arXiv preprint arXiv:2503.20920v2*, 2026. URL <https://doi.org/10.48550/arXiv.2503.20920>.
- [204] Meiyue Shao, Felipe H. da Jornada, Lin Lin, Chao Yang, Jack Deslippe, and Steven G. Louie. A structure preserving Lanczos algorithm for computing the optical absorption spectrum. *SIAM Journal on Matrix Analysis and Applications*, 39(2):683–711, 2018. URL <https://doi.org/10.1137/16M1102641>.
- [205] Meiyue Shao, Felipe H. da Jornada, Chao Yang, Jack Deslippe, and Steven G. Louie. Structure preserving parallel algorithms for solving the Bethe-Salpeter eigenvalue problem. *Linear Algebra and its Applications*, 488:148–167, 2016. URL <https://doi.org/10.1016/j.laa.2015.09.036>.
- [206] Anne Greenbaum, Ren-cang Li, and Michael L. Overton. First-order perturbation theory for eigenvalues and eigenvectors. *SIAM Review*, 62(2):463–482, 2020. URL <https://doi.org/10.1137/19M124784X>.

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- [207] Peter Puschnig, Christian Meisenbichler, and Claudia Draxl. Excited state properties of organic semiconductors: breakdown of the tamm-dancoff approximation. *arXiv preprint arXiv:1306.3790v2*, 2013. URL <https://doi.org/10.48550/arXiv.1306.3790>.
- [208] Robin Bajaj, Namana Venkatareddy, H. R. Krishnamurthy, and Manish Jain. Symmetries in zero and finite center-of-mass momenta excitons. *arXiv preprint arXiv:2508.16409v2*, 2025. URL <https://doi.org/10.48550/arXiv.2508.16409>.