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Electronic Structure and Reciprocal-Space Orbital Evolution in Linear Acenes

Bachelor's Thesis

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Abstract

This thesis presents a systematic investigation of the electronic structure and reciprocal-space orbital evolution of the homologous acene series, utilizing density functional theory (DFT). By transforming real-space molecular wave functions into computational k -space photoemission intensity distributions $I(k_x, k_y)$, this work models angle-resolved photoemission spectroscopy (ARPES) signatures of the investigated molecules, by approximating the photoelectron final state by a plane wave.

The predictive power and structural boundaries of the computational model are first critically benchmarked against experimental ARPES data sets for a series of increasing molecular lengths, spanning from tetracene (4A) to heptacene (7A). The simulations show a good agreement with the experimental data in terms of primary emission lobe positions, orbital symmetries, and the fundamental nodal structures for both the HOMO and LUMO. The remaining differences—including residual intensity in the nodal lines, and structural distortions in extended films—are discussed in terms of final-state scattering and substrate emissions.

Using this approach, the investigation is extended to a systematic theoretical analysis of the acene series from naphthalene (2A) up to decacene (10A) at a constant kinetic energy of 20 eV. As the molecules get longer, the emission patterns become significantly narrower in the k_y -direction. This transition from diffuse shapes to sharp, structured signals reflects the increasing number of repeating units in the acene chain. Mathematically, tracking the one-dimensional intensity profiles reveals a near-perfect linear correlation between the full width at half maximum (FWHM) of the emission lobes and the inverse molecular length ($1/L$). This scaling behavior demonstrates that the delocalized π -electron system of extended polyacenes can be well described by a simple one-dimensional particle-in-a-box model. Ultimately, this work demonstrates that computational modeling is an effective tool for exploring the electronic properties of longer acenes, which are often difficult to synthesize and measure experimentally.

Declaration on the Use of Generative AI Tools

It is acknowledged that generative AI-based tools were utilized as assistive technologies during the preparation of this thesis. Their application was strictly limited to stylistic and grammatical proofreading of the manuscript, as well as code optimization for data analysis and visualization. The underlying scientific content, data interpretation, and final conclusions remain entirely the author's own.

Contents

1	Introduction	5
2	Theoretical Framework	6
2.1	Fundamentals of Photoemission Orbital Spectroscopy	6
2.2	Photoemission Orbital Tomography and the Plane-Wave Approximation	6
2.3	Density Functional Theory and Electronic Structure Calculations with PySCF	7
2.4	The Homologous Series of Linear Polyacenes	10
2.5	Computational Simulation with <code>kmap.py</code>	11
3	Comparative Analysis: Experimental ARPES Data vs. Simulated k-Maps	14
3.1	Tetracene ($C_{18}H_{12}$)	14
3.2	Pentacene ($C_{22}H_{14}$)	16
3.3	Hexacene ($C_{26}H_{16}$)	18
3.4	Heptacene ($C_{30}H_{18}$)	20
3.5	Summary of Experimental Validation	21
4	Theoretical Trend Analysis and Quantum Scaling Laws	23
4.1	Evolution of Two-Dimensional Intensity Distributions	23
4.2	Analysis of One-Dimensional Intensity Profiles	25
4.3	Linear Scaling Laws and the One-Dimensional Particle-in-a-Box Model .	26
4.4	Summary of Theoretical Trends	28
5	Conclusion and Outlook	29
6	Python Scripts	30
	List of Figures	46
	Bibliography	47

1 Introduction

Consisting of linearly fused benzene rings, linear acenes represent a fundamental compound family in organic chemistry. These molecules are characterized by their rigid, planar geometry and their highly delocalized π -electron systems. Ranging from simple naphthalene to longer oligoacenes like decacene, these systems exhibit a unique evolution of their electronic properties as a direct function of their chain length. Extending their conjugated π -electron system shifts the energetic position of their frontier molecular orbitals and thereby narrows the fundamental energy gap. This is why they are the ideal subject for studying quantum mechanical structure-property relationships.

Because their electronic structure is highly tailorable, linear acenes have become a prime model system for investigating organic semiconductor devices such as organic field-effect transistors and organic light-emitting diodes. However, to fully use their potential in such applications, researchers must be not only able to look at the molecules in isolation, but also have to be able to directly probe and visualize the electron intensity distributions of these frontier orbitals in experimental thin films or single crystals.

To achieve this, angle-resolved photoemission spectroscopy (ARPES), combined with the tomographic framework known as photoemission orbital tomography (POT) [7], has emerged as an exceptionally powerful technique. Photoemission tomography gives researchers the opportunity to map the electron emission intensity directly in momentum space, which creates a unique, two dimensional fingerprint of the molecular orbitals. While those experimental maps provide direct insight into electronic states, interpreting the complex intensity patterns and assigning them to specific orbital symmetries typically requires a robust connection to theoretical modeling.

One widely established theoretical framework for decoding these maps is based on the plane-wave approximation of the photoemitted electron, which results in the fact that the experimental photoemission intensity is directly related to the Fourier transform of the real-space molecular orbital wave function. While density functional theory (DFT) calculations provide highly accurate real-space wave functions, transforming and visualizing their corresponding representations in momentum space requires efficient and accessible computational tools.

This work presents a systematic investigation of the momentum-space representations for a homologous series of linear polyacenes, ranging from naphthalene (2A) to decacene (10A), using the computational tool `kmap.py` [2]. Following a review of the underlying theoretical background, a detailed, case-by-case qualitative comparison of simulated HOMO and LUMO maps against experimental data is performed for the acene representatives tetracene (4A), pentacene (5A), hexacene (6A), and heptacene (7A). Finally, the scope is expanded to a generalized analysis encompassing all nine molecules in the series. This allows for tracking the evolution of orbital nodal structures, evaluating the predictive boundaries of the plane-wave approximation, and systematically uncovering electronic trends as the length of the acene chain increases.

2 Theoretical Framework

2.1 Fundamentals of Photoemission Orbital Spectroscopy

Angle-resolved photoemission spectroscopy (APRES) is based on the photoelectric effect. Photons can be absorbed by electrons bound in the material, when a monochromatic photon beam with energy $h\nu$ hits a sample. If the photon energy exceeds the characteristic work function Φ of the system, the electrons may be ejected into the vacuum as so called photoelectrons. The measured kinetic energy E_{kin} of the emitted electron and its initial binding energy E_B are then related through the conservation of energy:

$$E_{\text{kin}} = h\nu - \Phi - E_B \quad (2.1)$$

In such APRES experiments, the kinetic energy E_{kin} and the direction of emission of the emitted electrons are measured. Thereby the direction is typically described by the polar angle θ and the azimuthal angle ϕ relative to the surface normal.

At the interface to the vacuum, the system preserves translational symmetry parallel to the surface ([3, p. 64]), therefore the components of the electron momentum parallel to the interface ($\mathbf{k}_{\parallel}$) are strictly conserved during the transition from the material into the vacuum. For a free electron in vacuum with mass m_e using the kinematic relations, the experimental angles and energies can be directly converted into the two-dimensional wave vector $\mathbf{k}_{\parallel} = (k_x, k_y)$:

$$k_x = \frac{\sqrt{2m_e E_{\text{kin}}}}{\hbar} \sin \theta \cos \phi \quad (2.2)$$

$$k_y = \frac{\sqrt{2m_e E_{\text{kin}}}}{\hbar} \sin \theta \sin \phi \quad (2.3)$$

For the investigation of planar organic molecules adsorbed on surfaces, this two-dimensional momentum vector $\mathbf{k}_{\parallel}$ contains the complete information required to map the electronic structure. These equations define the exact grid of the momentum space maps (k -maps) that are theoretically simulated and analyzed in this work.

2.2 Photoemission Orbital Tomography and the Plane-Wave Approximation

Instead of measuring continuous energy bands, photoemission orbital tomography (POT) is used to measure discrete electronic states of adsorbed molecules, specifically their frontier molecular orbitals [7]. Here, a two dimensional intensity map in momentum space is obtained by recording the photoelectron intensity over a wide range of emission angles at a fixed binding energy (e.g. the energy of the highest occupied molecular orbital, HOMO). These momentum maps are the so called k -maps.

In order to model and interpret these k -maps, the quantum mechanical transition probability must be evaluated. According to Fermi's golden rule, the photoemission intensity I is proportional to the transition rate from an initial molecular state $|\psi_i\rangle$ to a final vacuum state $|\psi_f\rangle$. Within the dipole approximation this relationship is governed by the optical matrix element $M_{f,i}$:

$$I(\mathbf{k}) \propto |M_{f,i}|^2 = |\langle\psi_f| \mathbf{A} \cdot \mathbf{p} |\psi_i\rangle|^2 \quad (2.4)$$

where $\mathbf{A}$ represents the vector potential of the incident photon field and $\mathbf{p} = -i\hbar\nabla$.

The most important simplification in POT is the plane-wave-approximation. It states, that the emitted photoelectron can be described as a free-electron, thus a plane wave, in the vacuum, once it has escaped the attractive potential of the molecular layer and the underlying substrate. Consequently, the final state wave function $\psi_f(\mathbf{r})$ with the wave vector $\mathbf{k}$ is defined as

$$\psi_f(\mathbf{r}) \propto e^{i\mathbf{k}\cdot\mathbf{r}} \quad (2.5)$$

Substituting this plane-wave state into the dipol matrix element yields an integral over all space

$$M_{f,i} \propto \int e^{-i\mathbf{k}\cdot\mathbf{r}} [\mathbf{A} \cdot (-i\hbar\nabla) \psi_i(\mathbf{r})] d^3r \quad (2.6)$$

By utilizing the mathematical properties of the gradient operator and applying integration by parts, the momentum operator can be shifted to act directly on the plane wave, which pulls out the factor $\hbar\mathbf{k}$. This transforms the matrix element into:

$$M_{f,i} \propto (\mathbf{A} \cdot \mathbf{k}) \int \psi_i(\mathbf{r}) e^{-i\mathbf{k}\cdot\mathbf{r}} d^3r \quad (2.7)$$

The integral remaining in this expression is by definition the three-dimensional Fourier transform of the initial real-space molecular orbital, denoted as $\tilde{\psi}_i(\mathbf{k})$. Therefore, the photoemission intensity can be expressed as:

$$I(\mathbf{k}) \propto |\mathbf{A} \cdot \mathbf{k}|^2 \cdot |\tilde{\psi}_i(\mathbf{k})|^2 \quad (2.8)$$

This fundamental equation demonstrates that the measured intensity in momentum space is directly proportional to the absolute square of the Fourier transform of the real-space molecular orbital, modulated by a polarization-dependent factor $|\mathbf{A} \cdot \mathbf{k}|^2$.

2.3 Density Functional Theory and Electronic Structure Calculations with PySCF

Prior to the simulation of the momentum-space photoelectron intensity maps using the plane wave approximation, the spatial representation of the initial-state molecular orbital $\psi_i(\mathbf{r})$ has to be determined. Here, density functional theory (DFT) has established itself as the standard framework for calculating the electronic structure of complex multi-electron systems [4].

The quantum mechanical description of a molecular system containing N electrons and

M nuclei requires solving the time-independent, non-relativistic many-body Schrödinger Equation, defined by the eigenvalue problem

$$\hat{H}\Psi = E\Psi \quad (2.9)$$

Using the Born-Oppenheimer approximation, which lets one neglect the kinetic energy of the nuclei because of the massive inertia mismatch between the nuclei and the electrons ($m_n \gg m_e$), simplifies the electronic Hamiltonian $\hat{H}_e$ operating on the multi-particle wave-function $\Phi(\mathbf{r}_1, \dots, \mathbf{r}_N)$ to the explicit form:

$$\hat{H}_e = -\frac{\hbar^2}{2m_e} \sum_{i=1}^N \nabla_i^2 + \sum_{i=1}^N V_{\text{ext}}(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j}^N \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} \quad (2.10)$$

Here, the external potential arising from the Coulomb attraction of the fixed nuclei with atomic numbers Z_A at positions $\mathbf{R}_A$ is given by

$$V_{\text{ext}}(\mathbf{r}_i) = - \sum_{A=1}^M \frac{Z_A e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{R}_A|} \quad (2.11)$$

Even under this simplification, solving for the many-electron wave function remains intractable because Ψ depends simultaneously on $3N$ spatial and N spin coordinates. Due to the many-body electron-electron repulsion term, the variables cannot be separated, causing the computational complexity to scale exponentially with the particle number N [4].

Density functional theory circumvents this problem by shifting the the central observable from the complicated, non-observable many-body wave function to the physical ground-state electron density $\rho(\mathbf{r})$. This spatial density is a reduced three-dimensional variable obtained by integrating the absolute square of the wave function over all coordinates except one:

$$\rho(\mathbf{r}) = N \sum_{\sigma_1, \dots, \sigma_N} \int \dots \int |\Psi(\mathbf{r}_1, \sigma_1, \dots, \mathbf{r}_N, \sigma_N)|^2 d^3r_2 \dots d^3r_N \quad (2.12)$$

The physical foundation for this approach is established by the two Hohenberg-Kohn theorems [4]. The first theorem proves that the ground-state electron density $\rho_0(\mathbf{r})$ uniquely determines the external potential $V_{\text{ext}}(\mathbf{r})$. Since the external potential defines the Hamiltonian, the density therefore implicitly determines all physical properties of the system. This allows the total ground-state energy to be expressed as a unique functional of the density

$$E_0 = E[\rho_0]$$

The second theorem introduces a variational principle, stating that any trial density $\rho'(\mathbf{r})$, deviating from the ground state density, will always yield a total energy higher than or equal to the true ground-state energy

$$E[\rho'] \geq E_0,$$

providing a clear mathematical path to find the correct density by minimizing the energy functional.

Although these theorems prove that a universal energy functional exists, they do not reveal its exact mathematical form. To solve this practically, Walter Kohn and Lu Jeu Sham mapped the interacting electrons onto a fictitious system of N non-interacting particles moving within an effective single-particle potential $V_{\text{eff}}(\mathbf{r})$ that yields the identical ground-state density $\rho(\mathbf{r})$. Within this Kohn-Sham framework, the total energy functional is partitioned as [5]

$$E[\rho] = T_s[\rho] + \int \rho(\mathbf{r}) V_{\text{ext}}(\mathbf{r}) d^3r + E_H[\rho] + E_{\text{xc}}[\rho] \quad (2.13)$$

Here $T_s[\rho]$ is the non-interacting kinetic energy, $V_{\text{ext}}(\mathbf{r})$ represents the external nuclear potential, $E_H[\rho]$ is the classical electron-electron repulsion (also called Hartree energy) and $E_{\text{xc}}[\rho]$ is the exchange-correlation functional, which absorbs all non-classical multi-body effects like quantum mechanical exchange and electron correlation. Minimizing this functional under the constraint of orthonormal orbitals yields the decoupled single-particle Kohn-Sham equations

$$\left(-\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{eff}}(\mathbf{r}) \right) \psi_j^{\text{KS}}(\mathbf{r}) = \varepsilon_j \psi_j^{\text{KS}}(\mathbf{r}) \quad (2.14)$$

The effective potential is defined self-consistently as $V_{\text{eff}}(\mathbf{r}) = V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r})$, where V_{H} is the Hartree potential and $V_{\text{xc}}(\mathbf{r}) = \delta E_{\text{xc}} / \delta \rho$. Since V_{eff} depends on the density $\rho(\mathbf{r}) = \sum_j |\psi_j^{\text{KS}}(\mathbf{r})|^2$, which in turn depends on the orbitals, the equations must be solved iteratively using a self-consistent field algorithm. In POT, these single-particle Kohn-Sham orbitals, specifically the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), serve as the initial-state wave functions $\psi_i(\mathbf{r})$.

To solve these equations numerically, the continuous wave functions are projected onto a finite basis set. Specifically, when using the linear combination of atomic orbitals (LCAO) approximation, each molecular orbital is expanded as follows

$$\psi_j(\mathbf{r}) = \sum_i C_{ij} \chi_i(\mathbf{r}) \quad (2.15)$$

This transforms the differential eigenvalue problem into the algebraic Roothaan matrix equations:

$$\mathbf{H}_{KS} \mathbf{C} = \mathbf{S} \mathbf{C} \epsilon \quad (2.16)$$

Here $\mathbf{H}_{KS}$ is the Kohn-Sham matrix $H_{\mu\nu} = \langle \chi_\mu | \hat{h}_{KS} | \chi_\nu \rangle$, $\mathbf{S}$ is the overlap matrix $S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle$ and ϵ is a diagonal matrix of the orbital energies. Mostly, Gaussian-type orbitals (GTOs) are preferred as basis functions $\chi_i(\mathbf{r})$. This is because, according to the Gaussian product theorem, the product of two Gaussians forms another Gaussian, allowing for the exact analytical evaluation of multi-center integrals and drastically reducing computational overhead.

All electronic structure calculations in this work were performed using the open-source Python library PySCF [9]. First, the molecular geometries of the polyacenes are defined within a molecular environment object using the `gto.Mole()` function. Within this environment, the continuous wave functions are expanded using the standard 6-31G* basis

set. To ensure physical accuracy for these planar organic molecules, spherical harmonic basis functions are explicitly enforced by setting `mol.cart = False`, which systematically removes redundant Cartesian components from the calculation.

The self-consistent field equations are subsequently solved within a spin-restricted Kohn-Sham framework via the `dft.RKS()` module, which is ideally suited for the closed-shell electronic configuration of the investigated polyacene series. Once the iterative kernel achieves convergence, the PySCF framework directly provides the primary electronic outputs. These consist of the orbital occupancy numbers stored in `mf.mo_occ`, the discrete energy eigenvalues in `mf.mo_energy`, and the complete molecular orbital coefficient matrix in `mf.mo_coeff`. By mapping these numerical coefficients back to the analytical basis functions—specifically targeting the carbon $2p_z$ atomic orbitals that constitute the conjugated π -system—the real-space wave functions of the frontier molecular orbitals, namely the HOMO and LUMO, are reconstructed. These spatial distributions then serve as the direct input for the subsequent Fourier-space mapping tool `kmap.py` [2].

2.4 The Homologous Series of Linear Polyacenes

The real-space wave functions calculated via this framework are evaluated for the homologous series of linear polyacenes. This series consists of planar organic hydrocarbons composed of linearly fused benzene rings, starting from naphthalene ($C_{10}H_8$) and anthracene ($C_{14}H_{10}$) and extending up to decacene ($C_{42}H_{26}$). Here the electronic properties of these conjugated systems shift systematically, as the number of fused rings increases. As the linear polyacenes grow longer, the π -electrons become more delocalized across the molecule. Consequently, the energy gap between the HOMO and the LUMO decreases monotonically with increasing chain length as can be seen in figure 2.1.

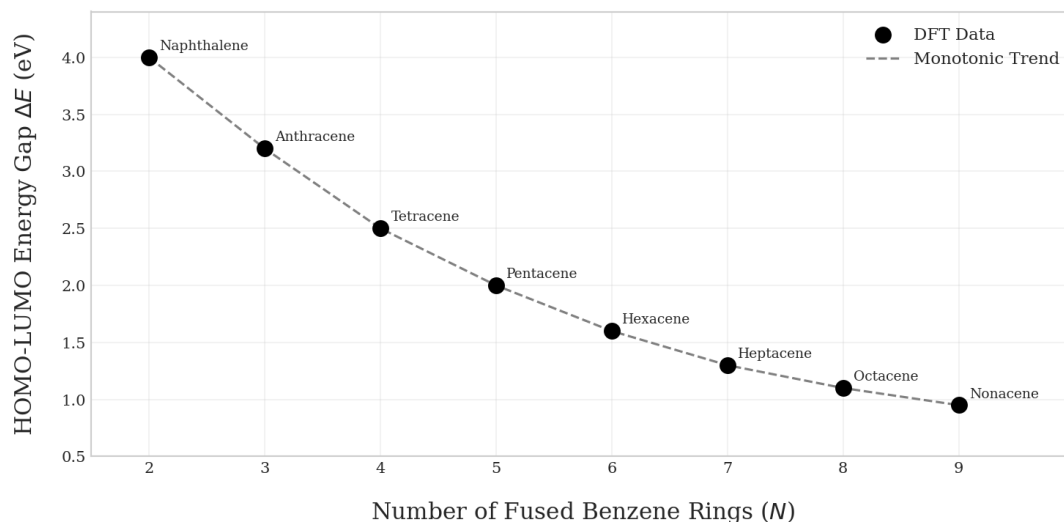


Figure 2.1: Calculated HOMO–LUMO energy gap ΔE as a function of the number of fused benzene rings (N) for the homologous linear polyacenes from naphthalene ($N = 2$) to decacene ($N = 10$). The energy gap decreases monotonically with increasing chain length, reflecting the enhanced delocalization of the π -electron system in longer molecules.

From a geometric perspective, all members of this linear polyacene series share a highly symmetric, planar structure. Because the molecules are planar and choosing the molecules to reside in the xy -plane, their frontier molecular orbitals are formed primarily by the linear combination of the vertical carbon $2p_z$ atomic orbitals. This arrangement makes the π -electron system inherently antisymmetric with respect to reflection across the molecular plane itself.

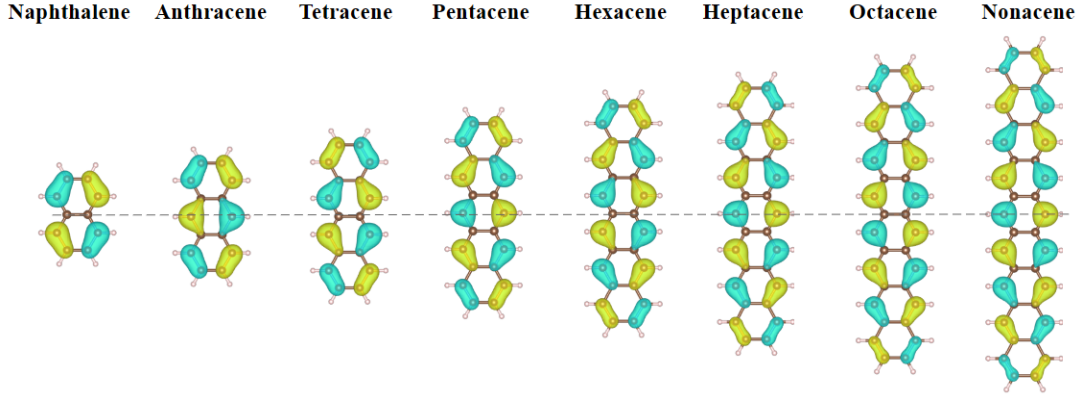


Figure 2.2: Real-space representation of the highest occupied molecular orbitals (HOMO) for the homologous series of linear acenes, ranging from naphthalene (2A) to nonacene (9A). The isosurfaces illustrate the characteristic nodal structure of the π -system, calculated via DFT and visualized using VESTA.

The linear polyacenes exhibit high geometric symmetry, featuring fixed orthogonal mirror axes within the molecular plane. These symmetries dictate the existence of vertical nodal planes where the wave function amplitude drops exactly to zero. For the frontier molecular orbitals, the number of these nodal structures along the long molecular axis increases linearly with the number of fused benzene rings. In POT, these real-space symmetries directly determine the positions of the emission maxima and dark regions within the simulated k -maps.

2.5 Computational Simulation with `kmap.py`

To bridge the gap between the real-space molecular orbitals obtained from the density functional theory calculations and the experimental momentum-space observables, a specialized numerical framework is required. In this work, the simulation of the photoelectron intensity distributions is performed using the Python library `kmap.py` [2]. This package is specifically designed to evaluate the transition matrix elements of angle-resolved photoemission spectroscopy within the plane-wave approximation for the final state, effectively acting as a simulation platform for POT.

The library `kmap.py` automates this complex spatial transformation by mapping the continuous real-space wave function grid onto a three-dimensional Cartesian reciprocal grid (k_x, k_y, k_z). It then calculates the kinetic energy E_{kin} and the corresponding total momentum vector $|\mathbf{k}| = \sqrt{2m_e E_{\text{kin}}}/\hbar$ governed by the experimental photon energy $h\nu$ and the molecular work function.

In the script developed for this work, the execution begins by initializing the calculation object using the central `KMap` class, passing the previously converged PySCF molecular environment object:

```
1 # Initialising a KMap-Object
2 kmap_obj = kmap.KMap(mol)
```

The library reads the atomic coordinates and the basis set configuration directly from the `mol` object, ensuring perfect geometric consistency. To evaluate the Fourier transform numerically, the continuous real-space initial-state wave function must be sampled on a dense spatial grid. This is achieved via the `.get_grid_ao()` method, which evaluates the atomic orbital basis functions at each discrete point in space:

```
1 # Calculating the real-space grid for the orbitals
2 ao_grid = ao_grid = kmap_obj.get_grid_ao(
3     nx=180, ny=120, nz=60,
4     xmin=-15, xmax=15,
5     ymin=-10, ymax=10,
6     zmin=-5,  zmax=5
7 )
```

Here, a three-dimensional grid spanning from -15 Bohr to $+15$ Bohr along all spatial axes with a resolution of $60 \times 60 \times 60$ points is constructed. This grid envelope is chosen to fully encompass the delocalized π -electron clouds of even the longest oligo-acenes, such as decacene, while maintaining a high spatial sampling rate to avoid aliasing artifacts during the subsequent fast Fourier transform. After setting up the atomic orbital grid, the molecular orbital wave function $\psi_i(\mathbf{r})$ is calculated by mapping the converged PySCF coefficient matrix C onto the spatial grid points. The final momentum-space intensity is then generated by selecting the relevant orbital index (e.g. the HOMO) and running the simulation kernel:

```
1 # Calculation of the k-maps
2 k_maps = kmap_obj.get_kmaps(
3     mo_coeff=mf.mo_coeff,
4     orbital_index=homo_idx,
5     ao_grid=ao_grid,
6     photon_energy=21.2,
7     work_function=4.3,
8     theta_max=90
9 )
```

The input parameters directly mirror standard experimental APRES conditions: while the photon energy of 21.2 eV corresponds to the widely used Helium I emission line, a work function of 4.3 eV represents a typical energetic barrier for organic thin films on metallic substrates. The parameter `theta_max=90` defines the full hemispherical acceptance angle of the electron analyzer.

Internally, `kmap.py` performs the three-dimensional FFT on the grid, cuts the resulting data cube along the specific hemispherical energy conservation surface dictated by $E_{\text{kin}} = h\nu - \Phi - E_{\text{binding}}$, and projects the spherical emission intensities onto the flat

two-dimensional detector plane (k_x, k_y) . The resulting output matrix `k_maps` contains the raw physical photoemission intensities, providing the high-fidelity theoretical maps that are directly comparable to experimental data.

3 Comparative Analysis: Experimental ARPES Data vs. Simulated k -Maps

The predictive power of the simulation pipeline is tested by comparing the simulated k -space k -maps with experimental ones. This comparison is thereby strictly focused on the four specific members of the linear polyacenes for which experimental data sets are available: tetracene ($C_{18}H_{12}$), pentacene ($C_{22}H_{14}$), hexacene ($C_{26}H_{16}$) and heptacene ($C_{30}H_{18}$). For each of these molecules, the simulated k -maps represent the emission intensities originating from both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). This enables a detailed qualitative analysis of the characteristic emission features, specifically focusing on how the orbital symmetry dictates the overall shape and structure of the simulated patterns across the entire series.

3.1 Tetracene ($C_{18}H_{12}$)

As can be seen from fig 3.1, the simulated k -maps predict highly localized, sharp intensity maxima precisely centered at their ideal reciprocal coordinates, while the experimental spectra exhibit a pronounced spatial broadening and blurring. Nevertheless, the underlying periodicity is fundamentally preserved, as the primary photoemission features in both the theoretical and experimental distributions are located at corresponding positions in momentum space.

Specifically, the simulated LUMO k -map predicts two dominant intensity maxima positioned strictly on the vertical axis at $k_x = 0 \text{ \AA}^{-1}$ and $k_y \approx \pm 1.5 \text{ \AA}^{-1}$. In contrast, the HOMO distribution shifts these primary emission centers off-axis, concentrating the intensity into four distinct pockets positioned at $k_y \approx \pm 1.0 \text{ \AA}^{-1}$ and $k_x \approx \pm 1.1 \text{ \AA}^{-1}$. Mechanistically, the good agreement between the calculated and measured maxima in momentum space demonstrates that the finite Pople-type basis set (6-31G*) implemented in PySCF accurately captures the real-space periodicity and expansion of the molecular π -system. Because ARPES essentially probes the Fourier transform of the initial state, the replication of these peak distances confirms that the theoretical model correctly evaluates the internal electronic wavelength of the respective molecule.

However, a closer inspection of the spatial profile also reveals some deviations regarding orbital symmetry and additionally effects due to experimental noise.. In the experimental LUMO, the characteristic broadening manifests in a largely isotropic, symmetric fashion around the primary centers. Conversely, the experimental HOMO shows a clear vertical intensity asymmetry, where the upper emission lobes appear significantly more intense than their lower counterparts. This asymmetry arises from the $|\mathbf{A} \cdot \mathbf{k}|^2$ polarization factor (see Eq. 2.8) which is disregarded in the simulated k -maps. Crucially, this asymmetry only modulates the local photoemission intensity with only minor shifts of the overall positions of the features; the experimental emission maxima remain in good alignment with the theoretical topology.

Furthermore, the simulation resolves fine structural details in the form of subtle secondary

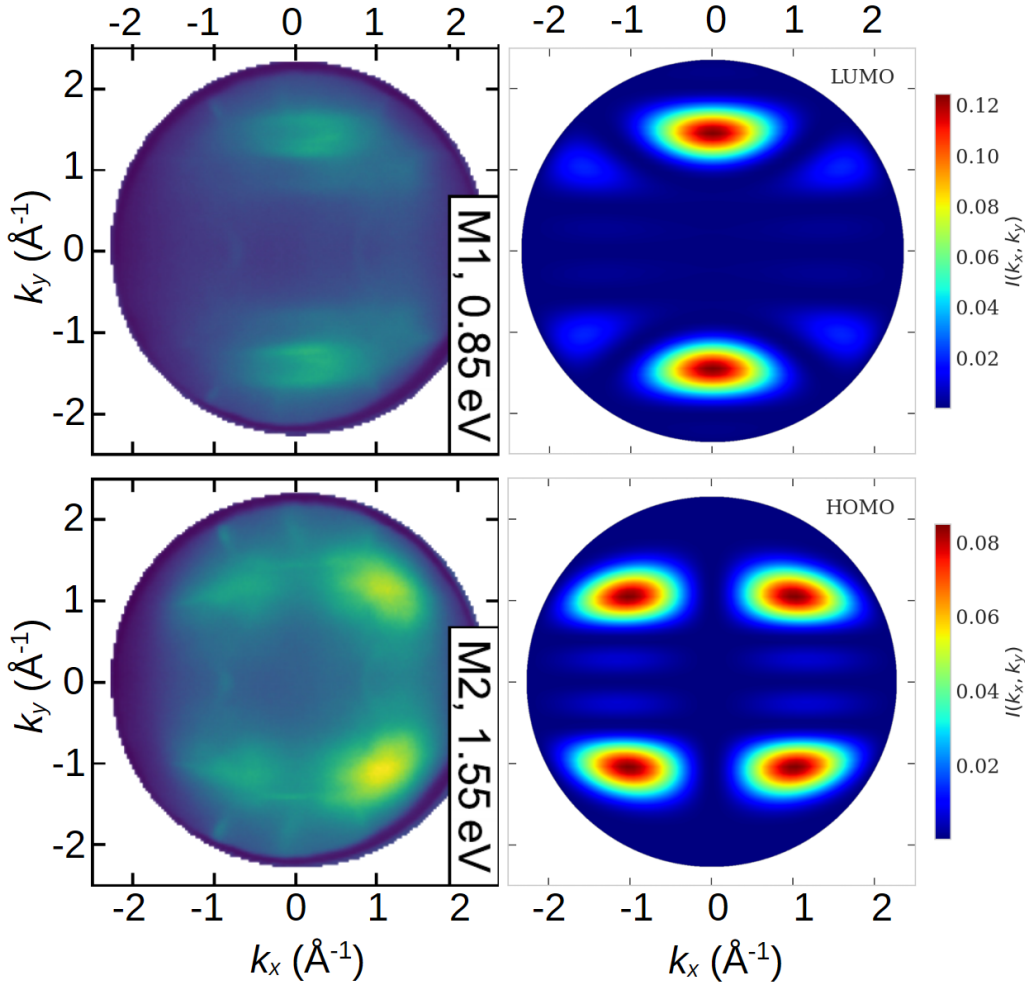


Figure 3.1: Qualitative comparison between the experimentally measured (left) and the numerically simulated (right) photoemission momentum maps for tetracene (4A). The experimental panel shows the emission intensities recorded at specific binding energies corresponding to the LUMO ($M1$, 0.85 eV) and the HOMO ($M2$, 1.55 eV). The right panel displays the calculated $I(k_x, k_y)$ intensity distributions for the LUMO ($E_{\text{kin}} = 25.40$ eV) and HOMO ($E_{\text{kin}} = 24.70$ eV) obtained via the `kmap.py` framework. Experimental data adapted from [10].

intensity maxima situated between the main lobes. For the LUMO, this manifests as four low-intensity satellite features facing one another, whereas in the HOMO, these four features are spatially compressed due to the proximity of the primary four-fold lobes. In the experiment, these delicate quantum interference features cannot be resolved due to the experimental resolution limit. However, the most striking difference between the calculated and experimental momentum maps is the appearance of continuous, vertical intensity features in the experimental data. While the gas-phase calculation predicts sharply bounded, slightly deformed ovals along the primary axes, the experimental reality exhibits additional curved, arc-like shapes. This is a direct consequence of the underlying

substrate, as the experiment is performed for a monolayer of tetracene (4A) on Ag(110). Even though ARPES with a photon energy of $h\nu \approx 30$ eV is extremely surface sensitive due to the very short mean free path of the photoelectrons (~ 1 nm), the experimental maps still contain strong signatures of emissions from the Ag sp -band. These substrate-related emissions can be clearly recognized as the sharp, line-like features crossing the k -maps, which superimpose with the rather broad emission lobes of molecular origin.

A final, robust marker for validating the wave function symmetry is the tracking of the dark interference corridors where destructive interference occurs. In the simulated LUMO k -map, a sharp, hard nodal line splits the two main lobes, where the intensity drops strictly to zero. The experimental LUMO tracks this behavior remarkably well, reproducing a profound central drop in photoemission intensity. For the HOMO k -map, however, this phase boundary is less defined. Due to the aforementioned broadening and the resulting formation of vertical intensity bands, no sharp, zero-intensity nodal line can be isolated in either axis direction; instead, a diffuse, faint cloud of residual intensity remains visible.

This mismatch highlights the limitations of the simple one-electron plane-wave approximation for the final state. By treating the escaping photoelectron as a completely unscattered free wave, the simulation neglects complex, low-energy forward scattering processes within the potential of the crystal lattice, which structurally redirect electrons into these theoretically forbidden nodal zones. In addition to such elastic electron scattering, however, the experimental k -maps exhibit an overall, largely k -independent background of electron emissions. This background is primarily caused by inelastic scattering processes with phonons (lattice vibrations). These interactions lead to a randomization of the electron momentum, which further contributes to the residual intensity within the nodal features. Nonetheless, the core structural blueprint remains discernible in all configurations, successfully confirming the fundamental nodal topology of the molecular orbitals.

3.2 Pentacene ($C_{22}H_{14}$)

In direct comparison to the shorter tetracene chain, the spatial profiles of pentacene depicted in fig. 3.2 exhibit a significantly higher degree of clarity. Both the calculated HOMO and LUMO distributions feature the characteristic sharp, oval-shaped emission lobes, which now appear visibly elongated and broadened along the primary emission axes. This real-space geometric expansion directly alters the reciprocal footprint: the extension of the conjugated π -system over five fused benzene rings narrows the emission lobes in momentum space.

For the formerly unoccupied state, the simulated LUMO predicts two primary intensity maxima centered precisely at $k_x = 0 \text{ \AA}^{-1}$ and $k_y \approx \pm 1.4 \text{ \AA}^{-1}$, a topology that is remarkably well-reproduced by the experimental ARPES spectrum. Similarly, the occupied state exhibits an outstanding spatial alignment; the theoretical HOMO concentrates its maximum intensity into four symmetric pockets located at $k_x \approx \pm 1.1 \text{ \AA}^{-1}$ and $k_y \approx \pm 1.1 \text{ \AA}^{-1}$, which matches the experimental peak positions almost perfectly. Crucially, the experimental data sets for pentacene suffer from significantly less blurring and spatial degradation than those of tetracene. Although the experimental countours remain inherently

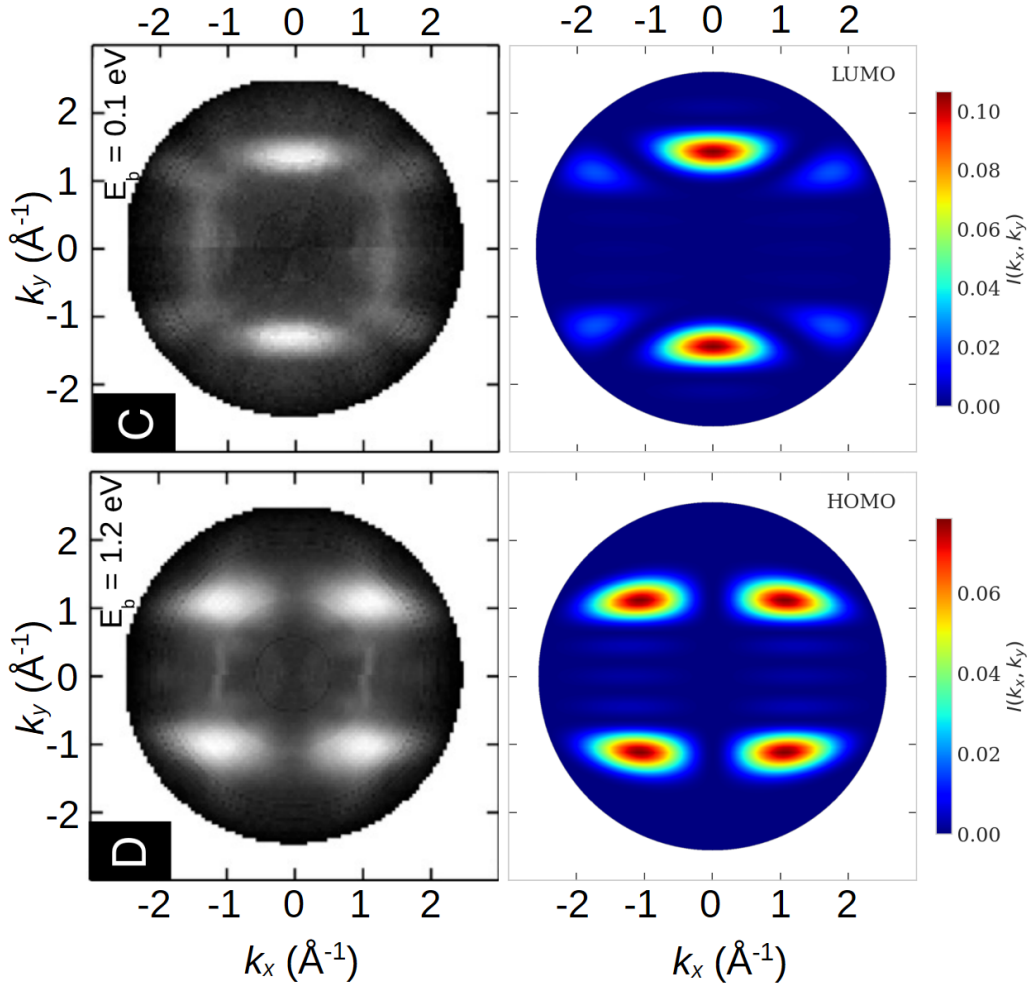


Figure 3.2: Comparison between experimental ARPES data (left) and simulated k -space intensity distributions (right) for pentacene (5A). Left panels show the measured LUMO ($E_B = 0.1$ eV) and HOMO ($E_B = 1.2$ eV). Right panels show the corresponding kmap.py simulations for the LUMO ($E_{\text{kin}} = 26.15$ eV) and HOMO ($E_{\text{kin}} = 25.05$ eV). Experimental data adapted from [6].

softer than the mathematically rigid contours of the calculation, the internal geometry and precise coordinates of the lobes can be evaluated with much higher fidelity.

This enhanced signal quality allows for a far more rigorous verification of the underlying wave function nodes. In the experimental momentum map, the k -region between the major emission lobes is not entirely dark but exhibits a systematic residual intensity. This features is a direct consequence of sample morphology; specifically, a minority of pentacene (5A) molecules is rotated by 90° with respect to the majority alignment on the Ag(110) substrate. The superposition of this rotated minority domain yields weak intensity remnants that wrap around the central core.

Conversely, the boundaries between the lobes within the HOMO reveal a more com-

plex behaviour. In the simulated HOMO, the sharp vertical and horizontal nodal planes create an ideal zero-intensity cross. In the experimental spectrum, a low-intensity residual cloud persists along the k_x direction, preventing the formation of a mathematically strict, hard nodal line at the core. Furthermore, while the simulation predicts three localized secondary interfering stripes compressed symmetrically along the k_y axis, these features remain invisible in the experimental maps. This striking divergence is attributed to finite-size effects within the numerical simulation. While the calculation is performed for an isolated, single molecule—leading to artificial interference fringes due to the spatial truncation of the wave function—the experiment probes a continuous, periodic layer of molecules where such boundary-induced oscillations are absent. Because the escaping photoelectron interacts strongly with the periodic potential of the surrounding crystal lattice, specific scattering pathways can undergo phase-matching conditions that either suppress expected intensity or redirect photoelectrons into classically forbidden regions. This underscores that while the primary orbital envelope is mapped with high quantitative accuracy, the exact fine structure of the occupied states is heavily modulated by solid-state matrix elements and final-state scattering effects.

3.3 Hexacene ($\text{C}_{26}\text{H}_{16}$)

The comparison between simulated and measured maps (fig. 3.3 for hexacene utilizes a direct split-screen comparison within the reference figures to evaluate the progression of the orbital features. The left panel of figure 3.3 presents a split-screen layout where the upper half displays simulated intensity data from an independent source [8], while the lower half contains the true experimental ARPES data. To maintain absolute consistency, the primary evaluation is conducted against the full, newly generated maps on the right.

For the lowest unoccupied molecular orbital (LUMO), the calculated momentum-map predicts two primary intensity maxima situated at $k_x = 0 \text{ \AA}^{-1}$ and $k_y \approx \pm 1.3 \text{ \AA}^{-1}$, a spatial positioning that is directly confirmed by the experimental ARPES distribution. The experimental k -maps are almost perfectly symmetric with respect to a horizontal mirror axis. However, a striking structural phenomenon is observed regarding the peak geometry. The lobes in the LUMO maps appear broader and more elongated along the k_y -axis, whereas the experimental features appear noticeably sharper, narrower, and more compressed. Furthermore, the delicate fine structure remains highly robust in this system: the secondary satellite peaks predicted by the theoretical model are clearly observable and empirically validated within the experimental map. In general, the photoemission features of the experimental hexacene k -map possess significantly sharper boundaries than those recorded for tetracene and pentacene, signaling an exceptional crystalline quality or highly favorable thin-film orientation within the sample.

An identical trend can be observed for the highest occupied molecular orbital (HOMO). The primary theoretical intensity pockets are located at $k_x \approx \pm 1.0 \text{ \AA}^{-1}$ and $k_y \approx \pm 1.0 \text{ \AA}^{-1}$. These lobes are distinctly narrower than those of its shorter precursors, establishing a systematic, monotonic evolution of peak narrowing with increasing chain length—a trend driven by the enhanced real-space delocalization of the π -electron sys-

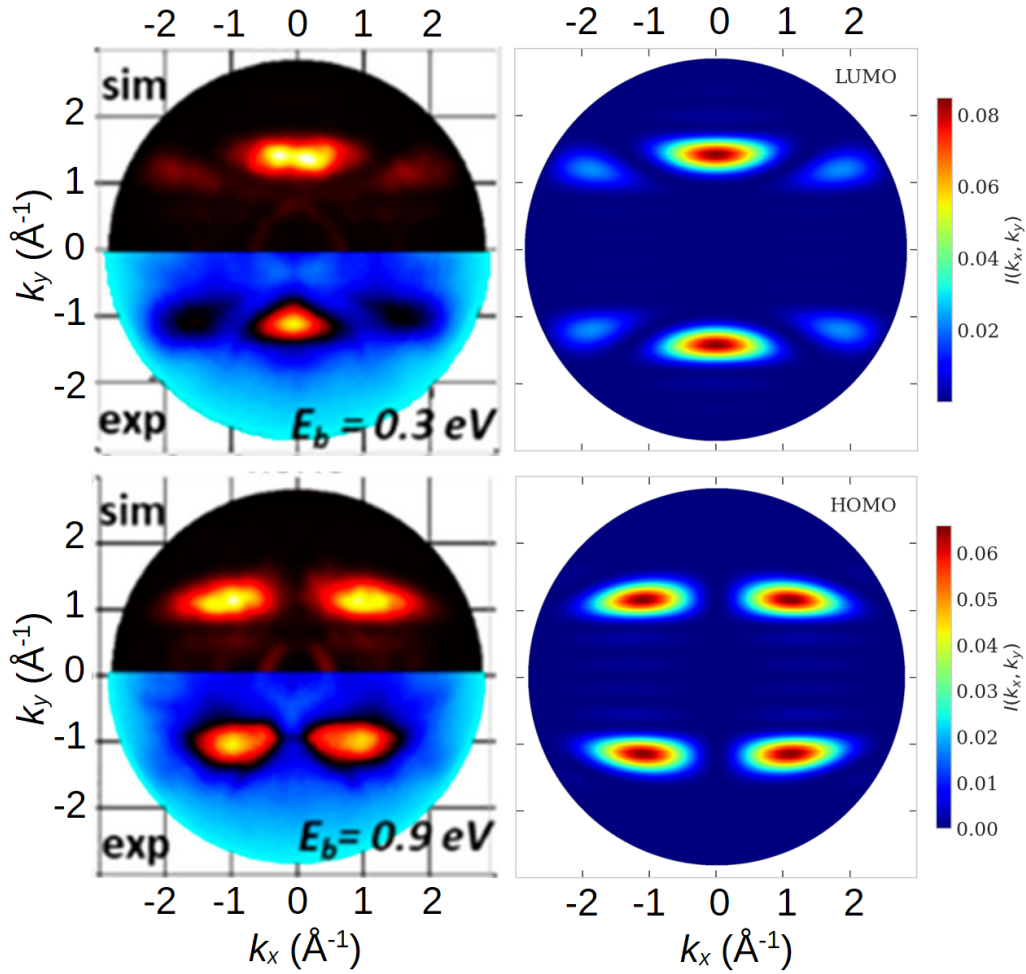


Figure 3.3: Comparison between experimental and simulated k -maps for hexacene. The left panel displays a split-view comparison of the LUMO ($E_B = 0.3$ eV) and HOMO ($E_B = 0.9$ eV), with simulated intensities (top) and experimental data (bottom). The right panel shows the corresponding full-scale `kmap.py` intensity distributions for the LUMO ($E_{\text{kin}} = 30.95$ eV) and HOMO ($E_{\text{kin}} = 30.35$ eV). Experimental data adapted from [8].

tem over the six fused benzene rings, which will be quantified in detail in a subsequent chapter. In the case of the HOMO, however, the stripes are heavily compressed and barely discernible within the calculation, rendering them entirely undetectable in the laboratory data.

Regarding the phase topology and destructive interference corridors, the theoretical models continue to project perfectly sharp, zero-intensity nodal lines. Although the sharper peak edges in the experimental data trace these underlying symmetry-driven boundaries with high fidelity, a complete intensity suppression is not achieved. Instead, a diffuse, thin background cloud of residual intensity spans across the entire reciprocal plane. Unlike the localized, structured artifacts observed in the previous systems, this continuous background lacks discrete features, indicating that as the molecular system grows longer,

multi-center electron scattering and inelastic background noise from underlying substrate layers increasingly contribute a uniform photoemission baseline that blurs the ideal destructive interference zones. Finally, an inspection of the experimental structural symmetry reveals a very subtle, asymmetric intensity drift toward the negative k_x -direction. This faint polarization- or geometry-induced matrix element effect remains exceptionally minor, leaving the central positions of the primary periodic peak positions fundamentally undisturbed.

3.4 Heptacene ($C_{30}H_{18}$)

The comparative analysis concludes with heptacene, the longest acene chain in this experimental series. Note that in the left panel in figure 3.4 the upper halves contain the experimental k -maps, while the lower halves show simulated momentum maps obtained for the 7A/Ag(110) interface [1]. The primary benchmark for the qualitative evaluation remains the uniform, full-scale maps generated on the right.

For the lowest unoccupied molecular orbital (LUMO), the calculated momentum-space map localizes its primary emission maxima at $k_x = 0 \text{ \AA}^{-1}$ and $k_y \approx \pm 1.3 \text{ \AA}^{-1}$. This spatial mapping is supported by the upper half of the experimental split-screen panel, where the primary intensity weight occupies the exact same reciprocal coordinates. The calculated HOMO distribution predicts four isolated and well-defined intensity pockets positioned at $k_x \approx \pm 1.0 \text{ \AA}^{-1}$ and $k_y \approx \pm 1.1 \text{ \AA}^{-1}$.

However, the experimental k -maps for both the HOMO and LUMO reveal additional features that set heptacene apart from its shorter homologues. Most notably, the experimental data exhibits an extra feature between the primary intensity pockets along the vertical axis, forming a continuous intensity baseline that connects the upper and lower peak pairs. This strong central intensity contribution arises from the underlying Ag sp -band emissions. Perhaps in this specific experiment for the 7A/Ag(110) interface, the Ag(110) substrate was not fully covered with a complete monolayer of 7A molecules. Such a lower molecular coverage logically explains why these substrate-related emissions appear to be noticeably stronger for the heptacene sample than for the shorter 4A, 5A, and 6A polyacene films.

Despite these substrate-related background emissions, the fundamental micro-structural features of the molecular orbitals can still be identified with sufficient clarity. The boundaries of the primary experimental peaks possess well-defined edges, allowing for a qualitative tracking of the expected destructive interference zones. While the simulated zero-intensity corridors partially disappear due to the diffuse background intensity from the silver substrate, the underlying nodal network remains discernible. This confirms that even for longer molecular systems like heptacene, where substrate contributions heavily modulate the overall intensity distribution, the essential wave function phase information remains encoded within the experimental k -maps.

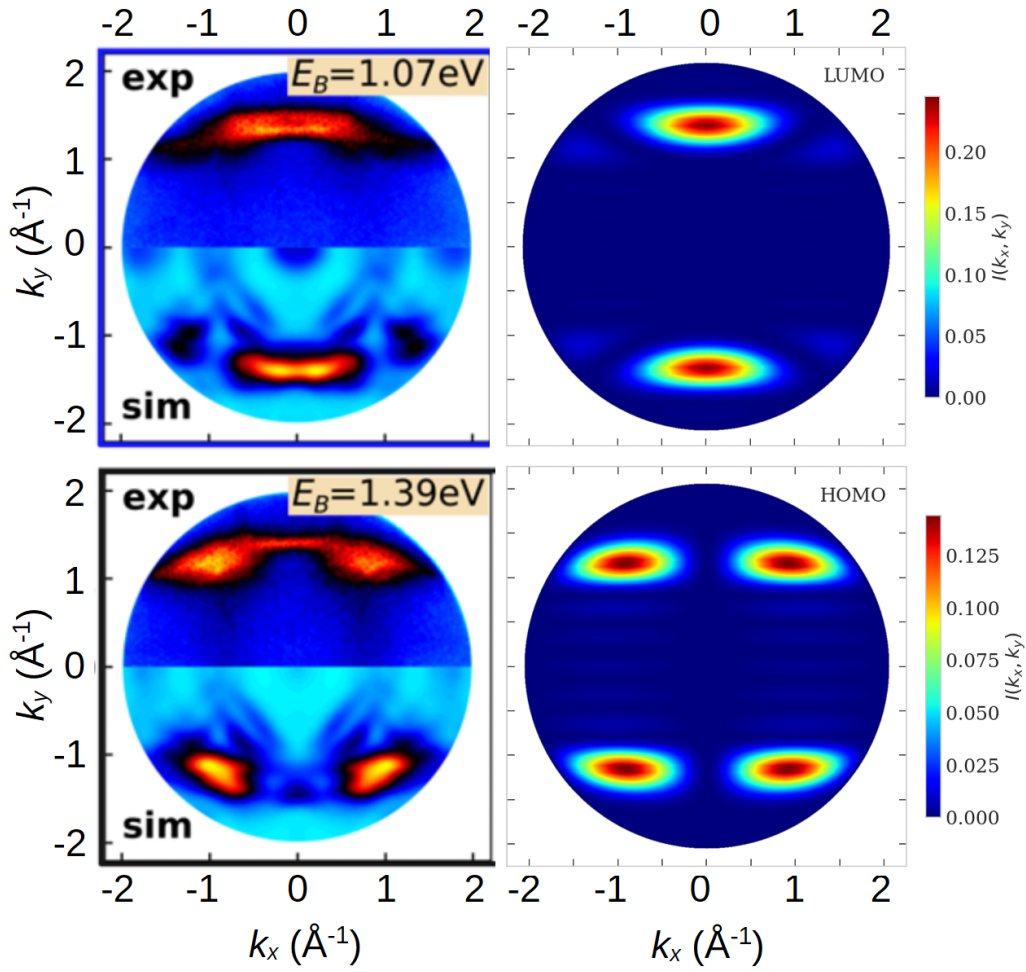


Figure 3.4: Comparison between experimental and simulated k -maps for heptacene. The left panel displays a split-view comparison of the LUMO ($E_B = 1.07$ eV) and HOMO ($E_B = 1.39$ eV), showing experimental data (top) and the simulated counterpart (bottom). The right panel shows the corresponding full-scale kmap.py intensity distributions for the LUMO ($E_{\text{kin}} = 30.18$ eV) and HOMO ($E_{\text{kin}} = 29.86$ eV). Experimental data adapted from [1].

3.5 Summary of Experimental Validation

In summary, the comparative analysis presented in this chapter successfully establishes a solid empirical benchmark for the computational framework by contrasting simulated k -space maps with experimental ARPES data sets from tetracene (4A) to heptacene (7A). The direct confrontation confirms that the model captures the primary spatial structure, orbital symmetries, and fundamental nodal networks of both the HOMO and LUMO with high quantitative fidelity.

The systematic review of the series revealed that the experimental momentum-space distributions are strongly modulated by sample-specific constraints. These range from substrate-induced intensity modulations and final-state scattering to distinct substrate-related background emissions, such as the Ag sp -band features observed in the longer

acene layers. Furthermore, the persistent background intensity observed within the experimental destructive interference corridors highlights the intrinsic limitations of the plane-wave final-state approximation, which inherently neglects multi-center forward scattering and inelastic substrate contributions, such as electron-phonon scattering. Ultimately, despite these intensity and background deviations, the exceptional reliability in reproducing the core topological features validates the plane-wave model within the experimental regime, providing the necessary foundation for its application to extended, purely theoretical molecular architectures.

4 Theoretical Trend Analysis and Quantum Scaling Laws

While the direct comparison with experimental data restricted the analysis to specific, experimentally accessible molecular sizes, the following purely theoretical study enables a systematic, clean investigation across the entire sequence from naphthalene to decacene under idealized, uniform conditions. To ensure absolute comparability and isolate structural trends, all computational k -space intensity distributions $I(k_x, k_y)$ were generated using a fixed kinetic energy of $E_{\text{kin}} = 20 \text{ eV}$.

The primary objective of this chapter is to map the physical evolution of the highest occupied molecular orbitals as the molecules are systematically elongated by the step-by-step addition of fused benzene rings. Therefore, the analysis in this section is divided into three consecutive stages:

First, the global transformation of the two-dimensional intensity topographies and the emergence of fine-structure interference features are evaluated. Second, one-dimensional intensity profiles extracted at a fixed momentum coordinate are utilized to quantify the simultaneous modulation of peak heights, positions and widths. Finally, the empirical line-shape variations are connected to fundamental quantum mechanics by benchmarking the scaling of the full width at half maximum against the inverse molecular length.

4.1 Evolution of Two-Dimensional Intensity Distributions

The systematic progression of the computed k -space maps from naphthalene to nonacene, as illustrated in Figure 4.1, reveals a striking transformation of the orbital signatures. Starting with naphthalene, the distribution is characterized by four broad, almost circular intensity maxima that occupy a large portion of the reciprocal plane, separated by a distinct central nodal cross that represents the fundamental phase boundaries of the HOMO wave function. As the molecular chain length increases, several key trends emerge seamlessly. Beginning with anthracene, the primary peaks undergo a significant contraction along the k_y -axis, becoming increasingly narrow and needle-like, while their lateral positions along the k_x -direction remain nearly constant.

Simultaneously, a characteristic higher-order interference pattern appears in the longer acenes, manifested as secondary intensity maxima located between the primary lobes along the k_y -direction. The number of these secondary features scales directly with the number of fused benzene rings, where anthracene displays two features, tetracene resolves into four, pentacene into six, and hexacene into eight distinct sub-peaks. Upon reaching the longest systems such as nonacene, these secondary features lose significant intensity and eventually vanish into a wide, low-intensity region between the primary peaks. The primary peaks themselves appear highly compressed, with their lower boundaries shifting toward higher k_y -values while the upper edges remain stable, effectively narrowing the vertical footprint of the orbital distribution.

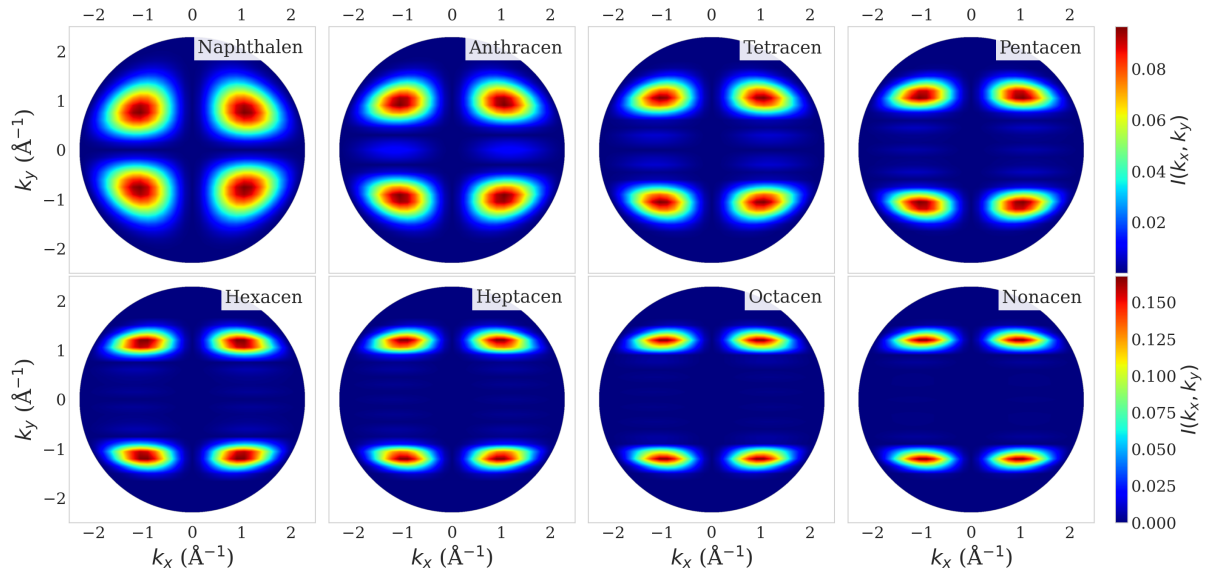


Figure 4.1: Simulated two-dimensional k -space photoemission intensity distributions $I(k_x, k_y)$ of the highest occupied molecular orbitals (HOMO) across the homologous linear acene series, spanning from naphthalene (2A) to nonacene (9A). All calculations were performed under uniform conditions at a fixed photoelectron kinetic energy of $E_{\text{kin}} = 20 \text{ eV}$.

These observations provide a direct visualization of the relationship between real-space delocalization and reciprocal-space interference. In organic semiconductors like the polyacene series, the π -electron system is delocalized over the entire length of the carbon backbone. As more benzene rings are added, the confinement box in which the electrons can freely move becomes longer, allowing for higher-frequency oscillations in the wave function. In the Fourier-transformed k -space, these quantum mechanical oscillations manifest as an increasing number of interference fringes that form the secondary peaks.

The structural narrowing of the k_y -profile is a classic hallmark of the Heisenberg uncertainty principle. As the spatial extent of the electron becomes less certain along the long molecular axis due to enhanced delocalization, its momentum becomes more precisely defined, leading to the observed sharpening of the peaks in k -space. From the perspective of organic electronics, this sharpening carries significant physical weight. In a molecular crystal, the overlap of these narrow momentum distributions between adjacent molecules directly dictates the charge transfer integral. A more localized momentum distribution in k -space implies a highly delocalized and potentially more mobile electronic state in real space, which is a key requirement for facilitating efficient charge transport in high-performance organic semiconductors. The transition from the broad, diffuse features of naphthalene to the highly directed, sharp emission of nonacene thus illustrates the maturation of a discrete molecule into a quasi-one-dimensional quantum wire.

4.2 Analysis of One-Dimensional Intensity Profiles

To quantitatively track the evolution of the photoemission profiles, one-dimensional intensity cuts were extracted from the calculated two-dimensional distributions along the k_y -axis at a fixed lateral momentum of $k_x \approx 1.0 \text{ \AA}^{-1}$, as compiled in Figure 4.2. This specific momentum coordinate was selected because it intersects precisely with the absolute maxima of the primary HOMO lobes, thereby yielding the most reliable and physically meaningful information regarding the quantum mechanical line-shape modulation.

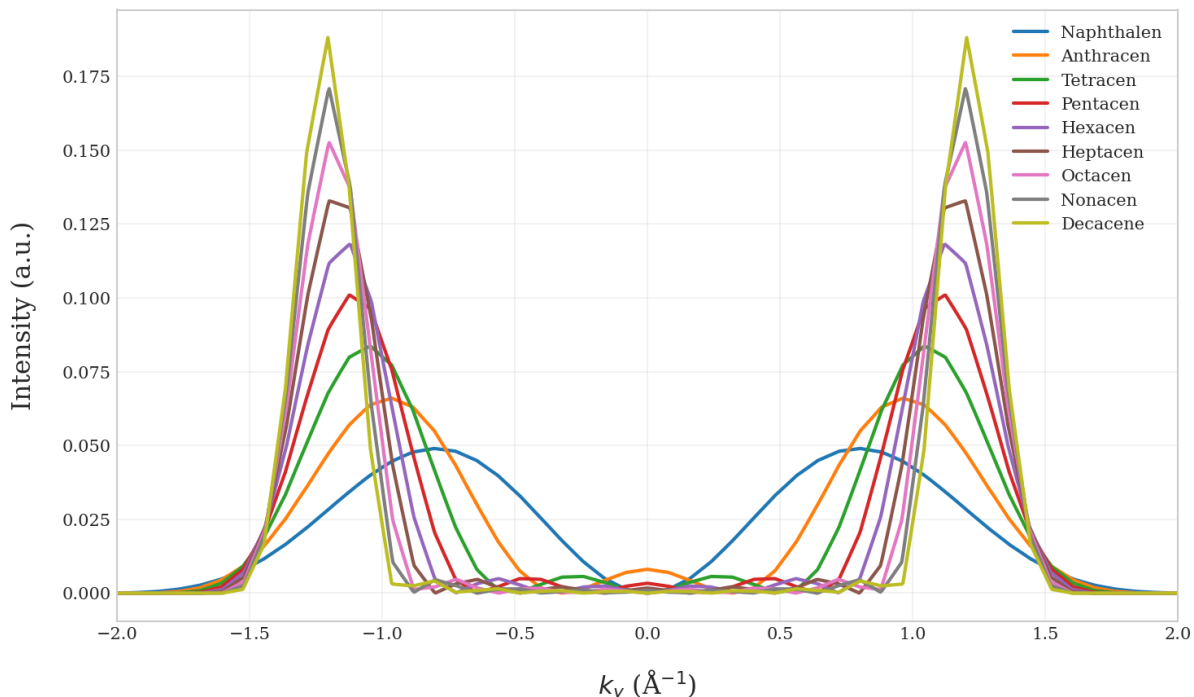


Figure 4.2: One-dimensional simulated k -space intensity profiles extracted along the k_y -axis at a fixed momentum coordinate of $k_x \approx 1.0 \text{ \AA}^{-1}$. The plot compares the complete homologous acene series from naphthalene to decacene ($E_{\text{kin}} = 20 \text{ eV}$).

The most prominent feature observed upon initial inspection of these profiles is the drastic, monotonic increase in peak amplitude with expanding molecular size. While naphthalene exhibits a remarkably flat, low-intensity curve, the maximum peak intensity scales upward by a factor of more than four when reaching decacene. This rapid surge in peak height is a direct consequence of the norm-conservation inherent to the calculated molecular wave functions. Because the total integrated electronic charge remains normalized across the series, the systematic spatial narrowing of the momentum distribution forces a concentration of the spectral weight into a progressively tighter region. Consequently, to conserve the total area under the probability density curve, the amplitude must rise dramatically, driving the transition from a broad, low-signal profile to an exceptionally intense, sharp resonance.

Simultaneously, a distinct and systematic movement of the absolute peak positions along

the k_y -axis is observed. For naphthalene, the maximum intensity pocket is localized relatively close to the reciprocal center at $k_y \approx \pm 1.0 \text{ \AA}^{-1}$. However, as additional benzene rings are incorporated into the aromatic backbone, these primary peaks shift continuously outward into the higher-momentum regime, eventually stabilizing at a asymptotic value of approximately $k_y \approx \pm 1.55 \text{ \AA}^{-1}$ for the longer acenes. This position shift is closely linked to the geometric stabilization and the internal periodicity of the carbon framework. In smaller oligomers, the electronic structure is highly dominated by boundary conditions and localized end-group effects. As the chain length increases, the central regions of the molecule increasingly resemble a perfect, periodic lattice with stabilized carbon-carbon bond lengths. The convergence of the peak positions at higher acene lengths demonstrates that the electronic system undergoes a fundamental transition from a finite, boundary-dominated molecular state to a quasi-infinite, periodic crystal band structure, where the fixed peak position reflects the intrinsic spatial frequency of the stabilized polyacene unit cell.

Finally, the peak shapes undergo a transformation from a broad, diffuse Gaussian-like envelope in naphthalene to ultra-sharp, needle-like peak structures in the higher-order homologues. Accompanying this narrowing is the development of multiple secondary interference oscillations between the two primary maxima, beginning noticeably with anthracene. Interestingly, these secondary satellite peaks are most prominent and clearly resolved within the intermediate acenes, whereas they begin to flatten significantly and damp out upon approaching decacene. This line-shape behavior reflects the delicate interplay of quantum coherence across the extended system. While the emergence of the fringes confirms that the phase information remains highly coherent across the entire molecular backbone for the medium-sized chains, the subsequent suppression of these secondary oscillations in the heaviest acenes indicates that the momentum distribution converges toward the absolute limits of a continuous, free-electron-like state, where the extreme real-space delocalization increasingly concentrates almost the entire kinetic energy signature exclusively within the primary Bragg-like emission channels.

4.3 Linear Scaling Laws and the One-Dimensional Particle-in-a-Box Model

To establish a quantitative link between the real-space geometry of the polyacenes and their computed reciprocal-space signatures, the full width at half maximum (FWHM) of the primary HOMO emission peaks along the k_y -axis was systematically evaluated. These numerical line-width values are plotted in Figure 4.3 as a function of the inverse molecular length ($1/L$), where L represents the physical longitudinal extension of the conjugated π -electron cloud in real space. The resulting distribution of the DFT-derived data points reveals an exceptionally clean, highly linear correlation across the entire molecular series, stretching from the short naphthalene system to the highly extended decacene framework. A linear regression fit applied to these data points reveals a consistent linear trend, confirming a direct proportionality between the momentum-space peak sharpness and the inverse geometric size of the molecule across the entire series.

This strict $1/L$ dependence provides a direct and elegant confirmation of the fundamental

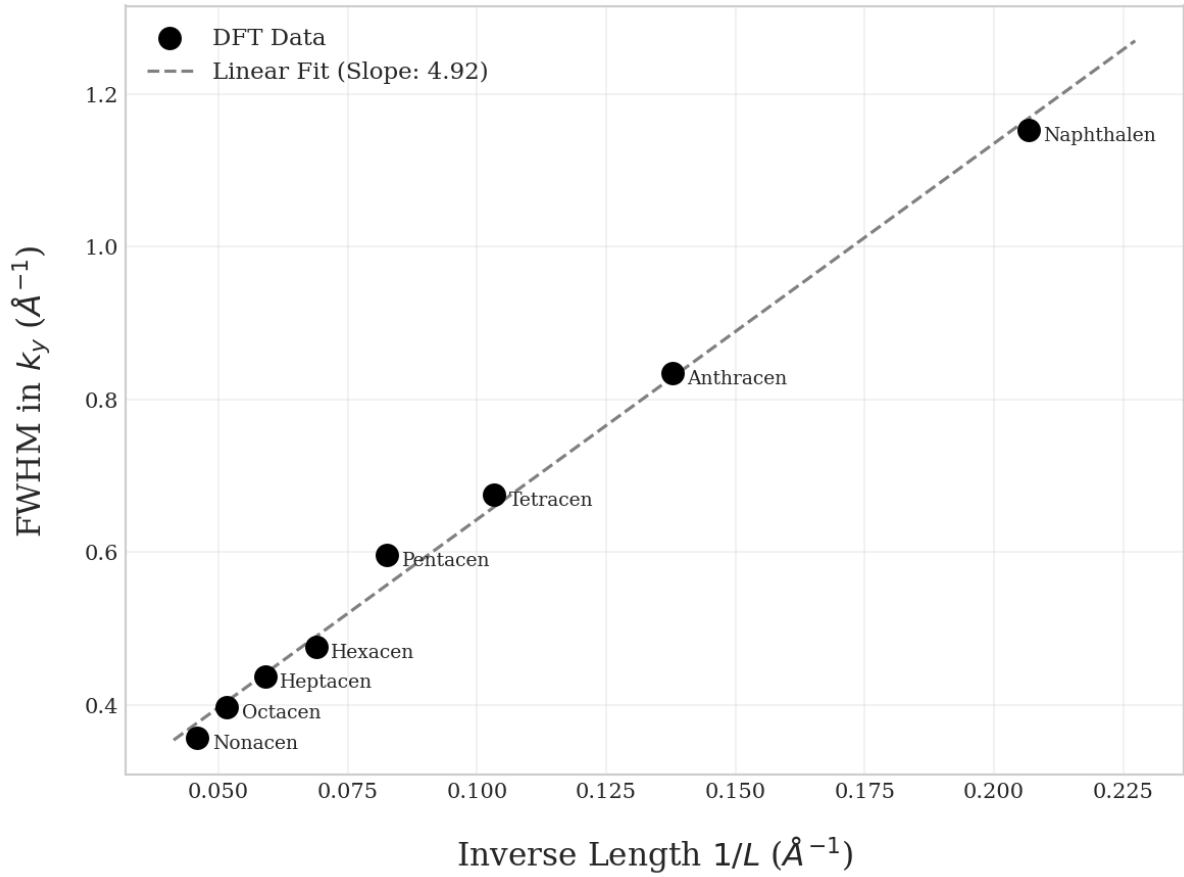


Figure 4.3: Linear scaling behavior of the simulated photoemission peak width (FWHM along the k_y -axis) as a function of the inverse molecular length ($1/L$) for the entire polyacene series from naphthalene to decacene ($E_{\text{kin}} = 20$ eV).

Heisenberg uncertainty principle and can be fully understood by mapping the electronic behavior onto the quantum mechanical model of an idealized one-dimensional particle-in-a-box. In this foundational model, an electron is confined within an infinitely deep potential well of length L , representing the boundaries of the linear carbon backbone. The spatial wave function $\psi(x)$ for the ground state or lowest-lying envelopes in such a box is mathematically described by a standing sine wave localized strictly within the boundaries:

$$\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad (4.1)$$

Because an ARPES experiment effectively measures the square of the Fourier transform of this spatial wave function, the corresponding momentum-space wave function $\phi(k)$ must be calculated by transitioning from real space to the k -domain via the Fourier integral. Performing this mathematical transformation on a truncated periodic wave function of finite length L yields a momentum distribution governed by the classic sinc-function architecture:

$$\phi(k) \propto \frac{\sin(kL/2)}{kL/2} \quad (4.2)$$

When evaluating the intensity profile $I(k) = |\phi(k)|^2$, the width of the resulting central

diffraction lobe is dictated entirely by the argument of the sinc-function. Mathematically, the first zero-crossings and consequently the full width at half maximum (Δk) of this intensity distribution are inversely proportional to the box length:

$$\Delta k \propto \frac{1}{L} \quad (4.3)$$

This inverse relationship is the exact physical mechanism driving the scaling law visualized in Figure 4.3. In short real-space systems like naphthalene, the tight spatial confinement forces a severe localization of the electron wave function, which inherently spreads the momentum distribution across a wide range of k -values, creating the broad, flat profiles observed previously. Conversely, as the polyacene chain is extended toward decacene, the spatial confinement is drastically relaxed along the longitudinal axis. The π -electrons can now delocalize freely over a much larger real-space domain. According to the Fourier relationship, this real-space delocalization forces a high degree of localization in the reciprocal domain, compressing the spectral weight into the ultra-sharp, needle-like peak geometries.

The fact that the calculated DFT data points follow this idealized 1D particle-in-a-box scaling law with a near-perfect linear fit underscores that the extended π -system of linear acenes behaves fundamentally like an unperturbed, one-dimensional organic quantum wire. It proves that the computational framework smoothly reproduces the transition from discrete molecular orbital confinement to the deterministic scaling laws that govern low-dimensional electronic materials.

4.4 Summary of Theoretical Trends

In conclusion, the systematic trend analysis presented in this chapter confirms that the electronic structure of the linear polyacene series follows highly predictable, fundamental quantum mechanical rules. By isolating the purely structural effects under uniform computational conditions with a fixed kinetic energy of $E_{\text{kin}} = 20$ eV, it was possible to track the precise evolution of the highest occupied molecular orbital from naphthalene (2A) up to decacene (10A).

The transition from broad, diffuse features to highly compressed, needle-like peaks—coupled with the appearance of quantized higher-order interference fringes—visually demonstrates the mathematical impact of expanding the aromatic backbone in reciprocal space. Quantitatively, this change is characterized by an increase in spectral weight, leading to higher peak amplitudes and more clearly defined peak positions. Most importantly, the near-perfect linear correlation between the full width at half maximum and the inverse molecular length ($1/L$) provides unambiguous quantitative proof that the extended π -electron system behaves in strict accordance with an idealized one-dimensional particle-in-a-box model. This successful transition from discrete molecular orbital tracking to deterministic quantum scaling laws establishes the final theoretical foundation required to contextualize the findings within the broader scope of the entire thesis.

5 Conclusion and Outlook

This thesis has successfully demonstrated the power and predictive capability of combining density functional theory with the plane-wave final-state approximation to model, validate, and understand the angle-resolved photoemission spectroscopy signatures of the homologous linear polyacene series. By comparing the initial experimental data with the calculated theoretical trends, a clear connection between laboratory observations and the underlying quantum mechanical properties of the molecules has been established.

The first major result of this work was the benchmarking in Chapter 3, where computational k -space simulations were directly compared with experimental ARPES data for tetracene, pentacene, hexacene, and heptacene. The qualitative agreement regarding peak positions, orbital symmetries, and the characteristic nodal patterns validated the chosen theoretical framework. It demonstrated that the plane-wave final-state approximation, despite its simplified treatment of photoelectron scattering dynamics, remains a robust and computationally efficient tool for capturing the emission characteristics of organic frontier molecular orbitals.

Building upon this validation, Chapter 4 used the framework to explore the electronic evolution across the series from naphthalene (2A) to decacene (10A). This systematic analysis shows the relationship between molecular length and reciprocal-space orbital transformations. As the linear carbon backbone elongates, the primary HOMO features compress along the k_y -axis, shifting from broad distributions into narrow resonances. This compression is associated with the delocalization of the π -system in real space, as indicated by the linear scaling of the peak width (FWHM) against the inverse molecular length ($1/L$). The extended acenes thus serve as a model system for studying one-dimensional electronic confinement in organic molecules.

Looking forward, this thesis underscores that computational modeling is a valuable predictive tool for materials science. For the longest acenes like nonacene and decacene, which are highly unstable and difficult to synthesize experimentally, simulations offer a reliable method to explore the electronic properties of these larger organic systems. The insights gained regarding highly directed momentum profiles and orbital delocalization can inform future molecular engineering strategies. Ultimately, this approach provides a basis for analyzing and optimizing charge transport properties, supporting the development of next-generation organic electronics.

6 Python Scripts

```
1 # --- BIBLIOTHEKEN --- #
2
3 import numpy as np
4 import matplotlib as mpl
5 import os
6
7 from pyscf import gto
8 from pyscf import scf, dft
9 from pyscf import lib
10 from scipy.signal import find_peaks
11
12 lib.num_threads(os.cpu_count())
```

```
1 # --- PLOTTING PARAMETER --- #
2
3 plt.style.use('seaborn-v0_8-whitegrid' if 'seaborn-v0_8-whitegrid'
4           ' in plt.style.available else 'default')
5
6 mpl.rcParams.update({
7     'font.family': 'serif',
8     'font.size': 15,
9     'axes.labelsize': 12,
10    'axes.titlesize': 12,
11    'xtick.labelsize': 10,
12    'ytick.labelsize': 10,
13    'figure.titlesize': 14,
14    'xtick.direction': 'in',
15    'ytick.direction': 'in',
16    'pdf.fonttype': 42,
17    'ps.fonttype': 42
18 })
19
20 COLOR_PROFILE = '#d62728'
21 COLOR_FWHM = '#1f77b4'
```

```
1 # --- DFT CALCULATIONS AND VOLUMETRIC DATA GENERATION --- #
2
3 acene_namen = {
4     "2A": "Naphthalen",
5     "3A": "Anthracen",
6     "4A": "Tetracen",
7     "5A": "Pentacen",
8     "6A": "Hexacen",
9     "7A": "Heptacen",
10    "8A": "Octacen",
11    "9A": "Nonacen",
```

```
12     "10A": "Decacen"
13 }
14
15 cube_output_dir = '[02] cube-Dateien'
16 if not os.path.exists(cube_output_dir):
17     os.makedirs(cube_output_dir)
18
19 # --- Function for generating the .cube file
20
21 def write_cube(mol, psi, x, y, z, cube_name):
22
23     num_atoms = mol.natm
24
25     dx = x[1] - x[0]
26     dy = y[1] - y[0]
27     dz = z[1] - z[0]
28     nx, ny, nz = psi.shape
29
30     with open(cube_name, 'w') as f:
31
32         f.write('cube file generated from PySCF\n')
33         f.write('Molecular orbital data\n')
34         f.write('%5i %15.10f %15.10f %15.10f \n' % (num_atoms,
35             x[0], y[0], z[0]))
36         f.write('%5i %15.10f %15.10f %15.10f \n' % (nx, dx, 0,
37             0))
38         f.write('%5i %15.10f %15.10f %15.10f \n' % (ny, 0, dy,
39             0))
40         f.write('%5i %15.10f %15.10f %15.10f \n' % (nz, 0, 0,
41             dz))
42
43     for i in range(num_atoms):
44         charge = mol.atom_charge(i)
45         coords = mol.atom_coord(i)
46         f.write('%5i %8.5f %15.10f %15.10f %15.10f \n' % (
47             charge, float(charge), coords[0], coords[1],
48             coords[2]))
49
50     for i in range(nx):
51         for j in range(ny):
52             for k in range(nz):
53                 f.write(' %13.5E' % psi[i, j, k])
54                 if (k + 1) % 6 == 0:
55                     f.write('\n')
56             if nz % 6 != 0:
57                 f.write('\n')
58
59
60 def get_xyz_grid(coords, add_space=4, grid_spacing=0.3):
```

```
61
62     x_min, y_min, z_min = np.min(coords, axis=0)
63     x_max, y_max, z_max = np.max(coords, axis=0)
64
65     x_min -= add_space
66     y_min -= add_space
67     z_min -= add_space
68     x_max += add_space
69     y_max += add_space
70     z_max += add_space
71
72     nx = int((x_max - x_min) / grid_spacing)
73     ny = int((y_max - y_min) / grid_spacing)
74     nz = int((z_max - z_min) / grid_spacing)
75
76     x = np.linspace(x_min, x_max, nx)
77     y = np.linspace(y_min, y_max, ny)
78     z = np.linspace(z_min, z_max, nz)
79
80     X, Y, Z = np.meshgrid(x, y, z, indexing='ij')
81
82     return X, Y, Z
83
84 # --- Loop over all acenes
85
86 for molecule_short, molecule_name in acene_namen.items():
87
88     molecule = f'[01] xyz-Dateien/{molecule_short}.xyz'
89
90     if not os.path.exists(molecule):
91         print(f"File not found: {molecule} -> skip {molecule_name}")
92         continue
93
94
95 # Energy and Molecular Orbitals
96
97 mol = gto.Mole()
98
99 all_lines = open(molecule).readlines()
100 mol.atom = "".join(all_lines[2:])
101
102 mol.basis = '6-31g*'
103 mol.cart = False
104 mol.build()
105
106 mol.max_memory = 26000 # Hardwareacceleration
107
108
```

```
109     atom_coords = mol.atom_coords()
110     for ib in range(mol.nbas):
111         atom = mol.bas_atom(ib)
112         R = atom_coords[atom]
113         nprim = mol.bas_nprim(ib)
114         l = mol.bas_angular(ib)
115         nctr = mol.bas_nctr(ib)
116         expnt = mol.bas_exp(ib)
117         coeff = mol.bas_ctr_coeff(ib)
118
119     # DFT-Calculation
120
121     mf = dft.RKS(mol)
122     mf.kernel()
123
124     # 3D-GRID
125
126     coords = mol.atom_coords()
127     X, Y, Z = get_xyz_grid(coords)
128     grid_coords = np.vstack([X.ravel(), Y.ravel(), Z.ravel()]).T
129
130     ao_values = mol.eval_gto('GTOval', grid_coords)
131
132     # Getting the HOMO and LUMO indices
133
134     occ_indices = np.where(mf.mo_occ > 0)[0]
135     homo_idx = occ_indices[-1]
136
137     unocc_indices = np.where(mf.mo_occ == 0)[0]
138     lumo_idx = unocc_indices[0]
139
140     # Calculation of the 3D-wavefunctions
141
142     psi_flat_homo = np.dot(ao_values, mf.mo_coeff[:, homo_idx])
143     psi_3d_homo = psi_flat_homo.reshape(X.shape)
144
145     psi_flat_lumo = np.dot(ao_values, mf.mo_coeff[:, lumo_idx])
146     psi_3d_lumo = psi_flat_lumo.reshape(X.shape)
147
148     x_axis = X[:, 0, 0]
149     y_axis = Y[0, :, 0]
150     z_axis = Z[0, 0, :]
151
152     write_cube(mol, psi_3d_homo, x_axis, y_axis, z_axis,
153               f'{cube_output_dir}/{molecule_short}_homo.cube')
154     write_cube(mol, psi_3d_lumo, x_axis, y_axis, z_axis,
155               f'{cube_output_dir}/{molecule_short}_lumo.cube')
```

```
1 # --- PLOTTING HOMO AND LUMO --- #
2
3 E_kin_default = 20          # [eV]
4 phi = 3.75                 # Workfunction [eV]
5 output_dir = '[03] Impuls-Karten'
6 if not os.path.exists(output_dir):
7     os.makedirs(output_dir)
8
9 # Photonenergies
10 h_nu_dict = {
11     '4A': 25,
12     '5A': 30.0,
13     '6A': 35.0,
14     '7A': 21.22
15 }
16
17 # Bindingenergies
18 Eb_dict = {
19     '4A': {'lumo': 0.10, 'homo': 1.50},
20     '5A': {'lumo': 0.1, 'homo': 1.2},
21     '6A': {'lumo': 0.3, 'homo': 0.9},
22     '7A': {'lumo': 1.07, 'homo': 1.39}
23 }
24
25 # All molecules
26 molecules = [
27     ('2A', 'Naphthalene'),
28     ('3A', 'Anthracene'),
29     ('4A', 'Tetracene'),
30     ('5A', 'Pentacene'),
31     ('6A', 'Hexacene'),
32     ('7A', 'Heptacene'),
33     ('8A', 'Octacene'),
34     ('9A', 'Nonacene'),
35     ('10A', 'Decacene')
36 ]
37
38 # Plotting limits
39 k_limits = {
40     "2A": (-3.0, 3.0),
41     "3A": (-3.0, 3.0),
42     '4A': (-2.5, 2.5),
43     '5A': (-3, 3),
44     '6A': (-3, 3),
45     '7A': (-2.25, 2.25),
46     "8A": (-3.0, 3.0),
47     "9A": (-3.0, 3.0),
48     "10A": (-3.0, 3.0)
```

```
49 }
50
51
52
53
54 # --- Loop over all molecules
55 for molecule_short, molecule_name in molecules:
56
57     lim = k_limits.get(molecule_short, (-3, 3))
58
59     fig, (ax1, ax2) = plt.subplots(2, 1, figsize=(6, 10),
60                                   dpi=150)
61
62     ax1.grid(False)
63     ax2.grid(False)
64
65     # Plotting the LUMO
66     file_lumo = rf'[02] cube-Dateien/{molecule_short}_lumo.cube'
67
68     if not os.path.exists(file_lumo):
69         print(f"Warning: {file_lumo} not found. Skipping
70               {molecule_name}.")
71         plt.close(fig)
72         continue
73
74     with open(file_lumo, 'r') as f:
75         cubefile_lumo = f.read()
76
77     if molecule_short in Eb_dict and 'lumo' in Eb_dict[
molecule_short]:
78         h_nu = h_nu_dict.get(molecule_short, 21.2)
79         E_kin_lumo = h_nu - phi - Eb_dict[molecule_short]['lumo']
80     else:
81         E_kin_lumo = E_kin_default
82
83     orbital_lumo = Orbital(cubefile_lumo, dk3D=0.08)
84     orbital_lumo.get_kmap(dk=0.005, E_kin=E_kin_lumo)
85
86     im_lumo = orbital_lumo.plot(ax1,
87                                title='',
88                                kxlim=lim, kylim=lim)
89
90     ax1.set_xlabel('')
91     ax1.set_ylabel('')
92     ax1.set_xticklabels([])
93     ax1.set_yticklabels([])
94
95     ax1.tick_params(axis='both',
96                     which='both',
```

```
97         direction='in',
98         top=True,
99         bottom=True,
100         left=True,
101         right=True,
102         length=6)
103
104     ax1.text(0.95, 0.95, 'LUMO',
105             transform=ax1.transAxes,
106             fontsize=font_size,
107             verticalalignment='top',
108             horizontalalignment='right',
109             bbox=dict(facecolor='white',
110                     alpha=0.7,
111                     edgecolor='none'))
112
113     if im_lumo is not None:
114         mappable_lumo = im_lumo
115     else:
116         mappable_lumo = ax1.images[0]
117
118     cbar_lumo = fig.colorbar(mappable_lumo,
119                             ax=ax1,
120                             shrink=0.7,
121                             pad=0.04
122                             )
123     cbar_lumo.ax.tick_params(labelsize=font_size)
124     cbar_lumo.set_label('$I(k_x, k_y)$', size=font_size)
125
126
127     # Plotting the HOMO
128     file_homo = rf'[02] cube-Dateien/{molecule_short}_homo.cube'
129     with open(file_homo, 'r') as f:
130         cubefile_homo = f.read()
131
132     if molecule_short in Eb_dict and 'homo' in Eb_dict[
133 molecule_short]:
134         h_nu = h_nu_dict.get(molecule_short, 21.2)
135         E_kin_homo = h_nu - phi - Eb_dict[molecule_short]['homo']
136     else:
137         E_kin_homo = E_kin_default
138
139     orbital_homo = Orbital(cubefile_homo, dk3D=0.08)
140     orbital_homo.get_kmap(dk=0.005, E_kin=E_kin_homo)
141
142     im_homo = orbital_homo.plot(ax2,
143                               title='',
144                               kxlim=lim, kylim=lim)
145
146     ax2.set_xlabel('')
```

```

145     ax2.set_ylabel('')
146
147     ax2.set_xticklabels([])
148     ax2.set_yticklabels([])
149
150     ax2.tick_params(axis='both',
151                    which='both',
152                    direction='in',
153                    top=True,
154                    bottom=True,
155                    left=True,
156                    right=True,
157                    length=6)
158
159     ax2.text(0.95, 0.95, 'HOMO', transform=ax2.transAxes,
160             fontsize=font_size,
161             verticalalignment='top',
162             horizontalalignment='right',
163             bbox=dict(facecolor='white',
164                     alpha=0.7,
165                     edgecolor='none'))
166
167     if im_homo is not None:
168         mappable_homo = im_homo
169     else:
170         mappable_homo = ax2.images[0]
171
172     cbar_homo = fig.colorbar(mappable_homo,
173                             ax=ax2,
174                             shrink=0.7,
175                             pad=0.04)
176     cbar_homo.ax.tick_params(labelsize=font_size)
177     cbar_homo.set_label('$I(k_x, k_y)$', size=font_size)
178
179     # Saving the Images
180     plt.tight_layout()
181
182     save_path = os.path.join(output_dir,
183                             f"{molecule_short}_homo_lumo.png")
184     plt.savefig(save_path, bbox_inches='tight')
185
186     plt.close(fig)
187

```

```

1  # --- PLOTTING THE 4x2 GRID --- #
2
3  E_kin = 20                                # [eV]
4
5  input_dir = '[02] cube-Dateien'

```

```
6 output_dir = '[03] Impuls-Karten'
7
8 cube_files = [f for f in os.listdir(input_dir) if f.endswith(".
    cube") and "10A" not in f]
9
10 cube_files.sort(key=lambda x: int(''.join(filter(str.isdigit, x))
    or 0))
11
12 if cube_files:
13
14     fig, axes = plt.subplots(2, 4, figsize=(18, 9), dpi=150)
15     axes_flat = axes.flatten()
16
17     reihe1_images = []
18     reihe2_images = []
19
20     for idx, (molecule_short, display_name) in enumerate(
acene_namen.items()):
21         ax = axes_flat[idx]
22
23         filename = f"{molecule_short}_homo.cube"
24         file_path = os.path.join(input_dir, filename)
25
26         cubefile = open(file_path).read()
27         orbital = Orbital(cubefile)
28
29         pdata = orbital.get_kmap(dk=0.005, E_kin=E_kin)
30         orbital.plot(ax,
31                     title='',
32                     kxlim=(-2.5, 2.5),
33                     kylim=(-2.5, 2.5))
34
35         ax.grid(False)
36
37         ax.text(0.95, 0.95,
38               rf'{display_name}',
39               transform=ax.transAxes,
40               fontsize=20,
41               verticalalignment='top',
42               horizontalalignment='right',
43               bbox=dict(facecolor='white',
44                       alpha=0.9,
45                       edgecolor='none'))
46
47         ax.xaxis.tick_top()
48         ax.tick_params(axis='both',
49                       which='both',
50                       labelleft=True,
51                       labeltop=True,
```

```

52         labelsizer=18)
53
54     if idx < 4:
55         ax.set_xlabel('')
56     else:
57         ax.xaxis.label.set_size(24)
58
59     if idx == 0 or idx == 4:
60         ax.yaxis.label.set_size(24)
61     else:
62         ax.set_ylabel('')
63
64     if ax.images:
65         if idx < 4:
66             reihe1_images.append(ax.images[0])
67         else:
68             reihe2_images.append(ax.images[0])
69
70     plt.tight_layout()
71
72     if reihe1_images:
73         cbar1 = fig.colorbar(reihe1_images[-1], ax=axes[0, :],
fraction=0.018, pad=0.02)
74         cbar1.set_label(r"$I(k_x, k_y)$", size=22)
75         cbar1.ax.tick_params(labelsizer=18)
76
77     if reihe2_images:
78         cbar2 = fig.colorbar(reihe2_images[-1], ax=axes[1, :],
fraction=0.018, pad=0.02)
79         cbar2.set_label(r"$I(k_x, k_y)$", size=22)
80         cbar2.ax.tick_params(labelsizer=18)
81
82     if not os.path.exists(output_dir):
83         os.makedirs(output_dir)
84
85     # Saving the Image
86     save_path = os.path.join(output_dir, "impulskarten_grid.png")
87     plt.savefig(save_path, bbox_inches='tight')
88     plt.show()
89
90

```

```

1 # --- 1D CUTS THROUGH k-MAPS --- #
2
3 E_kin = 20      # [eV]
4
5 fwhm_liste = []
6 vergleichs_daten = []
7

```

```
8 input_dir = '[02] cube-Dateien'
9 output_dir = '[03] Impuls-Karten'
10 output_plots_dir1 = "[04] 1D-Schnitte"
11 if not os.path.exists(output_plots_dir1):
12     os.makedirs(output_plots_dir1)
13
14 output_plots_dir2 = "[05] Vergleichsplots"
15 if not os.path.exists(output_plots_dir2):
16     os.makedirs(output_plots_dir2)
17
18 for file_basename, display_name in acene_namen.items():
19     file_path = os.path.join(input_dir, f"{file_basename}_homo.
20     cube")
21
22     if os.path.exists(file_path):
23         cubefile = open(file_path).read()
24         orbital = Orbital(cubefile, dk3D=0.08)
25         pdata = orbital.get_kmap(dk=0.005, E_kin=E_kin)
26
27         intensity_matrix = pdata.data.T
28
29         kx_vals = pdata.x_axis
30         ky_vals = pdata.y_axis
31
32         kx_idx = np.argmin(np.abs(kx_vals - 1.0))
33         intensity_1d = intensity_matrix[kx_idx, :]
34
35         lim = k_limits.get(file_basename, (-3.0, 3.0))
36
37         vergleichs_daten.append((ky_vals, intensity_1d,
38         display_name))
39
40         mask_r = ky_vals > 0
41         ky_r = ky_vals[mask_r]
42         int_r = intensity_1d[mask_r]
43
44         peaks, _ = find_peaks(int_r, height=0.01)
45
46         fwhm_val = 0
47         if len(peaks) > 0:
48             main_peak_idx = peaks[np.argmax(int_r[peaks])]
49             peak_height = int_r[main_peak_idx]
50             h_max = peak_height / 2.0
51
52             indices_above = np.where(int_r >= h_max)[0]
53
54             k_start = ky_r[indices_above[0]]
55             k_end = ky_r[indices_above[-1]]
56             fwhm_val = k_end - k_start
```

```

55     plt.figure(figsize=(8, 4), dpi=150)
56
57
58     plt.xlim(-2.0, 2.0)
59
60     plt.plot(ky_vals,
61              intensity_1d,
62              color='red',
63              label='Intensity Profile')
64
65     plt.hlines(y=h_max,
66               xmin=k_start,
67               xmax=k_end,
68               color='blue',
69               linestyle='--',
70               lw=2, zorder=5,
71               label=f'FWHM: {fwhm_val:.3f} Å')
72
73     plt.plot([k_start, k_end],
74              [h_max, h_max],
75              'bo', markersize=5, zorder=6)
76
77     plt.title(f"Vertical Cut: {display_name} at $k_x \backslash$
78               approx {kx_vals[kx_idx]:.2f}$ Å")
79     plt.xlabel(r"$k_y$ ($\AA^{-1}$)")
80     plt.ylabel("Intensity (a.u.)")
81     plt.xlim(lim[0], lim[1])
82     plt.legend()
83     plt.grid(True, alpha=0.3)
84
85     # Saving the Images
86     plot_filename = os.path.join(output_plots_dir1,
87                                   f"cut_{file_basename}.png")
88     plt.savefig(plot_filename, bbox_inches='tight')
89     plt.close()
90
91     fwhm_liste.append({'Molecule': display_name,
92                       'FWHM': fwhm_val})
93
94 # --- Plot for Comparison
95 if vergleiche_daten:
96     fig, ax = plt.subplots(figsize=(10, 6), dpi=150)
97
98     ax.set_xlim(-2.0, 2.0)
99
100    for ky, intens, label_name in vergleiche_daten:
101        ax.plot(ky, intens, label=label_name, lw=2)
102
103    ax.set_xlabel(r"$k_y$ ($\AA^{-1}$)", fontsize=15, labelpad=15)

```

```

104     ax.set_ylabel("Intensity (a.u.)", fontsize=15, labelpad=15)
105     ax.legend(loc='upper right', fontsize=10)
106     ax.grid(True, alpha=0.3)
107     plt.tight_layout()
108
109     # Saving the Image
110     comp_filename = os.path.join(output_plots_dir2, "
vergleichsplot_acene.png")
111     plt.savefig(comp_filename, bbox_inches='tight')
112     plt.show()
113
114 # -- Second Plot for comparison
115 if vergleichs_daten:
116     gewuenschte_acene = ["Tetracen", "Pentacen", "Hexacen", "
Heptacen"]
117
118     gefilterte_daten = [d for d in vergleichs_daten if d[2] in
gewuenschte_acene]
119
120     if gefilterte_daten:
121         fig_sel, ax_sel = plt.subplots(figsize=(10, 6), dpi=150)
122
123         plt.xlim(-2.0, 2.0)
124
125         for ky, intens, label_name in gefilterte_daten:
126             ax_sel.plot(ky, intens, label=label_name, lw=2)
127
128         plt.title(r"Comparison of Selected Acenes at $k_x$
\approx 1.0$ A$^{-1}$")
129         ax_sel.set_xlabel(r"$k_y$ (A$^{-1}$)")
130         ax_sel.set_ylabel("Intensity (a.u.)")
131         ax_sel.legend(bbox_to_anchor=(1.05, 1), loc='upper left')
132         ax_sel.grid(True, alpha=0.3)
133         plt.tight_layout()
134
135         comp_select_filename = os.path.join(output_plots_dir2,
"vergleichsplot_auswahl.png")
136         plt.savefig(comp_select_filename, bbox_inches='tight')
137         plt.close()
138
139
140

```

```

1  # --- FWHM VS MOLECULAR LENGTHS PLOT --- #
2
3  output_plots_dir = "[06] FWHM vs Molek ll ngen"
4  if not os.path.exists(output_plots_dir):
5      os.makedirs(output_plots_dir)
6
7  # Lengths of the molecules
8  laengen_dict = {

```

```
9     "Naphthalen": 4.84,
10     "Anthracen": 7.26,
11     "Tetracen": 9.68,
12     "Pentacen": 12.10,
13     "Hexacen": 14.52,
14     "Heptacen": 16.94,
15     "Octacen": 19.36,
16     "Nonacen": 21.78,
17     "Decacen": 24.20
18 }
19
20 plot_inv_L = []
21 plot_fwhm = []
22 plot_names = []
23
24 for entry in fwhm_liste:
25     name = entry['Molecule']
26     fwhm = entry['FWHM']
27
28     name_clean = name.replace("_homo", "").replace(".cube", "").strip()
29
30     if name_clean in acene_namen:
31         name_clean = acene_namen[name_clean]
32
33     if name_clean in laengen_dict and fwhm > 0:
34         plot_names.append(name_clean)
35         plot_fwhm.append(fwhm)
36         plot_inv_L.append(1.0 / laengen_dict[name_clean])
37
38 # --- Plotting
39 if len(plot_fwhm) > 0:
40     plt.figure(figsize=(8, 6), dpi=150)
41
42     plt.scatter(plot_inv_L,
43                 plot_fwhm,
44                 color='black',
45                 s=100, edgecolor='black',
46                 zorder=3, label='DFT Data')
47
48     m, b = np.polyfit(plot_inv_L, plot_fwhm, 1)
49     x_fit = np.linspace(min(plot_inv_L)*0.9,
50                          max(plot_inv_L)*1.1, 100)
51
52     plt.plot(x_fit, m*x_fit + b,
53              color='gray', linestyle='--',
54              label=f'Linear Fit (Slope: {m:.2f})')
55
56     for i, txt in enumerate(plot_names):
```

```

57     plt.annotate(txt, (plot_inv_L[i],
58                       plot_fwhm[i]),
59                   xytext=(7, -5),
60                   textcoords='offset points',
61                   fontsize=9)
62
63     plt.xlabel(r"Inverse Length  $1/L$  ( $\text{\AA}^{-1}$ )",
64               fontsize=15,
65               labelpad=15)
66     plt.ylabel(r"FWHM in  $k_y$  ( $\text{\AA}^{-1}$ )",
67               fontsize=15,
68               labelpad=15)
69     plt.grid(True, alpha=0.3)
70     plt.legend()
71     plt.tight_layout()
72
73     comp_select_filename = os.path.join(output_plots_dir,
74                                         "fwhm_vs_molecular_size.png")
75     plt.savefig(comp_select_filename, bbox_inches='tight')
76

```

```

1  # --- TREND: ENERGY GAP WITH SIZE --- #
2
3  output_plots_dir = "[06] FWHM vs Molekul l ngen" # Oder z. B.
4  "[07] HOMO-LUMO Gap"
5  if not os.path.exists(output_plots_dir):
6      os.makedirs(output_plots_dir)
7
8  rings = np.array([2, 3, 4, 5, 6, 7, 8, 10])
9  plot_names = ['Naphthalene',
10               'Anthracene',
11               'Tetracene',
12               'Pentacene',
13               'Hexacene',
14               'Heptacene',
15               'Octacene',
16               'Decacene']
17
18  gaps_eV = np.array([4.00, 3.20, 2.50, 2.00, 1.60,
19                     1.30, 1.10, 0.80])
20
21  if len(gaps_eV) > 0:
22      plt.figure(figsize=(10, 5), dpi=150)
23
24      plt.scatter(rings, gaps_eV, color='black',
25                 s=100, edgecolor='black',
26                 zorder=3, label='DFT Data')
27
28      plt.plot(rings, gaps_eV, color='gray',

```

```
28         linestyle='--', zorder=2,
29         label='Monotonic Trend')
30
31     for i, txt in enumerate(plot_names):
32         plt.annotate(txt, (rings[i], gaps_eV[i]),
33                        xytext=(7, 5),
34                        textcoords='offset points',
35                        fontsize=9)
36
37     plt.xlabel(r"Number of Fused Benzene Rings ($N$)",
38               fontsize=15, labelpad=15)
39     plt.ylabel(r"HOMO-LUMO Energy Gap $\Delta E$ (eV)",
40               fontsize=15, labelpad=15)
41
42     plt.xticks(rings)
43     plt.xlim(min(rings) - 0.5, max(rings) + 1)
44     plt.ylim(0.5, 4.4)
45
46     plt.grid(True, alpha=0.3)
47     plt.legend()
48     plt.tight_layout()
49
50     comp_select_filename = os.path.join(output_plots_dir,
51                                         "homo_lumo_gap_vs_size.png")
52     plt.savefig(comp_select_filename, bbox_inches='tight')
53
```

List of Figures

2.1	Calculated HOMO–LUMO energy gap.	10
2.2	Real-space HOMO wave functions of the polyacene series (2A–10A). . . .	11
3.1	Comparison between experimental and simulated k -space momentum maps for tetracene.	15
3.2	Comparison between experimental and simulated k -space momentum maps for pentacene.	17
3.3	Comparison between experimental and simulated k -space momentum maps for hexacene.	19
3.4	Comparison between experimental and simulated k -space momentum maps for heptacene	21
4.1	Simulated k -space intensity distributions of the acene series from naphthalene to nonacene.	24
4.2	One-dimensional k -space intensity profiles along k_y for the polyacene series up to decacene.	25
4.3	Linear scaling of the k -space peak width (FWHM) against the inverse molecular length ($1/L$) for the polyacene series.	27

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