Advanced Quantum Mechanics

Lecture in WS2025/26 at the KFU Graz

Axel Maas

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Chapter 1

Introduction

The lecture on quantum mechanics[1] provided the groundwork. It described the fundamental laws of quantum mechanics, and developed the necessary techniques to describe bound states, and some very simple physical systems, like the hydrogen atom. It also presented many of the conceptual aspects, like the different pictures, symmetries, and the path integral formulation. Finally, it covered various perturbative approaches for single-particle systems, one of the mainstays of even modern applications.

But, in the end, it covered only physics up to the mid 1950ies at most, and mostly only until the 1920ies. It also did not endeavor to describe interactions between multiple particles. Finally, almost all modern experiments in quantum physics utilize scattering, either as a probe or to entice interesting phenomena in the quantum system. It are these central aspects, which will be covered here.

As interactions always involve multiple particles, a first necessary step will be in chapter 2 to introduce the basics of treating more than one particle in a systematic way. Each particle may carry their own angular momentum. Thus, understanding consequences is an important step. This is aggravated by the existence of spin, which in non-relativistic quantum mechanics basically acts like a, little bit odd, angular momentum. This will be addressed in chapter 3. Likewise, many real-world system will be affected by electromagnetism. While a full treatment of electromagnetism will only be possible in the relativistic setting of the lecture "Quantum Field Theory", an extension beyond the hydrogen atom is possible and necessary, and will be conducted in chapter 4. This finally provides all the necessary elements to describe scattering, which will be

[1]Note that, throughout, the contents of my own lecture on "Quantum mechanics" will be considered known. If need be, the lecture notes are available from my homepage.

done in chapter 5.

The idea of particles, as they are described in quantum mechanics, is not tenable in a relativistic quantum theory, and needs to be replaced by fields. This is not surprising, as already issues like self-energy in classical electrodynamics suggests that the notion of point particles should be abandoned in favor of fields. While there are enough problems in non-relativistic quantum physics which do not need such a treatment, there are even in this case many which profit from the introduction of fields. This leads to quantum field theory, which, in their non-relativistic form, will be introduced in chapter 6. This will provide a new approach to the quantum many body theory, to be discussed din chapter 7.

In a final chapter 8 the always challenging issue of the measurement problem in quantum physics will be investigated anew.

There is a vast selection of textbooks on the topics. Those which were used in the preparation of these notes are

- Das "Lectures on Quantum Mechanics", Hindustan
- Nolting "Grundkurs der theoretischen Physik", Volumes 5 and 7, Vieweg
- Sakurai "Modern Quantum Mechanics", Addison Wesley
- Walecka, "Advanced modern physics", World Scientific

which are all old (but so are the topics of this lecture), and more modern (and more pedagogical) treatments are available.

Chapter 2

Many particle quantum mechanics I

Except for a very few items the first lecture on quantum mechanics was not concerned with multiple particle systems. Especially, interacting multiparticle systems were at most cursory touched upon, like the common example of helium to discuss variational techniques. This does not, however, reflect the actual situation. Most relevant systems involve multiple particles, which do interact. This will be introduced here using the operator formalism.

2.1 Hilbert space

2.1.1 General construction

The starting point is that the postulates of quantum mechanics retain their validity and form, no matter how many particles are involved. Indeed, a notion of particle is not even necessary. As the first postulate of quantum mechanics states, all information is contained in a vector (ket) in a Hilbert space $|k\rangle$. Measurements are still represented by the Born rule, i. e. a measurement needs to be described by a Hermitiean operator A with eigensystem $|a\rangle$, and the probability to measure the eigenvalue a is given by $|\langle a|\, k\rangle|^2$.

Time can be introduced into the Hilbert space by a Hamilton operator H, and the time evolution operator constructed from it. Here, already, implicitly an assumption is made about multi-particle systems: All particles experience the same, absolute time. Also, there is no inherent mechanism which yields the progression of time. Time is just a parameter of the system. It would require relativity to lift these restrictions, but this

will not be done here.

A system described in this way is considered to be a multi-particle system if it is a tensor product of subsystems, which individually are already representing quantum mechanical systems. For this to be the case, assume that there are n quantum-mechanical systems, i. e. n Hilbert spaces. Each system is describe by a Hamilton operator $H_{i=1,...n}$, which has an eigensystem $|m_i\rangle$ with eigenvalues E_{m_i} enumerated by the quantum number vectors m_i, and which can be discrete or continous. In many cases n identical copies will be used, but in principle each of these n systems can be different.

A non-interacting n-particle Hilbert space is then obtained by a tensor product

$$|\eta\rangle = |m_1\rangle \otimes ... \otimes |m_n\rangle \,. \tag{2.1}$$

Operators can be build likewise from each of the individual Hilbert spaces as

$$A = \sum_i \otimes_{j=1}^{i-1} \mathbf{1}_j \otimes A_i \otimes_{k=i+1}^{n} \mathbf{1}_k \tag{2.2}$$

where all A_i can be, in principle, different. Thus, operators act as

$$A\,|\eta\rangle = \sum_i \otimes_{j=1}^{i-1} |m_j\rangle \otimes A_i\,|m_i\rangle \otimes_{k=i+1}^{n} |m_k\rangle \,.$$

In particular, the time evolution operator is given by

$$U(t) = \sum_i \otimes_{j=1}^{i-1} \mathbf{1}_j \otimes U(t)_i \otimes_{k=i+1}^{n} \mathbf{1}_k, \tag{2.3}$$

where the above-mentioned assumption is made explicit that time proceeds for each particle in the same way.

So far, these particles do ignore each other. In particular, a wave function will have the form

$$\langle x|\eta\rangle = \Pi_i \eta(x_i)$$

and thus the states are not entangled. It is, of course, possible to write down already wave-functions which are entangled by choosing a state $|\psi\rangle$ which cannot be written like (2.1), but this is actually not the aim here. The more interesting question will be to replace (2.3). The time-evolution operator is so far given by a tensor sum of Hamilton operators H_i using (2.2). Thus, the time evolution of all particles ignores the existence of all other particles. For a genuine multi-particle system, this need to change.

Thus, the one-particle Hamilton-operators will now be extended by a set of interactions

$$H = \sum_i H_i + \sum_{i \neq j} H_{ij} + \sum_{ijk} H_{ijk} + ...$$

in which two-body interactions, three-body interactions, etc. are included. However, the full Hilbert space is still a product Hilbert space, the product of the one-particle Hilbert spaces can still be used as a basis. Thus, an arbitrary base vector can still be $|\{m_i\}\rangle$, but it will no longer be aproduct state. It may not even be a useful basis anymore, but this depends on the system in question.

2.1.2 A concrete example

Most continous multiparticle systems are non-trivial, if they cannot be rewritten in terms of new non-interacting systems. The latter is, e. g., the case for chains of oscillators, just like in classical mechanics. Thus, consider a discrete example.

The simplest one is a static, two-state system

$$H_i = \begin{pmatrix} a_i & b_i \\ b_i^* & a_i \end{pmatrix} \tag{2.4}$$

with eigenvalues $a_i \pm |b_i|$ and eigenvectors $(1, \pm 1)^\dagger$. Thus, the product eigenstates are $|i_1, i_2\rangle$, where the i_j run from 1 to 2. The combinations form all four basis vectors for the now 4×4 Hamilton operator, which has a 2×2-block-diagonal structure. A simple entangled state would be

$$|1, 1\rangle + |2, 2\rangle$$

as this state cannot be written as a simple product state, but only as a superposition of two product states.

A genuine two-body interaction can be introduced, e. g., by setting

$$H_{14} = H_{41}^* = c.$$

Select $a_i = a$ and $b_i = b$ for simplicity, while keeping the particles still distinguishable. What happens now is that the eigenstates themselves become entangled, though they can still be expressed in terms of the non-interacting eigenstates. Likewise, the eigenenergies, which before were doubly-degenerate, are now

$$E_i = a \pm \frac{1}{\sqrt{2}} \sqrt{2|b|^2 + |c|^2 \pm |c| \sqrt{4|b|^2 + |c|^2}}$$

with all possible combinations of the signs. As is visible, the original situation is obtained in the limit $c \to 0$, when the systems decouple.

That can be continued by adding more and more 'elementary' systems. It then depends on the choice of the non-block-diagonal elements of the Hamilton operator, how many particles interact. If only single matrix elements away from the block-diagonal are non-zero, these will add two-particle interactions. If, however, multiple will be non-zero, this becomes many-particle interactions. E. g., in the three-particle case setting

$$H_{14} = H_{41}^* = H_{16} = H_{61}^* = c$$

will create such a multi-particle system.

2.2 Bosons and fermions

One of the most intriguing features of fundamental physics are features of particles. The first feature is that particles come in certain types, and all particles of a given type are perfectly identical. This is very different from classical mechanics, where each particle can, in principle, be arbitrarily different from each other. Every type of particle is characterized by a set of quantum numbers, e. g. the electric charge.

While ominous at first, this can be understood once realizing that the concept of particles is actually an emerging one. The fundamental entities, to the best of our current knowledge, are quantum fields. They will be introduced in chapter 6. Individual particles of a given type then become excitations of a single field, thereby explaining that they are identical. How this happens will be discussed in more detail then.

Another feature is that all types belong to two categories, bosons and fermions. Fermions are particles which obey the Pauli principle, i. e. two fermions of the same type can never be at the same place. A product wave-function of both would always vanish at this point. Bosons do not obey this rule. Note that the Pauli principle only takes effect because particles are appear only as incarnation of certain types: Otherwise they all would be different, and the Pauli principle would have no consequence.

The implementation of the Pauli principle is at first not quite obvious. After all, $\psi(x)^2 = 0$ seems not to be useful, as this would require $\psi(x) = 0$. A simple example is to consider anti-commuting creation operator $b^\dagger$ and annihilation operator b, i. e.

satisfying

$$\begin{aligned} \{b, b^\dagger\} = bb^\dagger + b^\dagger b &= 1 \\ \{b, b\} = \{b^\dagger, b^\dagger\} &= 0. \end{aligned}$$

Thus, $(b^\dagger)^2 = 0$, and thus no state can contain more than one fermionic quanta.

How this works out can be seen for the Hamilton operator

$$H = \hbar\omega b^\dagger b,$$

which can be considered to describe a fermionic harmonic oscillator. This induces a number operator $N = b^\dagger b$ with the properties

$$\begin{aligned} \left[b^\dagger b, b\right] &= b^\dagger bb - bb^\dagger b = -(1 - b^\dagger b)b = -b & (2.5) \\ \left[b^\dagger b, b^\dagger\right] &= b^\dagger & (2.6) \end{aligned}$$

For any eigenstate $|E\rangle$ follows

$$Hb\,|E\rangle = ([H, b] - bH)\,|E\rangle = (E - \hbar\omega)b\,|E\rangle\,.$$

Thus, b indeed acts as its counterpart a by lowering the energy by one quanta $\hbar\omega$. Thus, a is called in this context also bosonic annihilation operator, and $a^\dagger$ bosonic creation operator. Likewise, it can be shown that $b^\dagger$ raises the energy by one quanta. But

$$\begin{aligned} b^\dagger b^\dagger\,|E\rangle &= 0 \\ bb\,|E\rangle &= 0 \end{aligned}$$

hold because of (2.6). Thus, there can be only two states with energy 0 and $\hbar\omega$, corresponding to zero and one quanta. This exemplifies how the Pauli principle can operate in quantum mechanics.

In terms of wave functions, it is a bit more involved. A systematic way will be discussed in chapter 6. For the moment, one possibility is requiring wave-functions to carry an additional internal representation, at least a two-dimensional vector space, with a non-Euclidean metric. A useful one is a symplectic metric, such that for two vectors $\vec{v}$ and $\vec{w}$ holds

$$\vec{v}^T \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \vec{w} = v_1 w_2 - v_2 w_1.$$

In such a metric, the norm of every vector automatically vanishes, $||\vec{v}|| = 0$. A fermionic wave-function would then be given as $\vec{\psi}(x)$. But what is the meaning of the second degree of freedom in the internal space?

This is linked to an interesting additional feature for both bosons and fermions. Both of them carry a new quantum number, which is called spin. At a very coarse level, a spin can be considered to be an intrinsic angular momentum of a point-like object. However, in contrast to the orbital angular momentum known, e. g., from atomic physics, it cannot be expressed in terms of the position operator and the momentum operator. Rather, it will have genuine own operators, the spin operators, $\vec{S}$. In particular, these spin operators obey the same algebra as orbital angular momentum operators,

$$[S_i, S_j] = i\hbar\epsilon_{ijk}S_k$$

and thus states with spin are characterized by two quantum numbers

$$\begin{aligned} \vec{S}^2 \left|s, m\right\rangle &= \hbar^2 s(s+1) \left|s, m\right\rangle \\ S_z \left|s, m\right\rangle &= \hbar m \left|s, m\right\rangle , \end{aligned}$$

where the commuting set of observables has been chosen like usual for angular momentum. It can now be shown that any fermion carries a half-integer spin, and every boson an integer spin. This is a consequence of having a (more than 1+1-dimensional) Minkowski space-time, and will be derived in the lecture quantum field theory I. Here, in non-relativistic physics, this spin-statistics theorem can only be considered an empirical fact. As will be seen in chapter 3, it is indeed possible to treat spin like an angular momentum in many respects. The reason for this stems also from special relativity, but there exists an even deeper, non-trivial relation stemming from (quantum) general relativity, which will be treated in the lecture on advanced general relativity and quantum gravity.

Now it becomes visible that any fermionic object, which thus has at least spin 1/2, will have at least two degrees of freedom, corresponding to $m = \pm 1/2$. Just like with orbital angular momentum, any wave-function can then be decomposed as

$$\psi_{\frac{1}{2}}(x) \left|1/2, 1/2\right\rangle + \psi_{-\frac{1}{2}}(x) \left|1/2, -1/2\right\rangle .$$

However, this would apparently require to introduce a non-trivial metric in spin space. This unnecessarily complicates the connection to angular momentum in chapter 3, and there exist a better solution.

2.3 Fock space

As noted, the Pauli principle is only relevant for identical particles. In addition, all particles having the same quantum numbers are identical - a set of quantum number uniquely characterizes a particle. The only quantity differing can be position, or momentum in Fourier space.

So consider two identical particles in position states $|x\rangle$ and $|y\rangle$. Because the particles are identical, it cannot be distinguished if the first particle occupies the first position state, or the second. Thus, the corresponding total state must satisfy

$$|x, y\rangle = e^{i\phi} |y, x\rangle ,$$

i. e. can at most differ by a phase. For fermions, the Pauli principle furthermore dictates $|x, x\rangle = 0$. It can then be shown, again a relativistic effect in four dimensions, that bosons have $\phi = 0$, i. e. their wave function is symmetric under the exchange of identical particles, while for fermions it is necessarily $\phi = \pi$. This actually implies the Pauli principle, as at the same point exchange of fermions implies

$$|x, x\rangle = - |x, x\rangle = 0,$$

as only a vanishing wave-function can fulfill this condition. The Pauli principle is thus a consequence of the antisymmetry of fermion wave functions under exchange, and not an independent principle.

One should note that the separation into fermions and bosons is true at a fundamental level. Effective theories may also offer situations in which the effective particles do not behave as either bosons or fermions. An particular example are wires, which are effectively one-dimensional. Thus, in non-relativistic quantum mechanics identical particles may be considered, which have no definite behavior under the exchange of two of them. As this is also true for classical particles, which can always be considered to be identifiable, such particles will be called classical in the following.

Considering again the elementary building blocks, this implies that for multi-particle states made from identical bosons or fermions not every state is admissible. E. g. a state made from two identical non-interacting boson states needs to be

$$\frac{1}{\sqrt{2}} \left(|x\rangle \otimes |y\rangle + |y\rangle \otimes |x\rangle \right) \tag{2.7}$$

while for fermion states only

$$\frac{1}{\sqrt{2}} \left(|x\rangle \otimes |y\rangle - |y\rangle \otimes |x\rangle \right) \tag{2.8}$$

is admissible. Any other product state would not have the correct properties under particle exchange. Thus, not every possible state in the product Hilbert is an admissible state in such cases. Only a subspace will contain physical states. All other states are mathematically valid, but unphysical. This physical subspace is called Fock space.

The necessity of introducing the Fock space, rather than having it automatically, is an artifact of the imposition of the concept of fermions and bosons. Just like time evolution, they represent an additional structure which is added to fundamental axioms of quantum mechanics. At the level of quantum mechanics, this is an empirical fact. If everything is treated consistently in a relativistic framework, this would come about automatically, and it would not be necessary to impose an additional structure. In that case, space time properties reduce the admissible vector spaces from an arbitrary complex vector space to a vector space carrying already the Fock space structure. Conversely, in a fully relativistic setup something like a classical particle could not be described.

A suitable basis for the Fock space as a subspace of the product Hilbert space can be constructed using the non-entangled states. In the bosonic case a totally symmetric state is constructed as

$$|b_1...b_n\rangle = \frac{1}{\sqrt{n!}} \sum_{P_{a_1...a_n}^{b_1...b_n}} |a_1\rangle \otimes ... \otimes |a_n\rangle$$

where the b_i signify the quantum numbers of the individual particle, and P creates all possible permutations. For the fermions, this is build as

$$|b_1...b_n\rangle = \frac{1}{\sqrt{n!}} \sum_{a_i} \epsilon_{a_1...a_n} |a_1\rangle \otimes ... \otimes |a_n\rangle ,$$

with ϵ the n-dimensional Levi-Civita tensor. Note that this will be zero if two quantum numbers b_i coincide, as expected from the Pauli principle. As this has the same structure as when building a determinant from its column, or row, vectors, this is called a Slater determinant. These bases consists out of pure states only, and entangled states will be linear combinations of them. Note that a linear combination retains its permutations properties, e. g.

$$|\gamma_1, \gamma_2\rangle = a |\alpha_1, \alpha_2\rangle + b |\beta_1, \beta_2\rangle = \pm a |\alpha_2, \alpha_1\rangle \pm b |\beta_2, \beta_1\rangle = \pm |\gamma_2, \gamma_1\rangle ,$$

and thus any superposition of Fock states remains in the Fock space. This allows for solving quantum mechanical problems basically as before, except that it is necessary to ensure that only states are admitted expressible in the Fock basis.

Consider the two-dimensional example from before. The product Hilbert space is four-dimensional. In the bosonic case, the Fock space is three-dimensional, with the admissible states

$$\begin{aligned} |1\rangle &= |11\rangle \\ |2\rangle &= |22\rangle \\ |3\rangle &= \frac{1}{\sqrt{2}} \left(|12\rangle + |21\rangle \right) . \end{aligned}$$

Thus, these represent the situations where both particles are in the same state, or a superposition where the two particles are occupying the same states, but it is not distinguishable which particle is in which state. In particular, the minimum energy of the system is twice the ground state energy. This is known as a Bose-Einstein condensate, in particular in the case of many particles.

For fermions, there is only a single state

$$|1\rangle = \frac{1}{\sqrt{2}} \left(|12\rangle - |21\rangle \right) .$$

The only possibility is that both particles occupy different states, and do this in an antisymmetric fashion. All states with both particles in the same state, particular the ground state, are forbidden. Thus, if there are no degenerate energy levels, the ground state energy of a fermionic system is always larger than the sum of the ground state energies. This can be different in case of degeneracies. An important example is the hydrogen atom.

In the case of non-identical particles, even if each would be bosonic or fermionic, the full Hilbert space is accessible, and any basis is working equally well.

Chapter 3

Angular momentum

3.1 Combined quantum numbers

In multiparticle systems, quantum numbers can be of two types. Either they only appear for one particle, or for more, or even all, of the particles. An example of the former is deuterium and electric charge. It is a two-particle system, but electric charge, a quantum number, is only carried by the proton. Thus, the total electric charge of deuterium is entirely given by the electric charge of the proton.

If multiple particles carry the same quantum number, the question arises what is the total value of it. To some extent, the answer is already given by (2.2). Given a Hermitiean operator A_i, for the individual particles, the total result is obtained from

$$A = \sum_i \otimes_{j=1}^{i-1} \mathbf{1}_j \otimes A_i \otimes_{k=i+1}^{n} \mathbf{1}_k. \tag{3.1}$$

This appears at first straight forward.

Consider two-particle systems, and consider electric charge. Then

$$Q\,|q_1, q_2\rangle = (Q_1 \otimes \mathbf{1}_2 + \mathbf{1}_1 \otimes Q_2)\,|q_1, q_2\rangle = (q_1 + q_2)\,|q_1, q_2\rangle = q\,|q\rangle = Q\,|q\rangle$$

where in the last step the state a quantum number q was introduced. However, this number is not unique, as any set of charges satisfying $q_1 + q_2 = q$ would have the same number. While it is often unnecessary to know the details of the individual q_i and only q is relevant, it should be kept in mind that only the full vector (q_1, q_2) uniquely identifies a state.

This is in particular interesting for superpositions. E. g.

$$a\,|q, q+1\rangle + b\,|q-1, q+2\rangle$$

is an eigenstate of Q, while it is not an eigenstate of the individual charge operators $Q_1 \otimes \mathbf{1}_2$ and $\mathbf{1}_1 \otimes Q_2$. In this case, the composite state can be thought of as a superposition of different possibilities how to realize the composite state. In particular, the subspace of fixed quantum number q can be described by different basis, and only one of them has the feature that it is simultaneously also an eigenbasis to the elementary operators Q_i. In practice, this may very well be not a convenient one. As the total charge is a sum of the individual charges, this is called an additive quantum number.

An alternative is given, e. g., by parity. If a state has a definite parity, it can only be 1 or -1. However, it was proven that for any state with definite parity, the eigenvalues can be only of this type. The issue is now that parity is a global space-time transformation. There is no notion of simply mirroring one particle. Thus, there exists no unit operator for parity. Parity acts on all subspace simultaneously, and the tensor operator is therefore necessarily given by

$$P = P_1 \oplus P_2$$

As a consequence, the parity of the tensorized state is the product of the individual parities, and the quantum number is multiplicative.

It may look at first surprising, as it is usually not as well associated as a quantum number, but the same is also true for momentum. In that case the product momentum operator $\vec{P}$ describes the center-of-mass momentum of the multi-particle state. Likewise, the position product operator $\vec{X}$ describes the center-of-mass of the particle ensemble. While translation appears at first to be a global space-time translation, this is indeed not necessary. After all, a single particle can be move relatively to another particle. Thus, momentum is an additive quantum number.

Note that as in single-particle quantum mechanics a state does not need to be an eigenstate of the position operator. What is still well-defined is the expectation value of the center-of-mass. Also, when performing a measurement, the probability to find the particles located at various positions is given by

$$|\langle x_1, ..., x_n | \, \alpha \rangle|^2 .$$

Note that if the particles are indistinguishable, then the probability is the statement that either of the two particles is found at a given position. In particular, also the test

state needs to be from the Fock space

$$\begin{aligned} |\langle\alpha|\,\beta\rangle|^2 &= \frac{1}{4}\left|\left(\langle y_1, y_2| \pm \langle y_2, y_1|\right)\left(|x_1, x_2\rangle \pm |x_2, x_1\rangle\right)\right|^2 \\ = \quad & \frac{1}{4}\left|\langle y_1, y_2|\, x_1, x_2\rangle + \langle y_2, y_1|\, x_2, x_1\rangle \pm \left(\langle y_1, y_2|\, x_2, x_1\rangle + \langle y_2, y_1|\, x_2, x_1\rangle\right)\right|^2 \end{aligned}$$

It is immediately visible that this expression vanishes when either $y_1 = y_2$ or $x_1 = x_2$ for fermions, implementing the Pauli principle. Moreover, for bosons this is immediately the average over the probability for any combination of possible positions of the two particles, as would be expected. In case of distinguishable particles, the second term would be absent, there would be no such exchange term. For fermions, this is different, and while the result is antisymmetric. The result can be somewhat straight-forwardly be interpreted, if it assumed that the two-particle wave-function will become continuously smaller if the two points approach each other. Then, the second term reduces the probability to find both fermions close by the closer the positions get, until it vanishes upon coincidence. Of course, in practice, this picture needs a calculation.

Consider, for example, two fermions affected by a harmonic potential of the same parameters. Their wave-functions are then given by

$$\frac{1}{2}\left(|n_1, n_2\rangle - |n_2, n_1\rangle\right)$$

Unsurprisingly, the wave-function always vanishes when $n_1 = n_2$, owing to the Pauli principle. Now, consider $n_1 = 0$ and $n_2 = 1$. This yields for the position space wave-function

$$\begin{aligned} \psi(x_1, x_2) &= \frac{\alpha}{4}\left(\langle x_1, x_2| - \langle x_2, x_1|\right)\left(|0, 1\rangle - |1, 0\rangle\right) \\ &= \frac{\alpha}{4} e^{-a(x_1^2+x_2^2)}\left(x_2 - x_1 - x_1 + x_2\right) = \frac{\alpha}{2}(x_1 - x_2)e^{-a(x_1^2+x_2^2)} \end{aligned}$$

which very directly shows the Pauli principle, as well as the aforementioned suppression of the wave-function when approaching coincidence. It may look strange that this happens now even if the two fermions appear to are in different states. However, the position basis is also an equivalent basis of the Fock space. Any basis needs to respect the Pauli principle. After all, as has been seen in quantum mechanics, asking for an exact position will change the momentum, and the state will be no longer in a definite energy eigenstate after measuring the position. Thus, this is just the statement that if a measurement tries to force both fermions to be at the same place, this will not work, if there are no degeneracies of the position eigenstates.

This is also seen when considering, e. g., the hydrogen atom. Consider two spinless electrons, one in the state $|111\rangle$ and the other one in $|11-1\rangle$. The antisymmetric wave function is

$$\frac{1}{\sqrt{2}}\left(|111;11-1\rangle - |11-1;111\rangle\right).$$

This yields the position space behavior

$$\psi_(x_1,x_2) = -\frac{i}{16\sqrt{2}a^5\pi} r_1 r_2 \sin\theta_1 \sin\theta_2 \sin(\phi_1-\phi_2). \tag{3.2}$$

This shows the same behavior. This does not vanish, except for the usual nodes of the individual wave functions, except for an additional node if the position of both fermions coincide. This stems from the Fock space quality of the position eigenstates.

However, an odd thing about (3.2) is that there appears to be a regularity in terms of the angular dependency, but no obvious way how to add the quantum numbers for the angular momentum. It is this which needs to be addressed next.

3.2 Angular momentum addition

As noted before, angular momentum seems to be strange when it comes to creating total quantum numbers. The reason is that, in contrast to the other ones encountered so far, it is associated with a non-commutative structure. E. g., charge or parity are commutative, and the quantum numbers add, or multiply. In fact, the main difference is that these operations are associated with an Abelian symmetry group, while angular momentum is associated with the non-Abelian rotation group SO(3). Building a tensorized state requires to ensure that the group structure is preserved.

On the other hand, objects like atoms have well-defined angular momentum. So, there must be a way to create their angular momentum from the individual components which composite it. This process is known as angular momentum addition, where addition is really misleading, or only true in a very generalized sense. There is a general theory of doing so for any non-Abelian group of the same type as the rotation group. This will be discussed in the optional lecture on advanced mathematical methods. However, the gist of the construction can be accessed without such additional information. This construction is known as the Clebsh-Gordan construction.

The starting point is the observation that states build from multiple particles behave like they have a common angular momentum. Consider the simplest case of two states building a composite state, Each having a definite angular momentum j_i. This will give

in total $(2j_1+1)(2j_2+1)$ possible states, due to the magnetic quantum numbers. If the composite state has any angular momentum $j \geq 0$, it will have a range up to $2j+1$ magnetic quantum numbers, each state being linearly independent. Since

$$(2j_1+1)(2j_2+1) = \sum_{n=|j_1-j_2|}^{j_1+j_2} (2n+1)$$

the number of states fit exactly if $|j_1 - j_2| \leq j \leq j_1 + j_2$ would hold, and all values in this range would be realized for the composite state. Lets see, whether this numerology can be substantiated.

To this end, angular momenta are Hermitiean operators. Thus (3.1) still holds. Thus

$$j(j+1)\,|j,m\rangle = J^2\,|j,m\rangle = (J^1 \otimes \mathbf{1}_2 + \mathbf{2} \otimes J^2)^2 \sum_{ij} c^{jm}_{j_1 m_1 j_2 m_i}\,|j_1 m_i\rangle \otimes |j_2 m_j\rangle \quad (3.3)$$

$$m\,|j,m\rangle = J_3\,|j,m\rangle = (J^1_3 \otimes \mathbf{1}_2 + \mathbf{2} \otimes J^2_3) \sum_{ij} c^{jm}_{j_1 m_1 j_2 m_i}\,|j_1 m_i\rangle \otimes |j_2 m_j\rangle \quad (3.4)$$

must be a valid eigenvalue equation for some values of the coefficients $c^{jm}_{j_1 m_1 j_2 m_i}$, called the Clebsh-Gordan coefficients. The problem hence reduces to finding them. This can be achieved by starting from the maximal values of j and $m = j$. Note that to actually calculate (3.3), it is necessary to consider the decomposition

$$J^2 = J_\mp J_\pm + J_3^2 \pm \hbar J_3,$$

and decompose each of the two operators into their well-defined action on the individual subspaces. Thus, the expression in (3.3) in terms of the individual operator needs to be taken rather as shorthand than actual definition.

In particular, select $j = j_1 + j_2$ and $m = j$. The only possibility how (3.3-3.4) can satisfy this if, if

$$|j,j\rangle = |j_1 m_1\rangle \otimes |j_2, m_2\rangle = \langle j_1 j_1; j_2 j_2\rangle$$

holds. But it is simultaneously always possible to construct such a state, which is uniquely characterized by its quantum numbers. To show the existence of further states, build the operators

$$J_\pm = \left(J^1_\pm \otimes \mathbf{1}_2 + \mathbf{1}_1 \otimes J^2_\pm\right).$$

It can be shown by explicit calculation that the ladder operators $J_\pm$ fulfill the commutation relations of angular momentum. This yields

$$J_-\,|j,j\rangle = (|j_1 j_1 - 1; j_2 j_2\rangle + |j_1 j_1; j_2 j_2 - 1\rangle) = |j\,j-1\rangle\,.$$

Application of (3.4) shows that the identification in the last step is justified. Further application of J_- will then yield further states, until the state

$$|j-j\rangle = |j_1 - j_1; j_2 - j_2\rangle$$

is reached, after which any further application of J_- will yield zero. The states need then to be normalized.

This only exhausts $2(j_1+j_2)+1$ of all states. To create a ladder for j_1+j_2-1 requires to build a state with $m = j_1+j_2-1$ and then start again from there. This state needs, of course, to be orthogonal to the state with the same m, but $j = j_1+j_2$, and also needs to be an eigenstate of J^2 to the corresponding eigenvalue. Because J_3 is linear in the individual J_3^i, this implies that the state must be of the form

$$|j_1+j_2-1 j_1+j_2-1\rangle \sum_{m_1+m_2=m} \sum a_{m_1 m_2} |j_1 m_1; j_2 m_2\rangle$$

and it is sufficient to fix the $a_{m_1m_2}$ subject to the conditions

$$\begin{aligned} \langle j_1+j_2 j_1+j_2-1|\, j_1+j_2-1 j_1+j_2-1\rangle &= 0 \\ \langle j_1+j_2-1 j_1+j_2-1|\, j_1+j_2-1 j_1+j_2-1\rangle &= 1, \end{aligned}$$

sufficient to provide a unique answer. This is repeated for all possible combinations of the j_i, yielding the desired number of linearly independent states. That they are in this fashion linearly independent follows from the fact that applying

$$\begin{aligned} & \langle j_1+j_2 j_1+j_2-2|\, j_1+j_2-1 j_1+j_2-2\rangle \\ \sim\ & (\langle j_1+j_2 j_1+j_2-1|\, J_-)\,(J_-\,|j_1+j_2-1 j_1+j_2-1\rangle) \\ =\ & (\langle j_1+j_2 j_1+j_2-1|)\,(J_+J_-\,|j_1+j_2-1 j_1+j_2-1\rangle) \\ \sim\ & (\langle j_1+j_2 j_1+j_2-1)(\,|j_1+j_2-1 j_1+j_2-1\rangle) = 0. \end{aligned}$$

This process is repeated for all possible values of the total angular momentum. The Clebsh-Gordan coefficients can then be read off the results, and have been tabulated[1]. Indeed, what has happened is really just a change of basis, and the Clebsh-Gordan coefficients are nothing but the elements of the corresponding transformation matrix.

[1] If they are, why care about the construction at all? Because the same construction can be generalized to other symmetries or theories with different (effective) space-time structure, where they are not readily available.

It is useful to study some examples. Before doing so, a very important insight is that nothing but the algebra in the corresponding subspaces has been used. Thus, as spin obeys the same algebra, this construction allows to freely mix orbital angular momentum and spin, and treat the resulting state as just an object obeying an algebra of the same type. This is again rooted in the fact that both spin and angular orbital momentum are rooted in the space-time structure of special relativity, and only appear in the non-relativistic setting to be separate entities.

As a first example, consider a trivial combination of $j_1 = 1$ and $j_2 = 0$. There are $3 \times 1 = 3$ states only, and the only possible value is $j = 1$. This yields

$$|1, 1\rangle = |11; 00\rangle$$

for the highest-weight state. As the lowering operators act only non-trivially on the $j_1 = 1$ states, yielding

$$\begin{aligned} |1, 0\rangle &= |10; 00\rangle \\ |1, -1\rangle &= |1 - 1; 00\rangle . \end{aligned}$$

The Clebsh-Gordan coefficients are thus

$$c^{1m=m_1}_{1m_100} = 1$$

and the transformation is diagonal.

The situation becomes more interesting with $j_1 = j_2 = 1/2$, with $2 \times 2 = 4$ states. The possible values for $j = 1$ and $j = 0$. Note that this implies (again) that two fermions can combine to make up a boson. The reverse is never true, as can be seen from the combination rule. Starting with the maximum state yields

$$|11\rangle = |1/21/2; 1/21/2\rangle .$$

Applying the lowering operator yields

$$\begin{aligned} |10\rangle &= J_- |11\rangle = \left(J^1_- \otimes \mathbf{1}_2 + \mathbf{1}_1 \otimes J^2_-\right) |1/21/2; 1/21/2\rangle \\ &= \frac{1}{\sqrt{2}} \left(|1/2 - 1/2; 1/21/2\rangle + |1/21/2; 1/2 - 1/2\rangle\right) \\ |1 - 1\rangle &= |1/2 - 1/2; 1/2 - 1/2\rangle . \end{aligned}$$

where it was used in the last line that the lowering operators annihilate the lowest state. This gives the three states necessary for $j = 1$. The fourth state must be the $j = 0$

state, and be orthogonal to the $j = 1$, $m = 0$ state. In this case, the necessary state can be directly read off

$$|00\rangle = \frac{1}{\sqrt{2}}\left(|1/2\,-1/2;1/21/2\rangle + |1/21/2;1/2\,-1/2\rangle\right),$$

rather than using the systematic construction. This yields the Clebsh-Gordan coefficients

$$\begin{aligned}
c^{11}_{\frac{1}{2}\frac{1}{2}\frac{1}{2}\frac{1}{2}} &= 1\\
c^{10}_{\frac{1}{2}-\frac{1}{2}\frac{1}{2}\frac{1}{2}} &= \frac{1}{\sqrt{2}}\\
c^{10}_{\frac{1}{2}\frac{1}{2}\frac{1}{2}-\frac{1}{2}} &= \frac{1}{\sqrt{2}}\\
c^{1-1}_{\frac{1}{2}-\frac{1}{2}\frac{1}{2}-\frac{1}{2}} &= 1\\
c^{00}_{\frac{1}{2}-\frac{1}{2}\frac{1}{2}\frac{1}{2}} &= \frac{1}{\sqrt{2}}\\
c^{00}_{\frac{1}{2}\frac{1}{2}\frac{1}{2}-\frac{1}{2}} &= -\frac{1}{\sqrt{2}}.
\end{aligned}$$

It is useful to visualize that as an actual transformation matrix

$$\begin{pmatrix} |11\rangle \\ |10\rangle \\ |1\,-1\rangle \\ |00\rangle \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 0 & 1 \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \end{pmatrix} = \begin{pmatrix} |1/21/2;1/21/2\rangle \\ |1/21/2;1/2\,-1/2\rangle \\ |1/2\,-1/2;1/21/2\rangle \\ |1/2\,-1/2;1/2\,-1/2\rangle \end{pmatrix}.$$

The matrix is explicitly unitary, as is necessary for a transformation matrix.

There are two more interesting features. One is that the $j = 1$ state is symmetric. On the other hand, the state $j = 0$ appears to be differently treating both constituents. However, both arise from the fact that the constituents are identical. Which has the minus sign for $j = 0$ does not matter, as both are indistinguishable. In fact, the state could be multiplied by minus 1, yielding an equally good state. The other comes from the fact that both constituents can have only a single highest state. There is no possibility thus than to be symmetric. However, the exchange operator does commute for identical particles with all operators, and thus this feature is inherited for all states obtained by J_-. Both features are thus generic. In particular, the largest j state build from two identical constituents is always symmetric, and bosonic.

To see what happens with more than two possibilities for j, consider the case with $j_1 = j_2 = 1$. This allows for $j = 2$, $j = 1$, and $j = 0$. Again, start with the largest j,

yielding in the same way

$$\begin{aligned}
|22\rangle &= |11;11\rangle \\
|21\rangle &= \frac{1}{\sqrt{2}}\left(|10;11\rangle + |11;10\rangle\right) \\
|20\rangle &= \frac{1}{\sqrt{6}}\left(|1-1;11\rangle + 2\,|10;10\rangle + |11;1-1\rangle\right) \\
|2-1\rangle &= \frac{1}{\sqrt{2}}\left(|1-1;10\rangle + |10;1-1\rangle\right) \\
|2-2\rangle &= |1-1;1-1\rangle\,.
\end{aligned}$$

The $j = 1$ sequence starts by orthogonalized to $|21\rangle$,

$$\begin{aligned}
|11\rangle &= \frac{1}{\sqrt{2}}\left(|10;11\rangle - |11;10\rangle\right) \\
|10\rangle &= \frac{1}{\sqrt{2}}\left(|1-1;11\rangle - |11;1-1\rangle\right) \\
|1-1\rangle &= \frac{1}{\sqrt{2}}\left(|1-1;10\rangle - |10;1-1\rangle\right),
\end{aligned}$$

and finally by orthogonalization

$$|00\rangle = \frac{1}{\sqrt{3}}\left(|1-1;11\rangle - |10;10\rangle + |11;1-1\rangle\right).$$

The same procedure can be continued as desired. Note that in this case the $j = 2$ state and $j = 0$ state are symmetric, while the $j = 1$ state is antisymmetric.

It is instructive to also see how the total spin comes about. Take the $j =$ case again. Then

$$\begin{aligned}
J^2\,|22\rangle = \left(J_-J_+ + J_3^2 + \hbar J_3\right)|22\rangle &= (0+4+2)\hbar^2\,|22\rangle = 2(2+1)\hbar^2\,|22\rangle \\
\left(J_-J_+J_3^2 + J_3\right)|11;11\rangle &= (0+(1+1)(1+1)+(1+1))\hbar^2\,|11;11\rangle \\
&= 2(2+1)\hbar^2\,|11;11\rangle\,.
\end{aligned}$$

This shows nicely how the total result is build up from the individual ones.

While this appears to be a bookkeeping device, it is more than that. It shows how constituents can build up states with properties that abstract from the individual constituents, and thus appear to be a single entity. The state $|jm\rangle$ does not refer back to its constituents, and the operators J^2 and J_3 act in a meaningful way on it, without referring back to the constituents. In this way, much more complicated objects can be

build up, only whose coarse properties are relevant. At the same time, it shows how complexity emerges. From simple, identical constituents, many states can be build.

E. g., add in a third $j = 1/2$ objects. There are now 8 different states ($2 \times 2 \times 2$), with values $j = 3/2$ (4), and $j = 1/2$ (2), but in the latter case there are two copies. These states are build as

$$\begin{aligned}
|3/23/2\rangle &= |1/21/2;1/21/2;1/21/2\rangle \\
|3/21/2\rangle &= \frac{1}{\sqrt{3}}\left(|1/21/2;1/21/2;1/2-1/2\rangle + |1/21/2;1/2-1/2;1/21/2\rangle\right. \\
&\quad \left. + |1/2-1/2;1/21/2;1/21/2\rangle\right) \\
|3/2-1/2\rangle &= \frac{1}{\sqrt{3}}\left(|1/21/2;1/2-1/2;1/2-1/2\rangle + |1/2-1/2;1/2-1/2;1/21/2\rangle\right. \\
&\quad \left. + |1/2-1/2;1/2-1/2;1/21/2\rangle\right) \\
|3/2-3/2\rangle &= |1/2-1/2;1/2-1/2;1/2-1/2\rangle\,,
\end{aligned}$$

very similar as before. But there are now two orthogonal possibilites for $j = 1/2$,

$$\begin{aligned}
|1/21/2\rangle_1 &= \frac{1}{\sqrt{2}}\left(|1/21/2;1/21/2;1/2-1/2\rangle - |1/21/2;1/2-1/2;1/21/2\rangle\right) \\
|1/2-1/2\rangle_1 &= \frac{1}{\sqrt{2}}\left(|1/21/2;-1/21/2;1/2-1/2\rangle - |1/2-1/2;1/2-1/2;1/21/2\rangle\right) \\
|1/21/2\rangle_2 &= \frac{1}{\sqrt{6}}\left(|1/21/2;1/2-1/2;1/2-1/2\rangle + |1/2-1/2;1/2-1/2;1/21/2\rangle\right. \\
&\quad \left. -2\,|1/2-1/2;1/2-1/2;1/21/2\rangle\right) \\
|1/2-1/2\rangle_2 &= \frac{1}{\sqrt{6}}\left(|1/21/2;1/2-1/2;1/2-1/2\rangle + |1/2-1/2;1/2-1/2;1/21/2\rangle\right. \\
&\quad \left. -2\,|1/2-1/2;1/2-1/2;1/21/2\rangle\right),
\end{aligned}$$

though there is some freedom in their choice.

It is noteworthy that the number of states is different than if constituents $j_1 = 1$ and $j_2 = 1/2$, despite the total angular momentum having the same possibilities. Two of the compound states have different inner structure. But they can only be distinguished when using measurements probing the internal structure. Just measuring the global quantum numbers j and m would not allow to distinguish them. Thus, while utilizing the compound could often be done only knowing its properties, a true understanding requires to analyze its structure.

3.3 Tensor operators

So far, states have been considered for angular momenta. However, operators are also related to angular momenta, most notably angular momentum itself, but also, e. g., the position operator and the momentum operator. This can be formalized, and will actually lead to a very powerful insight in section 3.4.

To this end, a tensor operator T^s_m of angular momentum s is defined to be a set of $2k+1$ operators, which satisfy the commutation relations

$$[J_3, T^s_m] = \hbar m T^s_m \tag{3.5}$$
$$[J_\pm, T^s_m] = \hbar\sqrt{(s \mp m)(s \pm m + 1)}T^s_{m\pm1}. \tag{3.6}$$

Explicit calculation show that the orbital angular momentum operator, the position operator, and the momentum operator satisfy this algebra with $s = 1$, i. e. they are all called vector operators. The Hamilton operator of rotational invariant system, e. g. the free particle, is a tensor operator with $s = 0$, as it commutes with all J_i. An operator with $s = 2$ would be the symmetric inertial momentum density operator,

$$I_{ij} = f(R^2)\left(R_i R_j - \frac{R_k R_k}{3}\delta_{ij}\right). \tag{3.7}$$

It has five different components. These are given as

$$\begin{aligned} I^2_{\pm2} &= R_\pm R_\pm f(R^2) \\ I^2_{\pm1} &= \sqrt{2} R_\pm R_3 f(R^2) \\ I^2_0 &= \sqrt{\frac{2}{3}}\left(R_+R_- + R_3R_3\right) f(R^2) \\ R_\pm &= R_1 + iR_2, \end{aligned}$$

where it was used that the R_i commute with each other.

In particular, the Clebsh-Gordan construction also applies to tensor operators,

$$T^s_m = \sum_{m_1,m_2} c^{sm}_{s_1m_1s_2m_2} U^{s_1}_{m_1} S^{s_2}_{m_2} \tag{3.8}$$

constructing a new one T from the individual ones U and V. If U and V do not commute, a choice has to be made. This can be shown by inserting the construction (3.8) into (3.5)top2, which is a lengthy exercise.

E. g., the result (3.7) can be seen to be the construction of twice the operator R using (3.8), where for convenience in the result the $R_\pm$ had been introduced.

It should be noted that the concept of tensor operators can be extended to any symmetry. Operators, just as states, can be classified, by the way how they transform under symmetry transformations. E. g., an operator can be a vector (like R and P) or a pseudovector (like J), depending on their transformation properties under parity. However, only for non-Abelian groups a construction like the one shown here is necessary, and this case will not appear further in this lecture. It is ubiquitous in many applications, and will turn up in most specialized courses in one way or another.

3.4 Wigner-Eckart theorem

Combining the concept of tensor operators with angular momentum eigenstates leads to a very powerful theorem, the Wigner-Eckart theorem. It will also clarify the role of symmetries in physics, and can be considered to be one of the most central theorems. It is also the one which is least conscienceless applied in every day research in quantum physics.

Its is a statement about tensor operators in eigenstates of angular momentum, and reads

$$\left\langle \alpha j m \left| T^s_q \right| \alpha' j' m' \right\rangle = c^{jm}_{sqj'm'} f^{jj'q}_{\alpha\alpha' T}, \tag{3.9}$$

where $f_{\alpha\alpha' T}$ no longer depends on m, m', or q. It is not a constructive theorem, i. e., it doe snot provide a way to calculate f. However, it states that it is sufficient to calculate f once to know it for any combinations of the angular momentum quantum numbers. It furthermore encodes selection rules: The matrix element is only non-vanishing if the corresponding Clebsh-Gordan coefficient is non-vanishing. Finally, it splits the full matrix element into one, which is purely geometrically and depends on the rotational properties of the system, the Clebsh-Gordan coefficient, and one, which is invariant under rotations, the function f. In particular, this implies that symmetry and dynamics are split. The symmetry part does not contain any non-trivial information. The non-trivial information is contained completely contained in the information invariant under the symmetry.

This statement can be generalized, though this will not be done in this lecture: If a physical system has a symmetry, any expectation value can be split into a product of a quantity containing all the physical information, which is invariant under the symmetry, and a part which depends only the mathematical properties of the symmetry group. Thus, symmetries in physics only redundant, geometrical information. Again, this is

not constructive, and in practice this knowledge may not be too helpful. But it is defining for the role of symmetries in physics.

Now it is about time to prove the special case (3.9) of the Wigner-Eckart theorem. Using (3.6) yields

$$\left\langle \alpha jm \left| \left[J_\pm, T^s_q \right] \right| \alpha' j' m' \right\rangle = \hbar \sqrt{(s \mp q)(s \pm q + 1)} \left\langle \alpha jm \left| T^s_{q\pm1} \right| \alpha' j' m' \right\rangle .$$

But, of course, the $J_\pm$ can also be applied to the states, yielding

$$\begin{aligned} & \sqrt{(s \mp q)(s \pm q + 1)} \left\langle \alpha jm \left| T^s_{q\pm1} \right| \alpha' j' m' \right\rangle \\ = \; & \sqrt{(j \pm m)(j \mp m + 1)} \left\langle \alpha jm \mp 1 \left| T^s_q \right| \alpha' j' m' \right\rangle \\ & - \sqrt{(j \mp m)(j \pm m + 1)} \left\langle \alpha jm \left| T^s_q \right| \alpha' j' m' \pm 1 \right\rangle . \end{aligned}$$

Doing this for all possible values of m, m', and q implies that the matrix elements satisfy a homogeneous system of linear equations, with coefficients given by the square-root expressions, which depend only on the angular quantum numbers, but not on $\alpha^{(\prime)}$, nor on the choice of T. In particular, up to a common constant, the system of equations has a unique solution, provided the coefficient matrix is non-singular.

It can be shown that the solution is, up to the common proportionality factors, are just the Clebsh-Gordan coefficients. To do so, consider

$$J_\pm \left| jm \right\rangle = (J^1_\pm \otimes \mathbf{1}_1 + \mathbf{1}_1 J^2_\pm) \sum_{m_1, m_2} c^{jm}_{j1m_1j_2m_2} \left| j_1 m1; j_2 m_2 \right\rangle$$

Multiplying with $\langle j_1 m_1; j_2 m_2|$ this after application yields the recursion relation

$$\begin{aligned} & \sqrt{(s \mp q)(s \pm q + 1)} c^{jm\pm1*}_{j_1m_1j_2m_2} \\ = \; & \sqrt{(j \pm m)(j \mp m + 1)} c^{jm}_{j_1m_1\mp1;j_2m_2} - \sqrt{(j \mp m)(j \pm m + 1)} c^{jm}_{j_1m_1;j_2m_2\pm1}. \end{aligned}$$

Thus, also the Clebsh-Gordan coefficients obey such a linear system of equations. In addition, this is a recursion relation allowing to calculate them. Finally, because the overall normalization is not fixed, it can be chosen such that all Clebsh-Gordan coefficients are real.

Returning to the original objective, this implies that, up to a proportionality constant, all matrix elements $\left\langle \alpha jm \left| T^s_q \right| \alpha' j' m' \right\rangle$ are given by the Clebsh-Gordan coefficients. But then the proportionality factor is just what is needed to fulfill (3.9), completing the proof.

Probably one of the most direct consequences of the Wigner-Eckart theorem are selection rules. Only if the corresponding Clebsh-Gordan coefficient is non-vanishing, a matrix element of tensor operators in angular-momentum eigenstates can be non-vanishing. E. g.,

$$\langle \alpha j m|_0^0 \, |\alpha' j' m'\rangle = \delta_{jj'}\delta_{mm'} f^{jj0}_{\alpha\alpha' T},$$

and thus expectation values of scalar operators will always vanish if not taken between the same angular momentum eigenstates, no matter any other quantum numbers. It is probably the latter which is striking: It is not even necessary to know the Hamilton operator to make this statement. It is sufficient to know that it is rotational invariant. Thus, this statement applies to the free particle, the isotropic harmonic oscillator, and the hydrogen atom simultaneously. In addition, if the state is not pure, but a superposition, it will project out a sum of expectation values between pure states.

Likewise, for the equally common case of a a vector operator

$$\langle \alpha j m| \, T^1_q \, |\alpha' j' m'\rangle = \delta_{jj'}\delta_{m,m'\pm q} f^{jj1}_{\alpha\alpha' T} + \delta_{j,j'\pm 1}\delta_{m,m'\pm q} f^{j,j\pm 1,1}_{\alpha\alpha' T}$$

holds. Thus, here different f can appear. In such a case multiple matrix elements will have to be evaluated explicitly, but still much less than the $3(2j+1)(2j'+1)$, which would be needed without the Wigner-Eckart theorem.

These are not very rare occurrences. Especially the fact that atomic or molecular transitions, mediated by electromagnetism, or nuclear transitions, mediated by all three fundamental forces, can all be described in terms of tensor operators implies that the existence, and especially absence, of a given transition can be traced back to the Wigner-Eckart theorem and the values of the Clebsh-Gordan coefficients. A large host of qualitative statements can thus be made without knowing any particular dynamics. In this context, transitions for which the Clebsh-Gordan coefficient vanish are often called forbidden transitions. Likewise, the relative strengths of non-forbidden transitions are given by the values of Clebsh-Gordan coefficients.

Of course, once reaching high precision, this will usually not suffice. E. g., when considering an atomic transition effects beyond the Coulomb potential get relevant, even things like recoil of the atom with respect to the emitted photon. But in many cases even these effects are described in term of tensor operators. Just that their independent matrix element may be much smaller, and thus the effect is small. So, many forbidden transition still occur - but due to an additional effect, which is described in terms of a different tensor operator. Hence, it is central to understand these concepts.

The reason why these are so important is again special relativity. Because all fundamental, non-gravitational forces, obey special relativity, everything is formulated in terms of quantities with a definite transformation property with respect to rotational symmetries. And thus are affected by the above. So, it is really special relativity which elevates the previous discussion.

Chapter 4

Electromagnetism

In quantum mechanics, electromagnetic phenomena where basically restricted to the Coulomb potential as an electrostatic phenomenon, and to external magnetic fields. From the practical point of view, neither of these were distinguishable from any other potential, which popped up as an empiric input into the Hamilton operator.

To a significant extent, this will not change in the following. The reason is that electromagnetism is already classically a relativistic theory. A real quantization must respect this. But to quantize a relativistic theory requires quantum fields. And while quantum fields will be, to some extent, this discussed in chapter 6, this will be non-relativistic quantum field theory only. Combining both is a very non-trivial step, and is relegated to the lecture Quantum Field Theory I. Here, thus, electromagnetism will remain classical, and thus no real feedback will be possible. But it will still substantially enlarge the number of phenomena treatable.

4.1 Classical electrodynamics as a gauge theory

For the sake of completeness, the following will briefly repeat the most pertinent points of classical electrodynamics. This will also fix notations.

Classical electrodynamics is governed by Maxwell's equations,

$$\vec{\partial} \cdot \vec{B} = 0 \tag{4.1}$$

$$\vec{\partial} \times \vec{E} + \partial_t \vec{B} = 0 \tag{4.2}$$

$$\vec{\partial} \cdot \vec{E} = \frac{1}{\epsilon_0}\rho \tag{4.3}$$

$$\vec{\partial} \times \vec{B} - \frac{1}{c^2}\partial_t \vec{E} = \mu_0 \vec{j}, \tag{4.4}$$

with the electric field $\vec{E}$, the magnetic field $\vec{B}$, the electric current $\vec{j}$ and the electric charge density ρ, which satisfy the continuity equation

$$\partial_t \rho + \vec{\partial}\vec{j} = 0.$$

The somewhat arbitrary placement of the constants ϵ_0, μ_0, and c is an artifact of the SI system. For a full theory, dynamical equations on the matter, like Newton's equation or the wave equation later, are needed to be supplemented. Here, however, the fields will remain classical, as noted before.

Maxwell's equation can be fulfilled, if the electric field and the magnetic field are given by

$$\vec{B} = \vec{\partial} \times \vec{A} \tag{4.5}$$

$$\vec{E} = -\vec{\partial} A_0 - \partial_t \vec{A}. \tag{4.6}$$

The second equation shows that in the static case A_0 is, up to a factor of c, the electric potential. The notation hints at the fact that A_0 and $\vec{A}$ combine into a four vector once moving to an explicitly relativistic notation. However, this will not be needed here explicitly.

That this is indeed a solution to Maxwell's equation can be seen from the fact that (4.1) is trivially fulfilled by (4.5), as any curl of a vector is automatically divergence-free. Likewise with the same argument

$$\vec{\partial} \times \vec{E} = -\vec{\partial} \times \partial_t \vec{A} = -\partial_t \vec{B},$$

and thus (4.2), follows. Thus the homogeneous Maxwell equations are satisfied by construction.

The inhomogeneous ones reduce to

$$\vec{\partial}^2 A_0 + \partial_t \vec{\partial} \cdot \vec{A} = -\frac{\rho}{\epsilon_0} \tag{4.7}$$

$$\left(\vec{\partial}^2 \vec{A} - \frac{1}{c^2}\partial_t^2 \vec{A}\right) - \vec{\partial} \cdot \left(\vec{\partial} \cdot \vec{A} + \frac{1}{c^2}\partial_t A_0\right) = -\mu_0 \vec{j}. \tag{4.8}$$

These are now four equations for four unknowns. Thus, the surplus constraint equations of the original Maxwell equations, after all 8 equations for 6 functions, have been resolved in this way.

However, this is a gauge theory. This means that for any value of the electric field and magnetic field there is an infinite number of possibilities for both $\vec{A}$ and A_0. This can be seen in the following way. Changing

$$\vec{A} \to \vec{A}' = \vec{A} + \vec{\partial} \cdot \omega \tag{4.9}$$

$$A_0 \to A_0' = A_0 + \partial_t \omega, \tag{4.10}$$

where Λ is an arbitrary function, will not change either the electric field nor the magnetic one. This follows for the magnetic field because the divergence of a curl is zero, and for the electric field because in (4.6) after exchange of both derivatives the contributions from both terms cancel. As (4.7-4.8) are just Maxwell's equations (4.3-4.4) with (4.5-4.6) inserted, neither will they. Thus, for any set of electric field and magnetic field there is an infinite number of possibilities for $\vec{A}$ and A_0.

This has two consequences. One is that this freedom can be used to introduce additional constraints on $\vec{A}$ and A_0, usually such as to simplify calculations. Such constraints are called gauge conditions. These may fix this freedom completely, or only partly. One choice is, e. g., Coulomb gauge, which imposes

$$\vec{\partial} \cdot \vec{A} = 0,$$

which reduces (4.7) to an equation which makes explicit the connection of A_0 and the electric potential. Another one is the Lorentz condition, which imposes

$$\vec{\partial} \cdot \vec{A} + \frac{1}{c^2} \partial_t A_0 = 0,$$

and which thus simplifies (4.8) to an inhomogeneous wave equation with the electric current as a source. Thus, both simplify the solution of Maxwell's equation considerable. In practice, it will depend on the specific form of ρ and $\vec{j}$ which is more advantegous. Once the solution is obtained, (4.5-4.6) can be used to obtain the electric field and the magnetic field.

4.2 States and redefinitions

Electromagnetism is a gauge theory. Furtheremore, already in classical mechanics matter was coupled to electromagnetism in the Hamiltonian formulation or Lagrangian formu-

lation in terms of a canonical momentum

$$\vec{p} - \frac{e}{c}\vec{A}$$

in which the gauge-dependent vector potential appeared. Of course, the gauge dependence eventually canceled in the trajectories. In quantum mechanics, of course, for all observables, like measurements, any gauge dependence need to cancel as well. But, in quantum mechanics also central quantities appear, which are not directly measurable, of foremost importance the wave function. There is no a-priori reason, why the wave function should not be gauge dependent. And, indeed, in the end it is.

This is a conceptually important insight: Because the wave function is not observable, it may be altered at will. In quantum mechanics this was already visible in terms of an arbitrary overall phase. However, here, the changes will be inherited from the gauge symmetry. It is worthwhile to understand this first for a simpler example.

In quantum mechanics, it is possible to redefine a potential by a constant as $V(x) \to V(x) + \omega$, where ω is constant. This can be used, e. g., to shift the lowest energy level of the hydrogen atom to zero, and the ionisation threshold to $+13.6$ eV, or to -3 eV and $+10.6$ eV, respectively. While a bit uncommon, there is nothing wrong with this, as only energy differences are measured.

As the shift is constant, this can be absorbed in the wave equation by introducing a time-dependent phase

$$|\alpha\rangle \to |\beta\rangle = e^{-\frac{i\omega t}{\hbar}} |\alpha\rangle$$

since

$$i\hbar\partial_t |\beta\rangle = e^{-\frac{i\omega t}{\hbar}} (\omega + i\hbar\partial_t) |\alpha\rangle = (H + \omega) |\beta\rangle = e^{-\frac{i\omega t}{\hbar}} (\omega + H) |\alpha\rangle .$$

Thus, this precisely compensates the effect. Also, even though the phase is not constant but time-dependent, this does not alter any probability densities nor any expectation values which do not involve a time derivative. In the latter case, this is necessary, as the time evolution involves the Hamilton operator, which also involves the shift. Thus, to compensate any effects in the time-dependence probed by a time derivative, this is necessary. Of course, the same can be absorbed in time-dependent phase in the Heisenberg picture.

4.3 Coupling to the vector potential

It turns out experimentally that canonical quantization delivers the correct quantum mechanical system in a classical electromagnetic field. Thus, the Hamilton operator is

$$H = \frac{1}{2m}\left(\vec{P} - \frac{e\vec{A}(\vec{X})}{c}\right)^2 + eA_0(\vec{X}) = \frac{1}{2m}\left(\vec{P}^2 - \frac{e}{c}\left(\vec{P}\vec{A} + \vec{A}\vec{P}\right) + \left(\frac{e}{c}\vec{A}\right)^2\right) + \frac{e}{c}A_0(\vec{X}). \tag{4.11}$$

Note that the dependence on the position operator effectively promotes the gauge field to an operator. What is classical is how the gauge field depends on the position operator. To emphasize this, just as for potentials, also a capital letter is used for the gauge field. This similarity implies already that the Ehrenfest relations will reestablish classical electromagnetic phenomena.

Note that this implies that the gauge field does not commute with the momentum operator. As a consequence the components of the canonical momentum operator $\vec{P}i = \vec{P} - e\vec{A}/c$ do not commute,

$$[\Pi_i, \Pi_j] = \frac{i\hbar e}{c}\epsilon_{kij}\epsilon_{klm}\partial_l \vec{A}_m = \frac{i\hbar e}{c}\epsilon_{ijk}B_k = \frac{i\hbar e}{c}F_{ij},$$

except for vanishing magnetic fields. Note that the latter does not imply that $\vec{A}$ needs to vanish. This is different from the canonical momentum operator, whose components commute, and thus care is needed.

As this explicitly demonstrates, the Hamilton operator involves the gauge-dependent gauge fields, rather than the gauge-invariant electric field and magnetic field. It would be possible to eliminate them , but at the expense of having non-local operators in the hamilton operators, i. e. quantities expressed as integrals. While conceptually possible, this is practically almost impossible to deal with in most cases. Thus, this route will not be pursued.

The next step is to establish the relation of the wave function to electric currents. Since the wave-function is the probability density for finding a particle, which in this case is charged, it is expected that this also yields the charge density. This is indeed the case. To show this, assume that $\rho = e|\psi|^2$ in position space is the charge density. Then the wave equation yields

$$\begin{aligned} \partial_t \rho + \Pi\vec{j} &= 0 \\ \vec{j} &= e\left(\frac{\hbar}{m}\Im\left(\psi^*\Pi\psi\right) - \frac{e}{mc}\vec{A}\rho\right) = \frac{\rho}{m}\left(\vec{\partial}\phi - \frac{e}{c}\vec{A}\right) \\ \psi &= \sqrt{\rho}e^{\frac{i\phi}{\hbar}} \end{aligned} \tag{4.12}$$

This has indeed the same form as the electromagnetic continuity equation for electric charge and electric current, with the given definition of the current. Also, when setting $\vec{A} = 0$, this reduces to the continuity equation for probability.

4.4 Gauge (in)variance

As noted, the vector potential can be changed by a gauge transformation, without changing electromagnetic phenomena. The question is whether this holds true in quantum physics. If one requires that physics is independent of the observer, this leaves only two possibilities. Either the gauge freedom is lost, and a unique gauge condition needs to be implemented in quantum physics or gauge symmetry may also not affect quantum observables, in particular expectation values. It is an experimental question which of both applies, and experiment clearly favors the latter, and such that the gauge transformations of the vector potential remain as in classical electrodynamics.

Thus, it requires to understand how gauge transformations are implemented in quantum physics. The electric current (4.12) provides a very good first step. If a gauge-transformation (4.9) is applied to the vector potential then

$$\frac{\rho}{m}\left(\vec{\partial}\phi - \frac{e}{c}\vec{A}\right) \to \frac{\rho}{m}\left(\vec{\partial}\phi - \frac{e}{c}\vec{A} - \frac{e}{c}\vec{\partial}\omega\right).$$

For this to remain invariant requires that the phase of the wave function also needs to change under a gauge transformation,

$$\phi \to \phi + \frac{e}{c}\omega \tag{4.13}$$

and thus the whole wave-function is multiplied by a phase

$$\psi \to e^{\frac{ie}{\hbar c}\omega}\psi.$$

I. e. the phase of the wave-function is changed at every point of space and time under the transformation. Thus, in contrast to the previous discussion in section 4.2 the phase is now locally changed. This is necessary to keep the electric current gauge invariant. Note that this does not imply that it is possible to arbitrarily just change the phase. Most importantly, it cannot be done without simultaneously changing also the vector potential by (4.9). Only changing both is a valid transformation. Note that also this implies that the probability density ρ is automatically invariant. Furthermore, replacing the canonical momentum operator with the covariant momentum operator will necessarily create invariant quantities.

It is a bit more awkward to discuss this in terms of arbitrary states. In this case, the gauge transformation is formally also operator-valued, to ensure that derivatives, mediated by the momentum operator, act correctly on it. While this is, in principle, clean, it is much simpler to stick with position space for now.

But then there is also the change to A_0 (4.10). This will affect the Hamilton operator, which will change under a gauge transformation. However, when analyzing the wave equation, this looks very different. The reason is the right-hand side, which changes according to

$$i\hbar\partial_t e^{\frac{ie}{\hbar c}\omega}\psi = i\hbar e^{\frac{ie}{\hbar c}\omega}\partial_t\psi - e^{\frac{ie}{\hbar c}\omega}\psi\frac{e}{c}\partial_t\omega$$

But this is exactly the term generated by the last term (4.11) by (4.10). Thus, this additional term cancels as well.

Finally,

$$\Pi' e^{\frac{ie}{\hbar c}\omega}\psi = \left(-i\hbar\vec{p} - \frac{e}{c}\vec{A} - \frac{e}{c}\vec{\partial}\omega\right) e^{\frac{ie}{\hbar c}\omega}\psi = e^{\frac{ie}{\hbar c}\omega}\Pi\psi.$$

Thus, the phase can be moved through. Hence, for the full wave equation

$$\begin{aligned} i\hbar\psi' &= \left(\frac{2m'^2}{\Pi} + \frac{e}{c}A_0\right)\psi' \\ e^{\frac{ie}{\hbar c}\omega}\left(i\hbar + \frac{e}{c}\partial_t\omega\right)\psi &= e^{\frac{ie}{\hbar c}\omega}\left(\frac{2m'^2}{\Pi} + \frac{e}{c}A_0 + \frac{e}{c}\partial_t\omega\right)\psi \end{aligned}$$

holds, and the gauge transformation drops out. Thus, the wave-equation itself is gauge-invariant, even though neither the Hamilton operator, nor the wave function are individually.

Note that this make sit a bit awkward to define what a static problem is, as a gauge transformation can make a static potential time-dependent. However, if there exists at least one gauge, in which the gauge fields $\vec{A}$ and A_0 become time-independent, then the problem can be solved in that gauge as a static problem. In particular, the energy spectrum is gauge-invariant, and independent of the choice of gauge. But it depends on the gauge, if the time-dependence of the eigenstates are then trivially $\exp(iEt/\hbar)$, or some arbitrary time-dependent phase $\exp(i(Et + e\omega/c)/\hbar)$.

4.5 The Aharanov-Bohm effect

A very interesting example of how electromagnetism can create novel effects in quantum physics is the Aharanov-Bohm effect. However, care needs to be taken in the implica-

tions of the results, due to the non-locality of quantum physics. It is often erroneously interpreted as that the gauge field is a real object. This is not the case.

The setup for this effect is a localized, constant magnetic field along the z-direction, e. g. $\vec{B} = B\vec{e}_z\theta(\rho - \rho_0)$ in cylindrical coordinates. The particle cannot enter this region. This can be created by an infinite, impenetrable coil of radius ρ aligned with the z-axis would create such a field. A possible gauge-fixed choice for the vector potential is $A_0 = 0$ and $\vec{A} = B\rho_0\vec{e}_\phi/\rho^2\delta(\rho - \rho_0) + \vec{\partial}\omega$, where ω is an arbitrary function, which can be non-zero everywhere. The question is what the transition probability is for a particle to move from a point a to a point b with and without magnetic field. In classical physics it would not matter if the magnetic field is zero or non-zero. In quantum mechanics it does.

Consider for this the transition amplitude between two points a and b, which is given by the transition amplitude

$$\langle a, t_a | b, t_b \rangle = \langle a, 0 | U(t_a, t_b) | b, 0 \rangle .$$

It is not entirely trivial, but eventually it can be shown that

$$\begin{aligned} |\langle a, t_a | b, t_b \rangle|^2 &= |\langle a, t_a | b, t_b \rangle_{\vec{B}=\vec{0}}|^2 \frac{1}{2} \left(1 + \cos \frac{e}{\hbar c} \int_{\mathcal{C}} \vec{A} \vec{dx} \right) \\ &= |\langle a, t_a | b, t_b \rangle_{\vec{B}=\vec{0}}|^2 \frac{1}{2} \left(1 + \cos \frac{e}{\hbar c} F_B \right) \end{aligned} \tag{4.14}$$

where $\mathcal{C}$ is any closed path which includes the points a and b, and F_B is the total magnetic flux in the coil. Thus, the probability is changed, deepening on the amount of magnetic flux, despite the fact that the particles does not appear to be able to notice the magnetic field, and at most the vector potential could be non-zero in its path. As noted, the effect is genuine quantum. This has been experimentally confirmed.

There are a few remarks. The first is that only the gauge-invariant magnetic flux contributes. This is also known as holonomy in this case. This quantity can be determined entirely without relying on the vector potential at all. Thus, apparently it is not the vector potential which plays a role, just the electromagnetic field. But then the effect appears to be entirely non-local. Also, this is not correct, and stems from too much thinking of a particle as a point-like object. However, particle-wave duality already teaches that this is different in quantum physics. What actually happens here is that the wave function needs to be really considered to be something everywhere, in particular also on the surface of the coil. Thus, there is a boundary. That one is also there if

the magnetic field is absent, so this alone cannot be the reason. However, the magnetic field changes discontinuously across the boundary. If, rather than just determining the phase difference (4.14), the whole wave function is determined, the boundary conditions with and without magnetic field yield the difference. Thus, because the wave-function is present throughout all of space, the existence of the discontinuous magnetic field on the boundary needs to be taken into account, and yields the effect. This is basically what happens when relating to the line integral in (4.14) to the area integral giving the flux. The information in the interior is stored on boundaries, as always in classical electromagnetism. And because the magnetic field is vanishing beyond the coil, the boundary can be arbitrarily deformed, also giving rise to the path-independence of (4.14). So, the Aharanov-Bohm effect is another example of the genuine non-local structure of quantum physics, like the violation of Bell's inequalities.

Note that the effects discussed in section 4.2 are working on the same structures.

4.6 The hydrogen atom beyond the Coulomb potential

Once one moves beyond the static case, also the hydrogen atom becomes more involved. There are three important effects:

1. Spin-orbit coupling: The movement of the electron induces a magnetic effect coupling to its spin

2. Hyperfinestructure: The magnetic moment of the nucleus also creates magnetic effects

3. Relativistic effects: The Coulomb potential is only the first terms in an expansion in the 'speed' of the electron

All of this originates as low-energy effects from the actual underlying quantum electrodynamics, which is a fully relativistic theory. Consider for the moment the case with a single electron only. Otherwise the interaction effects between electrons, which also include effects due to their spins, will be often of similar size, and unnecessarily complicate things conceptually. Though, of course, in actual multielectron systems these effects need to be kept.

An electric charge itself does not have a magnetic dipole moment, and thus in a suitable frame will not experience effects from a magnetic field. However, the electron has an intrinsic magnetic moment, due to its spin, of $\vec{\mu} = e\vec{s}/(m_e c)$. Classically, an object with a magnetic dipole moment moving in a static electric field experiences an additional potential. Canonically quantizing it, yields[1]

$$H = H_0 - \frac{1}{2m_e^2 c^2}\frac{\gamma}{r^3}\vec{L}\vec{S} \tag{4.15}$$

where the spin operator $\vec{S}$ satisfies the angular momentum algebra, and the electron is a $s = \hbar/2$ eigenstate, and H_0 is the spinless case. This term implies that the alignment between orbital angular momentum and the spin is relevant, thus the name spin-orbit coupling.

To understand the consequences, it is useful to switch to work with the total angular momentum $\vec{J}$, which is obtained from the orbital angular momentum and the spin by the Clebsh-Gordan construction. States are then described in terms of the eigenvalues j, l, s, and j_3. Note that $j = l \pm 1/2$, corresponding to whether the spin is aligned or anti-aligned with the orbital angular momentum. Furthermore, since $[L_i, S_j] = 0$, it follows that

$$\frac{1}{2}\vec{L}\vec{S} = \vec{J}^2 - \vec{L}^2 - \vec{S}^2.$$

Hence, total angular momentum states remain a suitable basis for this system, as they remain eigenstates. This is not true for the radial states, and a full solution is non-trivial. But it already shows a qualitative features, known as Lande's interval rule. For H_0, the states with $j = l \pm 1/2$ are degenerate, as $\vec{S}$ does not appear in H_0. Thus, every state appears twice, once for electrons with spin up and once for electrons with spin down. The spin-orbit coupling changes this, raising the energy levels with $j = l + 1/2$ and lowering those with $j = l - 1/2$. This is known as fine-structure (splitting).

This structure is further disrupted, if the nucleus of the atom has a non-vanishing magnetic moment, due to a non-zero spin. This is, e. g., the case already for the hydrogen atom. Neglecting still the movement of the nucleus beyond what is captured by the reduced mass, this leads to three non-trivial effects.

The first is a spin-orbit coupling between the electrons movement and the nucleus spin. This yields the same effect as (4.15), but with $\vec{S}$ replaced by $\vec{S}_N$, the nucleus' spin

[1] There is an additional factor of 2, which stems from quantum field theory. A relativistic particle of spin 1/2 has twice the classically expected magnetic moment.

operator. Also, the prefactors now differ, as the nucleus' magnetic moment appears, giving in total the contribution

$$H_1^H = -\frac{2a}{2m_e^2c^2r^3}\vec{L}\vec{S}_N,$$

where a summarizes the nucleus-specific constants. This also implies that the states are now more complicated, and need to be characterized by another angular momentum quantum number, which can be combined again into a total spin using the Clebsh-Gordan construction. However, this is often not the most useful basis. Since now both the electron and the nucleus have a magnetic moment, their relative alignment contributes. Taking this again from classical physics yields a second contribution

$$H_2^H = \frac{a}{2m_e^2c^2}\left(3(\vec{S}_N\vec{R})(\vec{S}\vec{R}) - \vec{S}_N\vec{S}\right),$$

with again the nucleus-specific constant a. The third term, called Fermi contact term, describes direct interaction between both kinds of spin, and reads

$$H_3^H = \frac{2a}{6m_e^2c^2}\delta^3(\vec{R})\vec{S}_N\vec{S}.$$

This is only a model of the actual microinteraction of spins, when the wave function of the electron appreciably overlaps with the nucleus itself. Similar to the ordinary contact term, this cannot be further motivated without a model of the nucleus itself.

All of these effects have been related to the spin of the electron. Since spin is really a relativistic effect, they already capture a substantial amount of relativistic effects. However, there are also corrections which would affect electrically charged particles with spin zero. These additional effects take the general form (in position space)

$$V_c(r) = -\frac{a}{r} + b\delta(\vec{r}) - \frac{a}{2}\left(\vec{\partial}^2\frac{1}{r} + \frac{1}{r}\vec{\partial}^2\right),$$

where the derivatives act on everything to the right in the wave equation, and a and b are again nucleus-specific constants. Thus, this can be understood as to modify the electric charge by an effective electric charge in the first term, provide an effect at the location of the nucleus, and finally have a momentum-dependent change of the potential. This will slightly change the energy levels. In particular, the last term introduces also the Lamb shift.

While all of these effects yields measurable consequence, a complete solution of all of them simultaneously is usually not possible beyond either numerical solutions or perturbative means. The latter is usually a good approximation, as the changes are small, at least for nuclei with small charge.