Advanced Quantum Mechanics

with partial content (chaps. 1,2,3) from the Bachelor course

Last updated January 27, 2025
Exam topics (WS2024-25) Chaps. 4, 6 (except Land’e g-factor), 7 (except 7.2), Chap 9 until 9.4 included), Chap 12 (until 12.1.3 included), Chap 10 (this last chapter only starting from the second exam)

Partially taken from the lecture notes of Prof. Wolfgang von der Linden.
Thanks to Katharina Rath, Lukas Bauer, and Lisanne Demelius for help with the translation

Contents

Chapter 1

Rotations and the angular momentum operator

1.1 Main goals in this chapter

- Motivation: in Chap. 2 we shall deal with **central potentials** for which **angular momentum is conserved**. We thus need to study the properties of **angular momentum in quantum mechanics**

- Determine algebra i.e. **commutation rules** of a generic **angular momentum operator $\hat{\mathbf{J}}$**.
  This is achieved by looking at the **algebra of rotation matrices**.

- From the commutation rules only find **eigenvalues** and properties of eigenvectors.

- Find expression for **orbital** angular momentum operator when acting on $\psi(\mathbf{r})$.

- Find its eigenvalues and properties of **eigenfunctions**, i.e. **spherical harmonics**.

1.2 Algebra of angular momentum operators

We have already seen that transformations, for example translations and time evolution, in quantum mechanics are represented by unitary transformations. These continuous transformations form a so-called **Lie groups** (see QM1) and have the general form

$$\hat{U}(\varphi) = e^{-i\varphi\hat{A}} . \tag{1.1}$$

with an hermitian operator $\hat{A}$ (**generator**) and a contiunuous real parameter φ. The transformation 1.1 can also be seen as a combination of infinitesimal transformations:

$$\hat{U}(\varphi) = \left(e^{-i\frac{\varphi}{N}\hat{A}}\right)^N \overset{N\to\infty}{=} (1 - i\frac{\varphi}{N}\hat{A})^N = (1 - i\varphi\hat{A} - \frac{1}{2}\varphi^2\hat{A}^2 + \cdots) \,. \tag{1.2}$$

A rotation in $\mathbb{R}^3$ can be specified by a corresponding rotation matrix $R_{\mathbf{n}}(\varphi)$

Definition: $R_{\mathbf{n}}(\varphi)$: rotation matrix by an angle φ around the axis $\mathbf{n}$.

The corresponding action on a quantum mechanical state is expressed by an unitary operator $\hat{U}(R_{\mathbf{n}}(\varphi))$, which according to 1.1 , can be expressed as

ROTATION OPERATOR

$$\hat{U}(R_{\mathbf{n}}(\varphi)) = e^{-i\varphi\hat{J}_{\mathbf{n}}/\hbar} \,. \tag{1.3}$$

where $\hat{J}_{\mathbf{n}}$ is the **generator** of rotations around the axis $\mathbf{n}$, i.e. the **Angular-Momentum** operator (Drehimpulsoperator). The form of these operators depend on the vector space one is considering. For example, in QM1 we have already met the corresponding operators $\hbar\hat{S}_x$, $\hbar\hat{S}_y$, $\hbar\hat{S}_z$ acting on Spin-$\frac{1}{2}$ states. For rotation in coordinate space, we will see that $\hat{\mathbf{J}}$ corresponds to the orbital angular momentum $\hat{\mathbf{L}}$

In the next sections we will study the properties of these operators.

1.2.1 Rotation matrices in $\mathbb{R}^3$

Let us start with what we know, namely ordinary rotation matrices in real space. These can also be expressed in a form similar to 1.3 , namely

$$R_{\mathbf{n}}(\varphi) = e^{-i\varphi A_{\mathbf{n}}} \,. \tag{1.4}$$

To illustrate this, we consider a rotation by an infinitesimal angle φ about the z axis:

$$R_{\mathbf{z}}(\varphi) = \begin{pmatrix} 1 & -\varphi & 0 \\ \varphi & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + O(\varphi^2) \tag{1.5}$$

using 1.2 to order $O(\varphi)$ with 1.4 identifies in this case

$$A_{\mathbf{z}} = i \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{1.6}$$

It is straightforward to show (proof): Sec. A.1 that for a finite φ one recovers the well known expression

$$R_{\mathbf{z}}(\varphi) = e^{-i\varphi A_{\mathbf{z}}} = \begin{pmatrix} \cos\varphi & -\sin\varphi & 0 \\ \sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix} . \tag{1.7}$$

Similarly, by cyclic permutation, [1] one obtains the two remaining generators:

$$A_{\mathbf{x}} = i \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix} \qquad A_{\mathbf{y}} = i \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{pmatrix} \tag{1.8}$$

This tells us the action of the rotation operators and of its generators on a three-dimensional vector space. We also know, from QM1, its action on a two-dimensional Spin-$\frac{1}{2}$ system. The question to address is now, what is their action on the infinite-dimensional Hilbert space of wavefunctions, in other words, what are the properties of its generators $\hat{\mathbf{J}}$.

To learn more about this issue, we first consider the fact that the combination of two rotations around different axes does not commute. For example, the combination

$$R_{\mathbf{y}}(-\varphi)R_{\mathbf{x}}(-\varphi)R_{\mathbf{y}}(\varphi)R_{\mathbf{x}}(\varphi) \tag{1.9}$$

is not equal to the identity. We evaluate 1.9 up to order φ^2, obtaining for 1.9 (details): Sec. A.2

$$1 + [A_{\mathbf{x}}, A_{\mathbf{y}}]\varphi^2 + \cdots . \tag{1.10}$$

The commutator is readily evaluated from 1.8

$$[A_{\mathbf{x}}, A_{\mathbf{y}}] = iA_{\mathbf{z}} . \tag{1.11}$$

This gives for 1.9

$$R_{\mathbf{y}}(-\varphi)R_{\mathbf{x}}(-\varphi)R_{\mathbf{y}}(\varphi)R_{\mathbf{x}}(\varphi) \approx 1 + i\varphi^2 A_{\mathbf{z}} + \cdots \approx R_{\mathbf{z}}(-\varphi^2) + \cdots . \tag{1.12}$$

The meaning of this is the following: Assume that one first rotates around the x-axis and then around the y-axis by a (small) angle φ, respectively, and then repeats the sequence of rotations in the same order by the angle $-\varphi$. This does not correspond to an identity transformation but results into a rotation around the z-axis by an angle $-\varphi^2$.

In general, we can write

$$R_\beta(-\varphi)R_\alpha(-\varphi)R_\beta(\varphi)R_\alpha(\varphi) = \varepsilon_{\alpha\beta\gamma}R_\gamma(-\varphi^2) + O(\varphi^3) \tag{1.13}$$

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[1] Here and below we will obtain results for a fixed cartesian component, and then generalize it to arbitrary components by means of a **cyclic permutation**, i.e. by exchanging everywhere $x \to y \to z \to x \to \cdots$

1.2.2 Commutation rules of angular momentum operators

If we now carry out these rotations on a quantum mechanical system, then both sides of Eq. 1.13 mut produce the same physical result. I. e.

$$\hat{U}(R_{\mathbf{y}}(-\varphi))\hat{U}(R_{\mathbf{x}}(-\varphi))\hat{U}(R_{\mathbf{y}}(\varphi))\hat{U}(R_{\mathbf{x}}(\varphi)) \overset{!}{=} e^{i\omega_z}\hat{U}(R_{\mathbf{z}}(-\varphi^2)) + O(\varphi^3) \quad (1.14)$$

where ω_z is a yet unknown φ-dependent phase. We exploit this property in order to learn more about $\hat{J}$.

Again, we expand 1.14 up to second order in φ. Comparing 1.3 with 1.4 , it is clear that the result of the left hand side of 1.14 is given by 1.10 whith $A_\alpha \to \hat{J}_\alpha/\hbar$, i.e.

$$1 + [\hat{J}_{\mathbf{x}}, \hat{J}_{\mathbf{y}}]\frac{\varphi^2}{\hbar^2} \quad (1.15)$$

Similarly, the r.h.s. of 1.14 becomes up to the same order, and neglecting the phase ω_z (See for a discussion): Sec. A.3

$$1 + i\frac{\varphi^2}{\hbar^2}\hbar\hat{J}_{\mathbf{z}} \quad (1.16)$$

comparing 1.15 with 1.16 gives $[\hat{J}_{\mathbf{x}}, \hat{J}_{\mathbf{y}}] = i\hbar\hat{J}_{\mathbf{z}}$. In general one gets the

COMMUTATION RULES OF THE ANGULAR MOMENTUM OPERATORS

$$[\hat{J}_\alpha, \hat{J}_\beta] = i\hbar\varepsilon_{\alpha\beta\gamma}\hat{J}_\gamma \qquad . \quad (1.17)$$

1.3 Scalar and Vector Operators

Scalar and vector quantities (observables) have well defined transformation properties under rotation. Here we show that these imply well defined commutation rules of the corresponding operators with the angular momentum operators.

Let us consider a scalar or vector operator $\hat{A}$, as well as one of its eigenstates $|\psi\rangle$:

$$\hat{A}\;|\psi\rangle = a\,|\psi\rangle \qquad .$$

Let us now consider a rotation R of the coordinate system. The operator is transformed into $\hat{A}'$ and the state vector $|\psi\rangle$ into $|\psi'\rangle = \hat{U}(R)\,|\psi\rangle$. The eigenvalue equation in the rotated system now reads

$$\begin{aligned}\hat{A}'\,\left|\psi'\right\rangle &= a\,\left|\psi'\right\rangle\\ \hat{A}'\,\hat{U}(R)\,\left|\psi\right\rangle &= a\,\hat{U}(R)\,\left|\psi\right\rangle\\ \hat{U}^{\dagger}(R)\hat{A}'\hat{U}(R)\,\left|\psi\right\rangle &= a\,\left|\psi\right\rangle \qquad .\end{aligned}$$

This observation holds for all eigenvectors of $\hat{A}$. Since these constitute a complete basis set, one has the identity $\hat{U}^{\dagger}(R)\hat{A}'\hat{U}(R)=\hat{A}$, or

$$\hat{A}'=\hat{U}(R)\hat{A}\hat{U}^{\dagger}(R) \qquad .$$

We assume again an infinitesimal rotation angle φ around the axis α and thus replace the unitary rotation operator

$$\hat{U}(R)=e^{-i\frac{\varphi}{\hbar}\hat{J}_{\alpha}}$$

with a series expansion up to linear order in φ

$$\begin{aligned}\hat{A}' &= (\mathbb{1}-\frac{i}{\hbar}\varphi\hat{J}_{\alpha})\hat{A}(\mathbb{1}+\frac{i}{\hbar}\varphi\hat{J}_{\alpha})+O(\varphi^{2})\\ \hat{A}' &= \hat{A}-\frac{i}{\hbar}\varphi[\hat{J}_{\alpha},\hat{A}]+O(\varphi^{2}) \qquad (1.18)\end{aligned}$$

If $\hat{A}$ is a scalar operator, the it is invariant under rotations, i.e. $\hat{A}'=\hat{A}$. From 1.18 it follows

SCALAR OPERATORS $\hat{A}$

$$[\hat{J}_{\alpha},\hat{A}]=0\,. \qquad (1.19)$$

An operator $\hat{\mathbf{A}}$ with vector-character consists in a set of three operators (for example in cartesian coordinates $\hat{A}_x,\hat{A}_y,\hat{A}_z$) which transform appropriately under rotations. A rotation R of the coordinate system corresponds to an inverse rotation of the components of $\hat{\mathbf{A}}$, i.e. by $R^{-1}=R^{T}$ (details): Sec. A.4 . We now consider specifically rotations around the z-axis by an angle φ. The corresponding rotation matrix is 1.5 . The rotation of the cartesian components $\hat{\mathbf{A}}'=R^{T}\ \hat{\mathbf{A}}$ is given explicitly by

$$\begin{aligned}\hat{A}'_x &= \hat{A}_x+\varphi\,\hat{A}_y\\ \hat{A}'_y &= \hat{A}_y-\varphi\,\hat{A}_x\\ \hat{A}'_z &= \hat{A}_z \qquad .\end{aligned}$$

We compare this with 1.18 and obtain

$$
\begin{aligned}
[\hat{J}_z, \hat{A}_x] &= i\hbar \hat{A}_y \\
[\hat{J}_z, \hat{A}_y] &= -i\hbar \hat{A}_x \\
[\hat{J}_z, \hat{A}_z] &= 0 \qquad .
\end{aligned}
$$

This can be summarized into

$$[\hat{J}_z, \hat{A}_\beta] = i\hbar \varepsilon_{z\beta\gamma} \hat{A}_\gamma \qquad .$$

A cyclical permutation of the above results leads to generalized transformation properties of

VECTOR-OPERATORS

$$[\hat{J}_\alpha, \hat{A}_\beta] = i\hbar\, \varepsilon_{\alpha\beta\gamma}\, \hat{A}_\gamma \qquad . \tag{1.20}$$

Notice that 1.17 is a special case of 1.20 , since $\hat{\mathbf{J}}$ is a vector.

1.4 Eigenvalue Problem for the Angular Momentum Operator

Systems with a central force are **invariant under rotation**. This means that their Hamiltonian $\hat{H}$ is a scalar, i.e. it commutes with each component $\hat{J}_\alpha$ (see 1.19). As discussed in QM1, this means that it is possible to find a common set of eigenfunctions (eigenvectors) of $\hat{H}$ and one of the $\hat{J}_\alpha$. As we will see, this allows to simplify the problem considerably and provides the opportunity to classify the eigenstates of the Hamiltonian.

Of course, one should try to take the maximum number of mutually commuting operators. Unfortunately, since the different $\hat{J}_\alpha$ do not commute with each other, we can take only one of them. However, there is one additional operator, namely $\hat{J}^2$, that commutes with all $\hat{J}_\alpha$ (and with a rotation-invariant Hamiltonian):

$$[\hat{J}^2, \hat{J}_\alpha] = 0\ . \tag{1.21}$$

To prove this it is sufficient to observe that $\hat{J}^2$, the square length of a vector, is a **scalar**, and thus 1.19 holds. (For a mathematical proof): Sec. A.6 .

As a consequence, $\hat{J}^2$ and, e.g., $\hat{J}_z$ (as well as the rotation invariant $\hat{H}$) admit a complete set of common eigenvectors. The remaining angular momentum operators cannot, however, be simultaneously diagonalized. Alternatively, one could also have chosen $\hat{J}^2$ and $\hat{J}_x$ or $\hat{J}^2$ and $\hat{J}_y$. One can, however, have just one of the three cartesian component. It has become established to use the z-component. The eigenvalue problem to be solved is, thus,

$$\begin{aligned}\hat{J}^2|j,m\rangle &= \hbar^2 a_j |j,m\rangle\\ \hat{J}_z|j,m\rangle &= \hbar\, m|j,m\rangle\ .\end{aligned}$$

The eigenstates $|j,m\rangle$ are characterized by two quantum numbers j and m, with corresponding eigenvalues $\hbar^2 a_j$ und $\hbar m$. We collected factors $\hbar$ from the eigenvalues, so that a_j and m are dimensionless ($\hat{\mathbf{J}}$ has the same dimensions as $\hbar$). Notice that we haven't yet specified what j,m (or even a_j) are, for the moment they are just dimensionless (in principle real) numbers used to specify the states $|j,m\rangle$.

Ladder operators

In many treatments of the angular momentum operator it is convenient to use a different representation of its components. We define

LADDER OPERATORS

$$\hat{J}_{\pm} = \hat{J}_x \pm i\hat{J}_y \qquad . \tag{1.22}$$

Clearly

$$\hat{J}_{\pm}^{\dagger} = \hat{J}_{\mp} \, . \tag{1.23}$$

From this we can obtain back the cartesian components of the angular momentum operator

$$\begin{aligned} \hat{J}_x &= \frac{(\hat{J}_+ + \hat{J}_-)}{2} \\ \hat{J}_y &= \frac{(\hat{J}_+ - \hat{J}_-)}{2i} \end{aligned}$$

The commutation rules for the new operators read Proof: Sec. A.6.

$$\begin{aligned} &[\hat{J}_z, \hat{J}_{\pm}] = \pm\hbar \hat{J}_{\pm} \\ &[\hat{J}_+, \hat{J}_-] = 2\hbar \hat{J}_z \\ &[\hat{J}^2, \hat{J}_{\pm}] = 0 \end{aligned} \tag{1.24}$$

The solution of the eigenvalue problem of the angular momentum operator from the results 1.24 follows a similar procedure as for the harmonic oscillator. The $\hat{J}_{\pm}$ are termed **ladder operators**, since they modify the quantum number m by ± 1:

$$\hat{J}_z(\hat{J}_{\pm}|j,m\rangle) = \hat{J}_{\pm} \underbrace{\hat{J}_z|j,m\rangle}_{m\,\hbar\cdot|j,m\rangle} + \underbrace{[\hat{J}_z, \hat{J}_{\pm}]}_{\pm\hbar\hat{J}_{\pm}}|j,m\rangle \tag{1.25}$$

$$= \hbar(m \pm 1)(\hat{J}_{\pm}|j,m\rangle) \tag{1.26}$$

I.e. $\hat{J}_{\pm}|j,m\rangle$ is an eigenstate of $\hat{J}_z$ with eigenvalue $\hbar(m \pm 1)$. This is the property of a ladder operator. $\hat{J}_{\pm}$ does not change a_j, the eigenvalue of $\hat{J}^2$, as $[\hat{J}^2, \hat{J}_{\pm}] = 0$, i.e.

$$\hat{J}^2(\hat{J}_\pm|j,m\rangle) = \hat{J}_\pm\hat{J}^2|j,m\rangle \tag{1.27}$$
$$= \hbar^2 a_j(\hat{J}_\pm|j,m\rangle) \tag{1.28}$$

and therefore $\hat{J}_\pm|j,m\rangle$ is eigenvector of $\hat{J}^2$ with eigenvalue $\hbar^2 a_j$. From this it follows

$$\hat{J}_\pm|j,m\rangle = C_{m\pm}|j,m\pm 1\rangle \tag{1.29}$$

The proportionality constants $C_{m\pm}$ will be determined later via normalisation. Can $\hat{J}_\pm$ be applied arbitrarily often, as in an harmonic oscillator? The answer is no, as can be shown by the following arguments. First of all, notice that

$$\hat{J}^2 - \hat{J}_z^2 = \hat{J}_x^2 + \hat{J}_y^2 \geq 0\,,$$

and therefore must be a nonnegative operator. Therefore,

$$\langle j,m|\hat{J}^2 - \hat{J}_z^2|j,m\rangle = \hbar^2(a_j - m^2) \geq 0 \Rightarrow a_j \geq m^2 \tag{1.30}$$

We therefor have following conditions:

1. $a_j \geq 0$, since the eigenvalues of $\hat{J}_z$ are real
2. $|m| \leq \sqrt{a_j}$

From the requirement that $\hat{J}_+|j,m\rangle$ must not lead to to large unallowed values of m, it follows that it exists a maximum (j-dependent) m_{max} for which

$$\hat{J}_+|j,m_{max}\rangle = 0 \qquad . \tag{1.31}$$

In order to determine m_{max}, we first transform the Operator $\hat{J}_-\hat{J}_+$ as follows:

$$\hat{J}_-\hat{J}_+ = (\hat{J}_x - i\hat{J}_y)(\hat{J}_x + i\hat{J}_y) = \hat{J}_x^2 + \hat{J}_y^2 + i\underbrace{[\hat{J}_x,\hat{J}_y]}_{i\hbar\hat{J}_z} = \hat{J}^2 - \hat{J}_z^2 - \hbar\hat{J}_z \tag{1.32}$$

One then has

$$0 = \hat{J}_-\hat{J}_+|j,m_{max}\rangle = \hbar^2(a_j - m_{max}^2 - m_{max})|j,m_{max}\rangle$$

and

$$a_j = m_{max}(m_{max}+1) \tag{1.33}$$

Due to 1.33 m_{max} determines uniquely the eigenvalue a_j. Therefore, we can identify the former with the quantum number j.

$$\mathbf{m_{max} = j} \tag{1.34}$$

Similarly, a m_{min} must exist with

$$\hat{J}_- \, |j, m_{min}\rangle = 0 \, .$$

Similar arguments as above lead to

$$\hat{J}_+\hat{J}_- = \hat{J}^2 - \hat{J}_z^2 + \hbar\hat{J}_z \tag{1.35}$$

and finally to

$$a_j = m_{min}(m_{min} - 1) \tag{1.36}$$

Combining 1.33 with 1.36 one gets. [2]

$$m_{min} = -j \tag{1.37}$$

Starting with $|j, m_{min}\rangle$ and repeatedly applying $\hat{J}_+$ one obtains (see 1.29)

$$\overbrace{\hat{J}_+ \cdots \hat{J}_+}^{n \text{ Mal}} |j, m_{min}\rangle \propto |j, m_{min} + n\rangle \ . \tag{1.38}$$

This works until $|j, j\rangle$ is reached. The next $\hat{J}_+$ destroys the state, according to 1.31 . In order to exactly reach $|j, j\rangle$, $j - m_{min} := n \in \mathbb{N}_0$ must be integer. Together with 1.37 one obtains

$$j = \frac{n}{2} \qquad n \in \mathbb{N}_0 \tag{1.39}$$

j is therefore half-integer or integer. 1.39 and 1.33 determine the possible eigenvalues of $\hat{J}^2$ und $\hat{J}_z$ as well as their relation. Accordingly, eigenstates are classified with following convention which represents the **Quantisation of Angular Momentum**.

Eigenvalues and Eigenvectors of Angular Momentum Operators

$$\begin{aligned} \hat{J}^2 |j, m\rangle &= \hbar^2 j(j+1) |j, m\rangle && \text{(1.40a)} \\ \hat{J}_z |j, m\rangle &= \hbar m |j, m\rangle && \text{(1.40b)} \end{aligned}$$

The notation and allowed values for these **Quantum numbers** are summarized in table 30. This result is completely general and follows simply from the com-

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[2] A second solution would be $j = m_{min} - 1$, which is obviously inconsistent

Symbol	Name	range of values
j	Angular momentum quantum n.	$j = \frac{n}{2} \qquad n \in \mathbb{N}_0$
m	magnetic quantum number	$m \in \{-j, -j+1, \ldots, j-1, j\}$

Table 1.1: Quantum numbers of angular momentum operators

mutation rules 1.17 .

We make the following interesting observation:

$$J_z^{max} = \hbar \cdot j; \Rightarrow \qquad (J_z^{max})^2 = \qquad \hbar^2 j^2 \tag{1.41}$$

$$\hat{J}^2 = \hbar^2 \cdot j(j+1) \qquad = \qquad \hbar^2 j^2 + \hbar^2 j \tag{1.42}$$

I.e., structure$\hat{J}^2$ is strictly larger than $\hat{J}_z^2$: the angular momentum operator cannot be completely aligned. This should be like that, since suppose one had $\hat{J}^2 = \hat{J}_z^2$, then it would follow $\hat{J}_x = 0$ and $\hat{J}_y = 0$. This would contradict Heisenberg's uncertainty principle. An exception is provided for $j = 0$ See why: Sec. A.7 .

Normalisation

Next we determine the proportionality constants $C_{m\pm}$ in 1.29 from normalisation (we use 1.32 and 1.35)

$$\langle j, m|\hat{J}_\pm^\dagger \hat{J}_\pm|j, m\rangle \overset{!}{=} |C_{m\pm}|^2 \underbrace{\langle j, m\pm 1|j, m\pm 1\rangle}_{=1}$$

$$\begin{aligned}
|C_{m\pm}|^2 &= \langle jm|\hat{J}_\mp \hat{J}_\pm|jm\rangle \\
&= \langle jm|(\hat{J}^2 - \hat{J}_z^2 \mp \hbar \hat{J}_z)|jm\rangle \\
&= \hbar^2(j(j+1) - m^2 \mp m) \\
&= \hbar^2(j(j+1) - m(m\pm 1))
\end{aligned}$$

The fact that $C_{m\pm} = 0$ for $m = \pm j$ is consistent with 1.34 and 1.37 .

The phase of $C_{m\pm}$ is in principle arbitrary. In the usual convention this is chosen real and positive. We thus obtain the following result

$$|j, m \pm 1\rangle = \frac{1}{\sqrt{j(j+1) - m(m \pm 1)}} \; \frac{\hat{J}_{\pm}}{\hbar} |j, m\rangle \quad . \tag{1.43}$$

With the help of 1.43 one can, starting from $|j, -j\rangle$ (or from an arbitrary $|j, m_0\rangle$) explicitly construct all other $|j, m\rangle$

We have derived all possible eigenvalues of $\hat{J}^2$ from the commutator algebra. This does not yet mean that all possible values of j are realized in nature. In particular $j = \frac{1}{2}$ does not correspond to a orbital angular momentum. On the other hand, we have identified $j = \frac{1}{2}$ with the spin of an electron in a Stern-Gerlach Experiment (QM1). The general rule is that orbital angular momenta have integer values of j (see Sec. 1.5). Half-integer values originate from the summation of spin with spin and/or with orbital angular momentum.

The vectorial angular momentum operator have a peculiar property which originates from the fact that its cartesian components do not commute. For normal vectors $\mathbf{v}$ the cross product $\mathbf{v} \times \mathbf{v}$ vanishes. This **does not hold** in the case of the operator $\hat{\mathbf{J}}$. Instead one has Proof: Sec. A.8 :

$$\hat{\mathbf{J}} \times \hat{\mathbf{J}} = i\hbar \hat{\mathbf{J}}$$

1.5 The Orbital Angular Momentum

Orbital angular momentum operator in real space

We have not jet specified the expression of the angular momentum operator $\hat{\mathbf{J}}$. Indeed, this depends on the space it acts on. When acting on wave functions without spin this indeed acquires the (quantized) form of the (orbital) angular momentum in classical physics.

To show this let us consider a wave function of the coordinates $\psi(\mathbf{r})$. This is a scalar, so that under a rotation its value on corresponding points in space remains unchanged:

$$\psi(\mathbf{r}) = \psi'(\mathbf{r}') = \hat{U}(R)\psi(R\mathbf{r}) \Rightarrow \hat{U}(R)^{\dagger}\psi(\mathbf{r}) = \psi(R\mathbf{r}) \,.$$

For an infinitesimal rotation φ, say around the z-axis (see 1.5 , 1.3) this gives ($\mathbf{r} \equiv (x,y,z)$)

$$\left(1 + i\frac{\varphi}{\hbar}\hat{J}_z\right)\psi(x,y,z) = \psi(x-\varphi y, y+\varphi x, z) + O(\varphi^2) = \\ = (1 + \varphi(-y\partial_x + x\partial_y))\,\psi(\mathbf{r}) + O(\varphi^2)\,. \tag{1.44}$$

This identifies

$$\hat{J}_z = -i\hbar(-y\partial_x + x\partial_y) = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x\,. \tag{1.45}$$

the latter is indeed the known expression for the z component of the orbital angular momentum operator $\hat{L}_z$. Generalisation to the other components is obtained by cyclic permutations.

Thus, in the case of a scalar wave function, the **generator of rotations** $\hat{\mathbf{J}}$ is the **orbital angular momentum**

$$\hat{\mathbf{J}} \Rightarrow \hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}}\,. \tag{1.46}$$

Notice that the order of the operators does not matter here. When the wave function has components, like in the case of a spinor considered in QM1, $\hat{\mathbf{J}}$ is the sum of $\hat{\mathbf{L}}$ plus other terms (e.g., the spin $\hat{\mathbf{S}}$).

It is straightforward to show (and should be expected from the discussion up to now) that $\hat{\mathbf{L}}$, being an operator generating rotations, has to obey the correct commutation relations 1.17 . In addition, the commutation relations 1.20 hold for the known vector operators $\hat{\mathbf{r}}$ and $\hat{\mathbf{p}}$ (proofs here): Sec. A.5 .

Eigenwerte

Von den Vertauschungsrelationen alleine wissen wir bereits, daß die Eigenwerte von $\hat{L}_z$ ganzzahlige oder halbzahlige Vielfache von $\hbar$ sind. Wir werden noch zeigen, daß die halbzahligen Drehimpulse aufgrund der inneren Struktur des Bahndrehimpulses ausscheiden.

As discussed, the (orbital) angular momentum $\hat{\mathbf{L}}$ is useful for problems with rotation symmetry, i.e. when the potential $V(\mathbf{r})$ only depends on $r \equiv |\mathbf{r}|$. In this case, it is also useful to work in spherical coordinates (r, θ, φ). It is, therefore, useful to express the operators $\hat{\mathbf{L}}$ in these coordinates. First, one can readily see that all components of $\hat{\mathbf{L}}$ only act on the angular part of the wave function, i.e. on $\Omega \equiv (\theta, \varphi)$. This can be deduced from the fact that (cf. 1.3) $e^{-i\varphi\hat{L}_\alpha/\hbar}$ produces a rotation of the coordinates, so it only acts on Ω, and it cannot act on r. As a consequence, also the $\hat{L}_\alpha$ only act on Ω. A second, more simple, argument comes from the fact that $\hat{L}_\alpha/\hbar$ is dimensionless and, therefore, can only act on dimensionless quantities.

The consequence is that if we write a wave function $\psi(r,\Omega)$ in the product form $r \equiv |\mathbf{r}|$

$$\psi(r,\Omega) = f(r)Y(\Omega)$$

then applying an arbitrary component of $\hat{\mathbf{L}}$ (or $\hat{L}^2$)

$$\hat{\mathbf{L}}\, f(r)Y(\Omega) = f(r)\, \hat{\mathbf{L}}\, Y(\Omega)\,. \tag{1.47}$$

As a consequence, the search for the common eigenfunctions of $\hat{L}^2, \hat{L}_z$ corresponding to the vectors $|l,m\rangle$, can be restricted to functions $Y(\Omega)$ of the angles Ω only. But 1.47 also means that given a common eigenfunction $Y(\Omega)$ of $\hat{L}^2, \hat{L}_z$, then one can multiply it by any function of r, and this will remain an eigenfunction of $\hat{L}^2, \hat{L}_z$ with the same eigenvalues. There is a large degeneracy. This also means that one chosen set of common eigenfunctions of $\hat{L}^2, \hat{L}_z$ do not represent a **complete** basis in the space of the $\psi(r,\Omega)$. It is, however, complete in the space of the $Y(\Omega)$, as we shall see below.

These eigenfunctions, classified according to their quantum numbers, are termed $Y_l^m(\Omega)$, and are the well-known **spherical harmonics** (Kugelflächenfunktionen). Here, m has the same meaning as in 1.40b, while it is convention to use l instead of j (1.40a) for the orbital angular momentum. In agreement with 1.40a and 1.40b one thus has

EIGENVALUE EQUATION FOR SPHERICAL HARMONICS

$$\hat{L}^2\, Y_l^m(\Omega) = \hbar^2\, l(l+1)\, Y_l^m(\Omega) \tag{1.48}$$
$$\hat{L}_z\, Y_l^m(\Omega) = \hbar m\, Y_l^m(\Omega)\,, \tag{1.49}$$

Below, we will show this result and derive the explicit expression of the operators $\hat{L}_z, \hat{L}_\pm$ as well as of their eigenfunctions Y_l^m in spherical coordinates.

1.5.1 Ortsraumeigenfunktionen des Bahndrehimpulses

Goals of this section are (a) to express the angular momentum operators in spherical coordinates and (b) to obtain the expression for the $Y_l^m(\theta,\varphi)$. The derivation is rather lengthy and tedious, so we will here only point out the steps one has to carry out, following the logics of the previous sessions, and show only the simpler calculations. The more tedious details can be found in the appendix: Sec. A.9 , In

order to understand the procedure, we will explicitly derive the lowest spherical harmonics, i.e. the ones with $l = 0$ and $l = 1$.
The steps are the following

- From the expression of the orbital angular momentum operator in cartesian coordinates (cf. 1.45),

  $$\hat{\mathbf{L}} = \hat{\mathbf{r}} \times \hat{\mathbf{p}} = -i\hbar\, \hat{\mathbf{r}} \times \boldsymbol{\nabla} \tag{1.50}$$

  write down the expression of the relevant operators $(\hat{L}_z, \hat{L}_\pm)$ in spherical coordinates. They will have the form of linear differential operators in θ, φ.

- $\hat{L}_z$ produces rotations around the z axis, and, thus, only acts on the angle φ. It has a very simple form,

  $$\boxed{\hat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial\varphi}} \tag{1.51}$$

  so we start by solving for the φ-part of the Y_l^m by using 1.49 . The eigenvalue equation

  $$\frac{\partial}{\partial\varphi} Y_l^m(\theta,\varphi) = im\, Y_l^m(\theta,\varphi)$$

  has a simple solution

  $$Y_l^m(\theta,\varphi) \propto e^{im\varphi} \,.$$

  Since the wave function must be single-valued, m **must be integer**. As a consequence, l must be integer as well. This fact excludes half-integer values for the orbital angular momentum quantum numbers l and m. In contrast , as seen in QM1, the spin angular momentum can be half-integer.

- Once we have the φ part, we write a differential equation (just in θ) for the wavefunction with maximum m (cf. 1.31):

  $$\hat{L}_+ Y_l^l(\theta,\varphi) = 0$$

  We solve it, the solution is relatively simple, and normalize the Y_l^l.

- Once we have the Y_l^l, we obtain the $Y_l^{l-1}, Y_l^{l-2}, \cdots$ by applying $\hat{L}_-$ and by normalizing, i.e. with 1.43 where $\hat{\mathbf{J}} \to \hat{\mathbf{L}}$ and $j \to l$.

The final result, i.e. the general form for the **spherical harmonics**, is given in A.14 .

Being a **complete orthonormal basis** in the space of functions $f(\theta,\varphi)$, the Y_l^m are

Orthonormal:

$$\int\int d\varphi\, d\cos\theta\; {Y_l^m}^*(\theta,\varphi) Y_{l'}^{m'}(\theta,\varphi) = \delta_{l,l'}\delta_{m,m'}\,. \tag{1.52}$$

Notice that the integration measure $d\cos\theta = \sin\theta d\theta$ is the one appropriate for spherical coordinates: $d\Omega \equiv d\varphi\ sin\theta d\theta$.

Complete

$$\sum_{l=0}^{\infty}\sum_{m=-l}^{l} {Y_l^m}^*(\theta,\varphi) Y_l^m(\theta',\varphi') = \delta(\cos\theta - \cos\theta')\delta(\varphi-\varphi') \tag{1.53}$$

Equivalently, this means that any function $f(\theta,\varphi)$ on the unit sphere can be expanded in terms of the Y_l^m:

$$f(\theta,\varphi) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} c_l^m\ Y_l^m(\theta,\varphi) \tag{1.54}$$

The coefficient, as usual, are evaluated by scalar multiplication from left with $\langle l', m'|$:

$$c_{l'}^{m'} = \int\int d\varphi\, d\cos\theta\, Y_{l'}^{m'}(\theta,\varphi)^*\ f(\theta,\varphi) \tag{1.55}$$

Explicit calculation for $l = 0$ and $l = 1$

For simplicity, we do this without normalisation

$\boxed{l = 0:}$

For $l = 0$, we have $m = 0$, therefore

$$\hat{L}_z Y_0^0 = 0 \quad \hat{L}_\pm Y_0^0 = 0 \Rightarrow \hat{L}_{x|y} Y_0^0 = 0\,.$$

Thus since all generators of rotation (cf. 1.3) give zero, this means that $Y_0^0(\theta,\varphi)$ is invariant under rotations, i.e. it is a **constant**.

$\boxed{l = 1:}$

Wir suchen zunächst nach $Y_1^{m=+1}$, was die Gleichung

$$\frac{\hat{L}_z}{\hbar} Y_1^{m=1} = -i\frac{\partial}{\partial\varphi} Y_1^{m=1} \overset{!}{=} 1\cdot Y_1^{m=1}$$

erfüllt, also

$$Y_1^1 = e^{i\varphi} f(\theta)$$

Die Gleichung (mit A.12)

$$\frac{\hat{L}_+}{\hbar} Y_1^{m=1} = e^{i\varphi}\left(\frac{\partial}{\partial\theta} f(\theta) - 1 \cdot \frac{\cos\theta}{\sin\theta} f(\theta)\right) \overset{!}{=} 0$$

hat die Lösung

$$f(\theta) \propto \sin\theta$$

Also

$$Y_1^1 \propto e^{i\varphi} \sin\theta$$

Anwenden des Leiteroperators A.12

$$Y_1^0 \propto \hat{L}_- Y_1^1 = e^{-i\varphi} e^{i\varphi}\left(-\frac{\partial}{\partial\theta} - \frac{\cos\theta}{\sin\theta}\right) \sin\theta \propto \cos\theta$$

ein zweites Mal

$$Y_1^{-1} \propto \hat{L}_- Y_1^0 = e^{-i\varphi}(-\frac{\partial}{\partial\theta}) \cos\theta \propto e^{-i\varphi} \sin\theta$$

Die niedrigsten Kugelflächenfunktionen sind in Tab. 50 angegeben

l	m	Kugelflächenfunktion
0	0	$Y_0^0 = \frac{1}{\sqrt{4\pi}}$
1	0	$Y_1^0 = \sqrt{\frac{3}{4\pi}}\cos\theta$
	±1	$Y_1^{\pm1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\varphi}$
2	0	$Y_2^0 = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1)$
	±1	$Y_2^{\pm1} = \mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta e^{\pm i\varphi}$
	±2	$Y_2^{\pm2} = \sqrt{\frac{15}{32\pi}}\sin^2\theta e^{\pm 2i\varphi}$

Table 1.2: Die ersten Kugelflächenfunktionen.

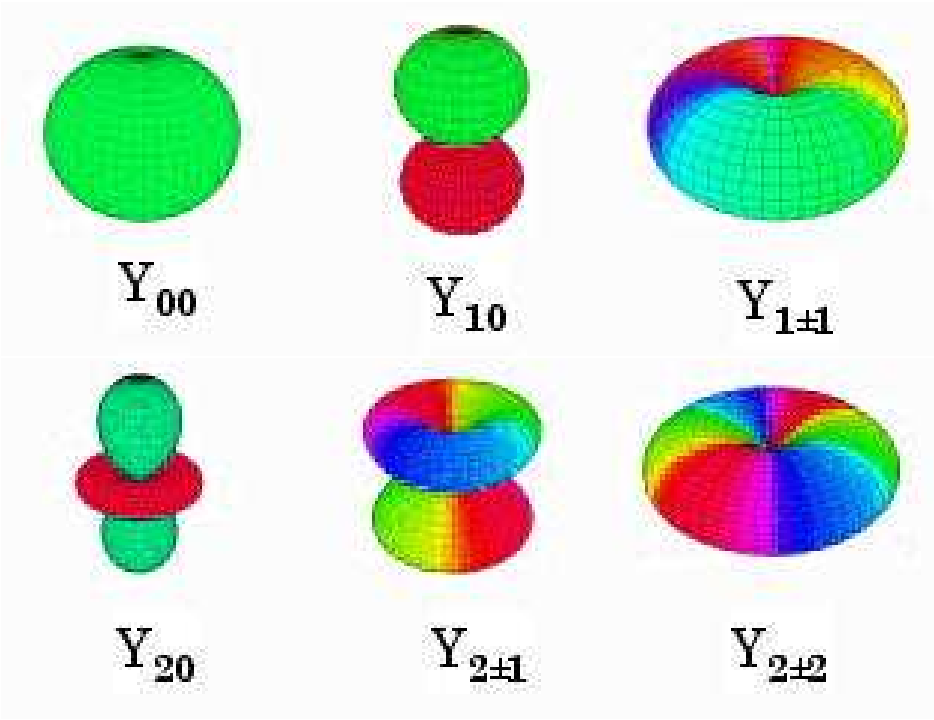

Figure 1.1: A plot of the first few spherical harmonics (50). The radius is proportional to $|Y_l^m|^2$, colors gives $\arg(Y_l^m)$, with green$=0$, red$=\pi$.

Chapter 2

Schrödinger equation in a central potential

2.1 Main results in this chapter (until Sec. 2.5)

- The Schrödinger equation for a particle in a **central potential** (i.e. rotation invariant) is written in **polar coordinates** r, θ, φ.
- Hereby one notices that the kinetic part can be splitted in a part acting only on r and one acting only on θ, φ.
- The part acting only on θ, φ is proportional to $\hat{\mathbf{L}}^2$.
- Therefore, one can look for solutions of the form $R(r)Y_l^m(\theta, \varphi)$, since the Y_l^m are eigenfunctions of $\hat{\mathbf{L}}^2$.
- After doing that one ends up with a **one-dimensional** eigenvalue equation for $R(r)$.
- Since the eigenvalue of $\hat{\mathbf{L}}^2$ does not depend on m, one has the general result that for a central potential **eigenfunctions with a given** l **have a** $2l+1$ **degeneracy**.

2.2 Radial- und Drehimpulsanteil

Der Hamiltonian für ein quantenmechanisches Teilchen im kugelsymmetrischen Potential (Zentralfeld) lautet

$$H = \frac{\hat{\mathbf{p}}^2}{2m} + V(r) \qquad . \tag{2.1}$$

Hierbei ist $r = |\mathbf{r}|$ die Norm des Ortsvektors. In der klassischen Mechanik ist der Drehimpuls l eine Erhaltungsgröße. Er ist durch die Anfangsbedingungen gegeben.

Der Term $\frac{\hat{\mathbf{p}}^2}{2m}$ wird in einem zentrifugal-Beitrag $\frac{\hat{\mathbf{L}}^2}{2mr^2}$ und einem radial-Teil $\frac{\hat{p}_r^2}{2m}$, aufgespaltet. Die Bewegungsgleichung des Teilchens reduziert sich somit auf die Radialgleichung in einem effektiven Potential

$$V_{eff}(r) = V(r) + \frac{\hat{\mathbf{L}}^2}{2mr^2} \qquad . \tag{2.2}$$

Wir werden versuchen, auch die Schrödingergleichung auf ein Radialproblem zu reduzieren. Dazu brauchen wir den Zusammenhang zwischen $\hat{\mathbf{p}}^2$ und $\hat{\mathbf{L}}^2$. Durch explizite Berechnung (details): Sec. A.10 erhalten wir

$$\hat{\mathbf{L}}^2 = \hat{\mathbf{r}}^{\,2}\hat{\mathbf{p}}^{\,2} + i\hbar\,\hat{\mathbf{r}}\cdot\hat{\mathbf{p}} - (\hat{\mathbf{r}}\cdot\hat{\mathbf{p}})^2$$

also

$$\hat{\mathbf{p}}^{\,2} = \frac{\hat{\mathbf{L}}^2 + (\hat{\mathbf{r}}\cdot\hat{\mathbf{p}})^2 - i\hbar\,(\hat{\mathbf{r}}\cdot\hat{\mathbf{p}})}{\hat{r}^{\,2}} \tag{2.3}$$

Man erkennt den Zusammenhang aus der klassischen Mechanik für $\hbar \to 0$. Der Hamiltonoperator nimmt hiermit die folgende Gestalt an

$$\hat{H} = \underbrace{\frac{(\hat{\mathbf{r}}\cdot\hat{\mathbf{p}})^2 - i\hbar\,(\hat{\mathbf{r}}\cdot\hat{\mathbf{p}})}{2m\,\hat{r}^2}}_{\hat{\hat{T}}} + V(r) + \frac{\hat{\mathbf{L}}^2}{2m\,\hat{r}^2} \tag{2.4}$$

Man erkennt bereits, dass $\hat{\hat{T}}$ nur die Komponente von $\mathbf{p}$ entlang $\mathbf{r}$ enthält.
Der Übergang in die Ortsdarstellung, mit der Zuordnung $\hat{\mathbf{r}} \to \mathbf{r}$ und $\hat{\mathbf{p}} \to -i\hbar\boldsymbol{\nabla}$, liefert aus 2.4

$$-\frac{2m}{\hbar^2}\hat{\hat{T}} \to \frac{\Big((\mathbf{r}\cdot\boldsymbol{\nabla})^2 + (\mathbf{r}\cdot\boldsymbol{\nabla})\Big)}{r^2}$$

In Kugelkoordinaten $\mathbf{r} = r\,\mathbf{e}_r$ und daher benötigen wir von $\boldsymbol{\nabla}$ nur die Komponente entlang $\mathbf{r}$:

$$\mathbf{r}\cdot\boldsymbol{\nabla} = r\frac{\partial}{\partial r}$$

also

$$\begin{aligned} -\frac{2m}{\hbar^2}\hat{\hat{T}} &\to \frac{1}{r^2}\Big(r\frac{\partial}{\partial r}r\frac{\partial}{\partial r}\Big) + \frac{1}{r^2}r\frac{\partial}{\partial r} = \frac{1}{r}\Big(\frac{\partial}{\partial r}r\frac{\partial}{\partial r} + \frac{\partial}{\partial r}\Big) \\ &= \frac{1}{r}\Big(\frac{\partial^2}{\partial\, r^2}r\Big) \end{aligned} \tag{2.5}$$

As expected, 2.5 is the radial part of the Laplace operator,[1] while $-\frac{\hat{\mathbf{L}}^2}{r^2\,\hbar^2}$ (cf. 2.4) its angular part.
Der Hamiltonoperator ist somit

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m}\frac{1}{r}\frac{\partial^2}{\partial r^2}r + V(r)}_{\hat{A}(r)} + \frac{1}{2m}\frac{\hat{\mathbf{L}}^2}{r^2} \qquad .$$

Man kann auch hier den letzten Term als Zentrifugalbeitrag erkennen (cf. 2.2).

2.3 Produktansatz für die Schrödingergleichung

Die Schrödingergleichung

$$\left(\hat{A}(r) + \frac{1}{2m}\frac{\hat{\mathbf{L}}^2}{r^2}\right)\psi(r,\theta,\varphi) = E\psi(r,\theta,\varphi)$$

kann durch einen Produktansatz $\psi(r,\theta,\varphi) = R(r)\cdot Y(\theta,\varphi)$ weiter vereinfacht werden. Nach Multiplikation mit r^2 wird diese zu

$$R(r)\frac{\hat{\mathbf{L}}^2}{2m}Y(\theta,\varphi) = Y(\theta,\varphi)r^2(E-\hat{A}(r))R(r)$$

da L^2 nur auf θ,φ und $\hat{A}(r)$ nur auf r wirkt. Nach Multiplikation mit $(R(r)\cdot Y(\theta,\varphi))^{-1}$ von links erhält man

$$\frac{1}{Y(\theta,\varphi)}\frac{\hat{\mathbf{L}}^2}{2m}Y(\theta,\varphi) \quad = \quad \frac{1}{R(r)}\left(r^2(E-\hat{A}(r))R(r)\right) = \kappa \qquad .$$

Da die linke Seite nur θ und φ, die rechte Seite hingegen nur r enthält, muß κ eine Konstante sein und wir erhalten zwei in Winkel- und Radialanteil getrennte Differentialgleichungen

$$\frac{\hat{\mathbf{L}}^2}{2m}Y_l^m(\theta,\varphi) \quad = \quad \kappa Y_l^m(\theta,\varphi) \tag{2.6}$$

$$(\hat{A}(r) + \frac{\kappa}{r^2})R(r) \quad = \quad ER(r) \tag{2.7}$$

2.6 ist die bereits gelöste Eigenwertgleichung des Drehimpulsoperators, deren Eigenwerte den Parameter $\kappa = \frac{\hbar^2}{2m}l(l+1)$ mit der Drehimpulsquantenzahl in Verbindung bringen.

---

[1] This result is only valid provided the wave function is non singular for $r \to 0$. Consider for example, the case $\psi \propto 1/r$. In that case $\hat{T}^2\psi \propto \nabla^2\psi \propto \delta(\mathbf{r})$.

Einsetzen in die Radialgleichung 2.7 ergibt

$$-\frac{\hbar^2}{2m}\frac{1}{r}\frac{d^2}{dr^2}(r\,R(r))+\left(V(r)+\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right)R(r)=ER(r)$$

Multiplikation von links mit r und Verwendung der Abkürzung $\chi(r) := r\,R(r)$ liefert schließlich die

SCHRÖDINGERGLEICHUNG FÜR DEN
RADIALANTEIL DER WELLENFUNKTION

$$-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}\chi(r)+\underbrace{\left(V(r)+\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right)}_{V_{eff}(r)}\chi(r)=E\,\chi(r) \qquad . \tag{2.8}$$

Die Lösung dieser Differentialgleichung hängt vom jeweiligen Potential $V(r)$ ab und muß je nach Problem neu gelöst werden. Die gesamte Wellenfunktion ψ ist dann

$$\psi_{lm}(r,\theta,\varphi)=\frac{1}{r}\chi(r)\cdot Y_l^m(\theta,\varphi) \qquad , \tag{2.9}$$

wobei nur die Quantenzahlen des Drehimpulses explizit angegeben wurden. Die Quantenzahlen, die sich aus dem Radialanteil ergeben, werden später eingeführt. Allgemein können wir bereits erkennen, daß die Energien, wegen der Rotationsinvarianz in m, $(2l+1)$-fach entartet sind .

2.4 Entartung bei unterschiedlichen m

Die Entartung der Zuständen mit unterschiedlichen m bei festem l ist eine direkte Folgerung der Rotationsinvarianz. Diese gilt also allgemein für Systeme, in der der Hamiltonian H mit allen Komponenten des Drehimpulsoperators $\hat{\mathbf{J}}$ (Erinnerung, hier $\hat{\mathbf{J}}=\hat{\mathbf{L}}$) vertauscht. Das kann folgendermaßen gezeigt werden:
Wir haben bereits gezeigt, dass $\hat{\mathbf{J}}^2$ und $\hat{J}_z$ zusammen mit dem Hamiltonian diagonalisiert werden können. Die gemeinsame Eigenzustände von $H,\hat{\mathbf{J}}^2,\hat{J}_z$ können

also dargestellt werden als

$$|n, j, m\rangle$$

wo n eine zusätzliche Quantenzahl ist. Die Eigenwertgleichung lautet

$$\hat{H}\,|n, j, m\rangle = E_{n,j,m}\,|n, j, m\rangle \ . \tag{2.10}$$

wendet man auf beiden Seiten den Leiteroperator $\hat{J}_-$ an, und betrachtet man die Tatsache, dass $[\hat{H}, \hat{J}_-] = 0$, erhält man

$$\hat{H}\hat{J}_-\,|n, j, m\rangle = E_{n,j,m}\hat{J}_-\,|n, j, m\rangle \ .$$

mit 1.43

$$\hat{J}_-\,|n, j, m\rangle = \text{const.}\ |n, j, m-1\rangle$$

erhält man

$$\hat{H}\,|n, j, m-1\rangle = E_{n,j,m}\,|n, j, m-1\rangle \ .$$

also, verglichen mit 2.10 haben wir

$$E_{n,j,m-1} = E_{n,j,m} \equiv E_{n,j}$$

unabhängig von m, wie gesagt.

2.5 Wasserstoff und H-ähnliche Probleme

2.5.1 Summary

- For the **Hydrogen Atom**, one has a Coulomb potential $V \propto -1/r$.
- We look for **bound states**, i.e. states with $E < 0$. The solution of the corresponding equation for $R(r)$ is obtained in two steps.
- First one looks for the asymptotic solution at $r \to \infty$. Here the requirement is that $R(r)$ vanishes exponentially.
- For the short-r part one makes a polynomial Ansatz. Inserting into the Schrödinger equation, one obtains a recursive equation for the coefficient of the polynomial.
- The requirement that the recursive equation stops at some point (i.e. the polynomial has finite order), leads to the **eigenvalue condition** for the energy.
- For the case that the recursive equation does not stop the sequence leads to an **exponential behavior** of the wave function, which is not allowed.

Das Wasserstoffatom **H** und seine Isotopen $^2\mathbf{H} = \mathbf{D}$ und $^3\mathbf{H} = \mathbf{T}$, sowie die Ionen $\mathbf{He}^+$,$\mathbf{Li}^{2+}$,$\mathbf{Be}^{3+}$ sind die einfachsten atomaren Systeme.

Ihre Kernladung ist ein ganzzahliges Vielfaches der Elementarladung und die Elektronenhülle besteht ausschließlich aus einem Elektron.

Ohne äußere Kräfte wirkt nur die Coulombwechselwirkung zwischen Kern und Elektron.

2.5.2 Center of mass coordinates

This is a two-body-problem. However, as in classical mechanics one can introduce center of mass coordinates $\mathbf{R} \equiv m_1\mathbf{r}_1 + m_2\mathbf{r}_2$, $\mathbf{P} = \mathbf{p}_1 + \mathbf{p}_2$ $(1,2$ indicate the two particles), and relative coordinates $\mathbf{r} \equiv \mathbf{r}_1 - \mathbf{r}_2$, $\mathbf{p} = m_{red}(\frac{\mathbf{p}_1}{m_1} - \frac{\mathbf{p}_2}{m_2})$, where $m_{red} \equiv (\frac{1}{m_1} + \frac{1}{m_2})^{-1}$ is the reduced mass. This is a canonical transformation, so it is easy to show that the correct commutation rules for the new variables hold. The advantage is that now the Hamiltonian separates

$$H = \frac{\mathbf{P}^2}{2(m_1+m_2)} + \frac{\mathbf{p}^2}{2m_{red}} + V(r)$$

and one can solve separately for the center of mas motion, which is free, and the relative motion, which describes a **single body** with mass m_{red} in the potential $V(r)$.
In the case of Hydrogen, since the nucleus is much heavier than the electron, m_{red} is essentially given by the electron mass. In the following , for simplicity, we will use the electron mass m instead of m_{red}. We will also leave out the center of mass part of the Hamiltonian, which is trivial. Results for two particles with similar masses, such as for example positronium, are easily recovered by replacing m with m_{red}.

2.5.3 Eigenvalue equation

Wir verwenden folgende Abkürzungen

m = Masse des Elektrons
+Ze = Ladung des Kerns
-e = Ladung des Elektrons

Die potentielle Energie (Coulombenergie) des Systems ist in Gaußschen Einheiten[2] gegeben durch

$$V(r) = -\frac{Ze^2}{r}$$

Die Schrödingergleichung wird dann zu

$$\hat{H}\psi(\mathbf{r}) = (-\frac{\hbar^2}{2m}\nabla^2 + V(r))\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

Aus 2.9 wissen wir bereits, daß

$$\psi(\mathbf{r}) = \psi(r,\theta,\varphi) = \frac{\chi(r)}{r}\cdot Y_l^m(\theta,\varphi) \qquad ,$$

wobei $\chi(r)$ der Radialanteil der Schrödingergleichung ist, dessen Quantenzahlen noch nicht spezifiziert sind.

$$-\frac{\hbar^2}{2m}\frac{d^2}{dr^2}\chi(r) + (-\frac{Ze^2}{r} + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2})\chi(r) = E\chi(r)$$

$$\chi''(r) + (\underbrace{\frac{Ze^2 2m}{\hbar^2}}_{=:\frac{2Z}{a_0}}\frac{1}{r} - \frac{l(l+1)}{r^2} + \frac{2mE}{\hbar^2})\chi(r) = 0 \qquad . \tag{2.11}$$

In dieser Gleichung tritt eine charakteristische Länge atomarer Systeme auf, der sogenannte Bohrsche Radius.

$$a_0 = \frac{\hbar^2}{me^2} = 0.529\mathring{A} \qquad . \tag{2.12}$$

Für $r \to \infty$ vereinfacht sich 2.11 zu

$$\chi''(r) = -\frac{2mE}{\hbar^2}\chi(r) \qquad .$$

Wir untersuchen hier gebundene Zustände, das sind solche mit negativer Energie. Wenn die Energie negativ ist, wird $E - V(r)$ für $r \to \infty$ negativ und die Schrödingergleichung führt zu einem exponentiellen Abfall der Wellenfunktion.

---

[2] Für mikroskopische Phänomene sind Gaußsche Einheiten bequemer als die SI-Einheiten, da viele Vorfaktoren einfacher werden.

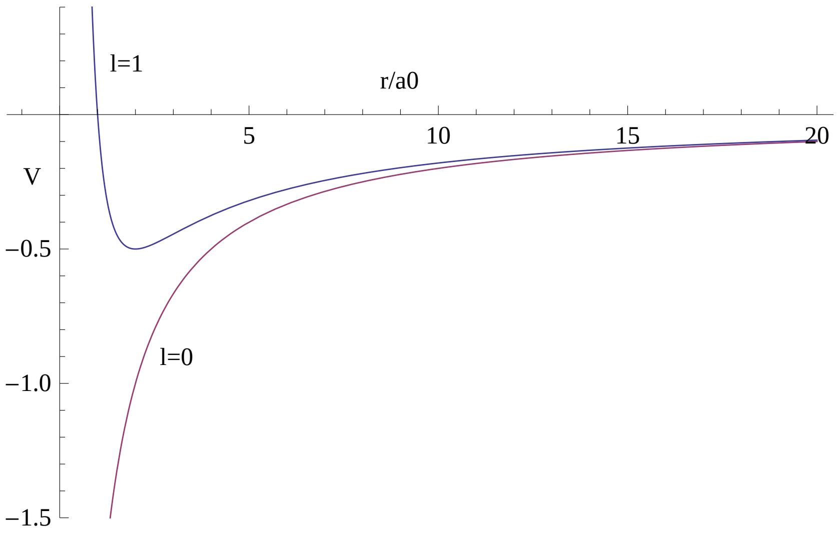

Figure 2.1: Effective Coulomb-Potential $V_{eff}(r)$ in atomic units for $l = 0$ and $l = 1$

Neben den gebundenen Zuständen gibt es noch Streuzustände mit positiver Energie. Für $r \to \infty$ lautet die Differentialgleichung 2.11 somit

$$\chi^{''}(r) \;=\; -\frac{2mE}{\hbar^2}\chi(r) \;=\; \gamma^2\,\chi(r) \qquad .$$

Die Lösung dieser Differentialgleichung ist bekanntlich

$$\chi(r) \;=\; ae^{-\gamma r} + be^{+\gamma r} \qquad .$$

Der zweite Summand ist nicht normierbar. Er beschreibt also keinen gebundenen Zustand und wir setzen deshalb aus physikalischen Gründen $b = 0$.

Für beliebige r machen wir den Ansatz

$$\chi(r) \;=\; F(r)e^{-\gamma r} \tag{2.13}$$

und setzen ihn in 2.11 ein. Zusammen mit

$$\frac{d^2}{dr^2}\chi(r) = e^{-\gamma r}(F^{''}(r) - 2\gamma F^{'}(r) + \gamma^2 F(r))$$

erhalten wir

$$e^{-\gamma r}\left(F^{''}(r) - 2\gamma\,F^{'}(r) + \gamma^2 F(r) + (\frac{2Z}{a_0}\frac{1}{r} - \frac{l(l+1)}{r^2} - \gamma^2)F(r)\right) = 0$$

$$F^{''}(r) - 2\gamma\,F^{'}(r) + (\frac{2Z}{a_0}r - l(l+1))\frac{1}{r^2}F(r) = 0 \tag{2.14}$$

Die Lösung der Differentialgleichung läßt sich als eine Potenzreihe ansetzen

$$\begin{aligned} F(r) &= r^{\sigma} \sum_{\mu=0}^{\infty} c_{\mu} r^{\mu} \\ &= \sum_{\mu=0}^{\infty} c_{\mu} r^{\mu+\sigma} \end{aligned} \tag{2.15}$$

Einsetzen von 2.15 in die Differentialgleichung 2.14 ergibt

$$\begin{aligned} &\sum_{\mu=0}^{\infty} c_{\mu}(\mu+\sigma)(\mu+\sigma-1) r^{\mu+\sigma-2} - 2\gamma \sum_{\mu=0}^{\infty} c_{\mu}(\mu+\sigma) r^{\mu+\sigma-1} \\ &\qquad + \frac{2Z}{a_0} \sum_{\mu=0}^{\infty} c_{\mu} r^{\mu+\sigma-1} - l(l+1) \sum_{\mu=0}^{\infty} c_{\mu} r^{\mu+\sigma-2} = 0 \qquad . \end{aligned}$$

Wir fassen Terme gleicher Potenz in r zusammen

$$\begin{aligned} &c_0(\sigma(\sigma-1) - l(l+1)) r^{\sigma-2} + \\ &\quad + \sum_{\mu=0}^{\infty} \Big\{ c_{\mu+1}(\mu+1+\sigma)(\mu+\sigma) - 2\gamma c_{\mu}(\mu+\sigma) + \\ &\quad + \frac{2Z}{a_0} c_{\mu} - l(l+1) c_{\mu+1} \Big\} r^{\mu+\sigma-1} = 0 \end{aligned} \tag{2.16}$$

Die Koeffizienten der Potenzen r^l müssen individuell verschwinden, da die Gleichung für beliebige Werte von r gelten muß und die $\{r^l\}$ ein vollständiges, linear unabhängiges Basissystem bilden. Zunächst folgt aus der Bedingung $c_0 \neq 0$ für σ die Bedingung

$$\sigma(\sigma-1) = l(l+1) \qquad . \tag{2.17}$$

Das ergibt (the second solution must be discarded, see: Sec. A.11)

$$\sigma = l + 1 \; . \tag{2.18}$$

Einsetzen in 2.16 liefert die Bestimmungsgleichungen der Koeffizienten c_{μ}. Für alle $\mu \geq 0$ gilt

$$\frac{c_{\mu+1}}{c_{\mu}} = \frac{2\gamma(\mu+l+1) - 2\frac{Z}{a_0}}{(\mu+l+2)(\mu+l+1) - l(l+1)} \qquad . \tag{2.19}$$

Das Verhalten für $\mu \gg 1$ ist

$$\frac{c_{\mu+1}}{c_{\mu}} \underset{\mu \gg 1}{\longrightarrow} \frac{2\gamma}{\mu+1} \qquad .$$

Das heisst, der Beitrag aus großen μ liefert

$$\sum_{\mu}^{\infty} \frac{(2\gamma)^{\mu}}{\mu!} r^{\mu} \sim e^{2\gamma r} \tag{2.20}$$

Da die hohen Potenzen $\mu \gg 1$ das Verhalten der Funktion für große r bestimmen, verhält sich χ für große r wie

$$\chi(r) = F(r)\, e^{-\gamma r} = r^{l+1}\, e^{2\gamma r} \cdot e^{-\gamma r} \quad = \quad r^{l+1}\, e^{\gamma \cdot r} \qquad .$$

Wenn die Potenzreihe nicht abbricht, divergiert $\chi(r)$ für $r \to \infty$ und beschreibt wieder keinen normierbaren, gebundenen Zustand. Wir müssen also erreichen, daß die Reihe abbricht. Es kann in der Tat erreicht werden, daß ein Koeffizient c_{μ^*+1} in 2.19 , und somit alle nachfolgenden, verschwinden. Das ist genau dann der Fall, wenn

$$\gamma = \frac{\frac{2Z}{a_0}}{2(\mu^* + l + 1)} = \frac{Z}{a_0\ (\mu^* + l + 1)} \quad ; \quad \mu^* \in \mathbb{N}_0 \qquad . \tag{2.21}$$

Für die Energie bedeutet das

$$E \quad = \quad -\frac{\hbar^2}{2m}\gamma^2 \quad = \quad -\frac{\hbar^2}{2m} \frac{\frac{Z^2}{a_0^2}}{(\mu^* + l + 1)^2} = -\frac{\hbar^2}{2m}\left(\frac{m^2 e^4}{\hbar^4}\right) \frac{Z^2}{(\mu^* + \mathbf{l} + \mathbf{1})^2} \qquad .$$

Die Energie ist also quantisiert. Es ist üblich eine modifizierte Quantenzahl

$$n = \mu^* + l + 1 \tag{2.22}$$

anstelle von μ^* einzuführen. Aus $\mu^* \geq 0$ und $l \geq 0$ folgt $n \geq 1$ und die erlaubten Energien der gebundenen Zustände sind

$$\boxed{\begin{aligned} E_n \quad &= \quad -\frac{me^4}{2\hbar^2}\frac{Z^2}{n^2} \qquad n = 1, 2, 3, \ldots \\ E_n \quad &= \quad -\mathrm{Ry}\frac{Z^2}{n^2} \qquad . \end{aligned}} \tag{2.23}$$

Die natürliche Einheit der Energie ist das

RYDBERG

$$1Ry = \frac{me^4}{2\hbar^2} \qquad . \tag{2.24}$$

Wegen $\mu^* + l + 1 = n$ sind bei gegebener Hauptquantenzahl n nur Drehimpulsquantenzahlen $l < n$ erlaubt.

Symbol	Name	erlaubte Werte
n	Hauptquantenzahl	$n = 1, 2, 3, \dots$
l	Drehimpulsquantenzahl	$l = 0, 1, 2, \dots, n-1$
m	magnetische Quantenzahl	$m = \{-l, -l+1, \dots, +l-1, l\}$ $2l+1$ mögliche Werte

Table 2.1: *Quantenzahlen des H-Atoms mit Wertebereichen.*

2.5.4 Entartung

Wir haben schon gesehen (Sec. 2.4), dass für ein rotationsinvariantes Hamiltonian, die Energie nicht von der Quantenzahl m abhängig ist.
Im Fall vom Wasserstoffatom hängt aber die Energie E_n nur von der Hauptquantenzahl n, also auch nicht von l ab. Zu festem n, also für eine gegebene Energie, kann die Drehimpulsquantenzahl die Werte $l = 0, 1, \dots, n-1$ annehmen. Zu jedem l wiederum sind $2l+1$ Werte für die magnetische Quantenzahl möglich. Die Anzahl der entarteten Zustände ist somit

$$\begin{aligned}
\text{Entartung} &= \sum_{l=0}^{n-1} (2l+1) \\
&= 2\sum_{l=0}^{n-1} l + n \\
&= 2\frac{n(n-1)}{2} + n = n^2
\end{aligned}$$

Die Entartung ist also n^2.

- Die Drehimpulserhaltung erklärt nur die $(2l+1)$-fache Entartung der magnetischen Q.Z.
- Die höhere Entartung bedeutet, daß es hier eine weitere Erhaltungsgröße, nämlich den Runge-Lenz Vektor gibt. Er ist klassisch definiert als

  $$\mathbf{N} = \mathbf{p} \times \mathbf{L} - e^2 Zm\, \mathbf{e_r}$$

  Quantenmechanisch

  $$\hat{\mathbf{N}} = \frac{1}{2}(\hat{\mathbf{p}} \times \hat{\mathbf{L}} + \hat{\mathbf{L}} \times \hat{\mathbf{p}}) - e^2 Zm\mathbf{e_r}$$

  Dieser Vektor ist nur im $\frac{1}{r}$-Potential eine Erhaltungsgröße. Man spricht daher auch von zufälliger Entartung.

2.5.5 Energieschema des H-Atoms (Z=1)

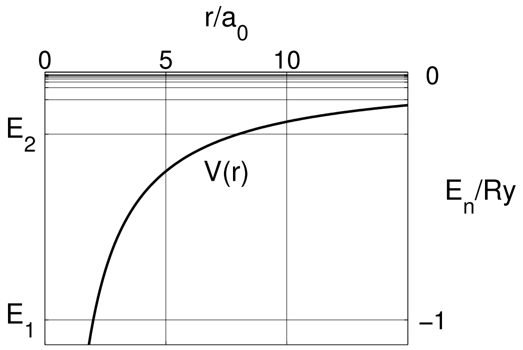

Figure 2.2: *Energieniveaus des H-Atoms in Ry und Coulombpotential (durchgezogene Kurve).*

Das H-Atom definiert charakteristische Werte für Energie und Länge

$$1\ \text{Ry} = \frac{me^4}{2\hbar^2} = 13.6\ \text{eV}$$
$$a_0 = \frac{\hbar^2}{me^2} = 0.529\mathring{A} \quad .$$

2.5.6 Lichtemission

Nach den Gesetzen der klassischen Elektrodynamik strahlt beschleunigte Ladung Energie ab. Das hieße, daß das Elektron, das klassisch auf einer Ellipsenbahn um den Kern kreist, permanent Energie abstrahlen würde. Es müßte dadurch spiralförmig in den Kern stürzen. Das steht natürlich im Widerspruch zur Beobachtung stabiler Atome.

Zudem erwartet man klassisch ein kontinuierliches Emissionsspektrum. Man findet aber experimentell isolierte Spektrallinien. Quantenmechanisch sind im Atom nur die Energien E_n erlaubt. Wenn ein Elektron einen Übergang $E_{n_i} \to E_{n_f}$ (initial $\to$ final) macht, wird die freiwerdende Energie $E_{n_i} - E_{n_f}$ in Form eines Photons mit der Energie

$$\hbar\omega = -\mathrm{Ry}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) = \left(\frac{n_i^2 - n_f^2}{n_i^2 n_f^2}\right)\mathrm{Ry}$$

emittiert. Experimentell wurden anfänglich drei Typen von Übergängen beobachtet, die Lyman, Balmer und Paschen Serien

Zur Erinnerung

$$\begin{aligned} E &= h\cdot\nu = \frac{h\cdot c}{\lambda} \\ \Rightarrow \quad \lambda &= \frac{h\cdot c}{E} \\ \mathbf{h\cdot c} &= \mathbf{1.2\cdot 10^{-6} \quad eV\cdot m} \end{aligned}$$

Lyman Serie $(n_f = 1)$:

$$\begin{aligned} \lambda &= \frac{h\cdot c}{\mathrm{Ry}}\left(\frac{n^2}{n^2-1}\right) \qquad n = 2,3,\ldots \\ \lambda &= (9\ldots 12)\cdot 10^{-8}\ \mathrm{m} \\ \mathrm{UV} &: \ (1\ldots 40)\cdot 10^{-8}\ \mathrm{m} \end{aligned}$$

Balmer Serie $(n_f = 2)$:

$$\begin{aligned} \lambda &= \frac{h\cdot c}{\mathrm{Ry}}\left(\frac{n^2\cdot 4}{n^2-4}\right) \qquad n = 3,4,\ldots \\ \lambda &= (3.6\ldots 6.6)\cdot 10^{-7}\ \mathrm{m} \\ \text{Sichtbar} &: \ (4\ldots 8)\cdot 10^{-7}\ \mathrm{m} \end{aligned}$$

Paschen Serie ($n_f = 3$) :

$$\begin{array}{rcl} \lambda & = & \frac{h \cdot c}{\mathrm{Ry}}(\frac{n^2 \cdot 9}{n^2 - 9}) \qquad n = 4, 5, \ldots \\ \lambda & = & (0.8 \ldots 1.9) \cdot 10^{-6}\ \mathrm{m} \\ \text{Infrarot} & = & (1 \ldots 100) \cdot 10^{-6}\ \mathrm{m} \end{array}$$

Isotopeneffekt

Für Wasserstoff bzw Deuterium gilt

$$\begin{array}{lcl} \mathrm{H} & : & M{=}M_p \\ \mathrm{D} & : & M \approx 2M_p \end{array} \quad ,$$

wo M die Masses des Kernes ist. Da das Massenverhältnis

$$\frac{m_e}{M_p} = \frac{1}{1836}$$

sehr klein ist, kann man die effektive Masse m_{red} schreiben als

$$m_{red} \approx m(1 - \frac{m}{M})$$

Die Berücksichtigung der Kernbewegung führt also nur zu geringen Modifikationen der Energie 2.23

$$\begin{array}{rcl} E & = & \frac{m_e \cdot e^2}{2\hbar \cdot n^2}(1 - \frac{m_e}{M}) \\ & = & \frac{\mathrm{Ry}}{n^2}(1 - \frac{m_e}{M}) \\ \Rightarrow & & \\ \Delta E_n & \equiv & E_n^D - E_n^H = \frac{\mathrm{Ry}}{n^2}(\frac{m_e}{M_p} - \frac{m_e}{2M_p}) \\ & = & \frac{\mathrm{Ry}}{n^2} \cdot \underbrace{\frac{m_e}{2M_p}}_{2{,}7 \cdot 10^{-4}} \\ \Rightarrow \left|\frac{\Delta\lambda}{\lambda}\right| & = & 2{,}7 \cdot 10^{-4} \Rightarrow |\Delta\lambda| = O(1\ \overset{\circ}{A}) \qquad . \end{array}$$

Weitere Korrekturen zum Wasserstoffspektrum rühren von relativistischen Effekten her. Diese Korrekturen sind von der Ordnung O(0.1 $\overset{\circ}{A}$). Weitere Details sind Inhalt der Atom- und Molekülphysik.

2.5.7 Wasserstoff-Wellenfunktion

Aus 2.22 hat der letzte nicht verschwindende Term in der Reihe (2.15) den Index $\mu^* = n - l - 1$. Die Reihe lautet somit

$$F(r) = r^{l+1} \sum_{\mu=0}^{n-l-1} c_\mu \, r^\mu \qquad . \tag{2.25}$$

Die Funktion $F(r)$ ist somit ein Polynom n-ten Grades.
Die Wasserstoff-Wellenfunktion lautet

$$\Psi_{nlm}(\mathbf{r}) = \frac{\chi_{nl}(r)}{r} \, Y_l^m(\theta, \varphi) \qquad .$$

Wir fassen nun die Ergebnisse für den Radialteil der Wellenfunktion zusammen, wobei wir nun alle Quantenzahlen explizit berücksichtigen (cf. 2.15 , 2.18)

$$R_{nl}(r) = \frac{\chi_{nl}(r)}{r} = e^{-\gamma r} \, r^l \sum_{\mu=0}^{n-l-1} c_\mu \, r^\mu \tag{2.26}$$

$$\gamma = \frac{Z}{n a_0} \qquad . \tag{2.27}$$

Eine detailiertere Rechnung (details in: Sec. A.12) führt zum

Ortsanteil der Wasserstoff-Wellenfunktionen

$$\begin{aligned}
\frac{\chi_{nl}(r)}{r} &= (2\gamma)^{3/2} \left(\frac{(n-l-1)!}{2n(n+l)!} \right)^{1/2} (2\gamma r)^l \, e^{-\gamma r} \, L_{n-l-1}^{2l+1}(2\gamma r) \\
\frac{\chi_{nl}(r)}{r} &= (2\gamma)^{3/2} \left(\frac{(n+l)!}{2n(n-l-1)!} \right)^{1/2} \frac{1}{(2l+1)!} \, (2\gamma r)^l \, e^{-\gamma r} \\
&* \quad {}_1\mathrm{F}_1(l+1-n, 2l+2; 2\gamma r) \qquad .
\end{aligned} \tag{2.28}$$

Normierung

Die Normierung der Wellenfunktion ist so gewählt, daß

$$\int_0^\infty R_{nl}(r)^2 r^2 dr = \int_0^\infty \left(\frac{\chi_{nl}(r)}{r} \right)^2 r^2 dr = 1 \qquad . \tag{2.29}$$

Der Faktor r^2 stammt vom Volumenelement $d^3r = r^2 dr d\Omega$ und stellt sicher, daß die Wellenfunktionen zusammen mit dem Winkelanteil (cf. 1.52) orthonormal sind:

$$\int |\Psi_{nlm}(r, \theta, \varphi)|^2 \, r^2 dr \, d\cos\theta \, d\varphi = 1$$

Spezialfälle

Interessant im Vergleich mit der Bohr-Sommerfeld-Theorie ist der **Fall mit maximalem Drehimpuls** $l = n - 1$ (siehe 2.26). In diesem Fall ist ${}_1\mathrm{F}_1(0, 2n; r) = 1$ und der Radialanteil der Wellenfunktion vereinfacht sich zu

$$\frac{\chi_{n,n-1}(r)}{r} = (2\gamma)^{3/2} \left(\frac{1}{2n(2n-1)!} \right)^{1/2} (2\gamma r)^{n-1} \, e^{-\gamma r} \qquad .$$

Die radiale Wahrscheinlichkeitsdichte ist

$$p(r) = |\chi_{n,n-1}(r)|^2 \propto (2\gamma r)^{2n} e^{-2\gamma r} = e^{-2\gamma r + (2n)\ln(2\gamma r)} \qquad .$$

Sie hat das Maximum bei $r = \frac{n}{\gamma} = n^2 a_0$. Diese Werte stimmen mit denen der Bohr-Sommerfeld-Theorie überein. Diese Übereinstimmung sollte aber nicht überbewertet werden, da die Elektronen nicht auf klassischen stationären Bahnen umlaufen.

Mit der Wellenfunktion Ψ_{nlm} können folgende, oft benötigten Erwartungswerte berechnet werden

$$\langle r \rangle = \frac{a_0}{2Z} \Big(3n^2 - l(l+1) \Big) \tag{2.30a}$$

$$\langle r^2 \rangle = \frac{a_0^2 n^2}{2Z^2} \Big(5n^2 + 1 - 3l(l+1) \Big) \tag{2.30b}$$

$$\langle \frac{1}{r} \rangle = \frac{Z}{n^2 a_0} \qquad . \tag{2.30c}$$

Für spätere Rechnungen benötigen wir die Grundzustandswellenfunktion, i.e. $n = 1, l = m = 0$.

GRUNDZUSTANDSWELLENFUNKTION DES H-ÄHNLICHEN ATOMS

$$\psi_{100}(r, \theta, \varphi) = \left(\frac{Z^3}{a_0^3 \, \pi} \right)^{1/2} e^{-Zr/a_0} \qquad . \tag{2.31}$$

The first few radial wave functions R_{nl} (normalized according to 2.29) are

$$
\begin{aligned}
R_{10}(r) &= 2\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-Zr/a_0} && (2.32)\\
R_{20}(r) &= 2\left(\frac{Z}{2a_0}\right)^{\frac{3}{2}} \left(1-\frac{Zr}{2a_0}\right) e^{-Zr/(2a_0)}\\
R_{21}(r) &= \frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{\frac{3}{2}} \frac{Zr}{a_0} e^{-Zr/(2a_0)}
\end{aligned}
$$

Chapter 3

Time dependent perturbation theory

3.1 Zeitabhängige (Diracsche) Störungstheorie

Häufig interessiert man sich für zeitabhängige Hamilton-Operatoren. Z.B. könnte man daran interessiert sein, was mit einem Atom passiert, wenn man elektromagnetische Wellen einstrahlt. Man kann versuchen, die zeitabhängige Schrödingergleichung analytisch exakt zu lösen. Das gelingt allerdings nur in den seltensten Fällen. Der Ausweg sind entweder numerische Verfahren, die in den letzten Jahren rasant an Leistungsfähigkeit und Bedeutung zugenommen haben. Alternativ hat man die Möglichkeit, das Problem perturbativ zu lösen. Wir gehen davon aus, daß der Hamilton-Operator $H = H_0 + H_1(t)$ aus einem zeitunabhängigen Teil H_0 und einer zeitabhängigen Störung $H_1(t)$ besteht. Für das Folgende gehen wir davon aus, daß das Eigenwertproblem von H_0

$$H_0|\Phi_n\rangle = \varepsilon_n|\Phi_n\rangle$$

gelöst ist. In der Praxis benutzt man die Lösung des zeitabhängigen Problems, um experimentell Rückschlüsse auf das Eigenwertspektrum von H_0 zu gewinnen.

Z.B. kann man einen klassischen Oszillator von außen mit einer periodischen Kraft mit einer Frequenz ω anregen. Wenn wir ω kontinuierlich variieren, wird die Amplitude der erzwungenen Schwingung bei der Eigenfrequenz des ungestörten Oszillators maximal sein. Wir können also auf diese Weise auf die Eigenfrequenz (bzw. Federkraft) und die Reibungskräfte rückschließen. In Quantensystemen ist diese Vorgehensweise die einzig mögliche, das mikroskopische System zu untersuchen. In diesem Zusammenhang hat man allerdings die Stärke des Störterms H_1 unter Kontrolle und kann erreichen, daß „ $H_1 \ll H_0$" Die Aufteilung der Dynamik in Anteile, die von H_0 und solche, die von H_1 herrühren, führt zur Einführung des Wechselwirkungsbildes.

3.1.1 Das Wechselwirkungsbild

Die Zeitentwicklung eines Zustandes nach dem Gesamthamiltonian $H = H_0 + H_1(t)$ wird durch die zeitabhängige Schrödingergleichung bestimmt:

$$i\hbar\frac{d}{dt}|\Psi^S(t)\rangle = \Big(H_0 + H_1(t)\Big)|\Psi^S(t)\rangle\ . \tag{3.1}$$

der superscript “S” steht für “Schrödinger Bild”.
Die Zeitentwicklung eines beliebigen Anfangszustands $|\Phi\rangle$ im zeitunabhängigen ungestörten System lautet bekanntlich

$$|\Phi(t)\rangle = e^{-\frac{i}{\hbar}H_0 t}|\Phi(t=0)\rangle \qquad .$$

Es ist sinnvoll, den “einfachen” Teil der Dynamik, beschrieben durch H_0, explizit im wechselwirkenden Zustandsvektor $|\Psi\rangle$ zu eliminieren durch Einführung des **Wechselwirkungsbildes (Interaction representation)**. Der Zustand im Wechselwirkungsbild wird mit dem index “I” (interaction) bezeichnet.

$$|\Psi^I(t)\rangle =: e^{\frac{i}{\hbar}H_0 t}|\Psi^S(t)\rangle\ . \tag{3.2}$$

Die Zeitableitung von 3.2 liefert

$$i\hbar\,\frac{d}{dt}|\Psi^I(t)\rangle = -H_0\ e^{\frac{i}{\hbar}H_0 t}\ \Big|\Psi^S(t)\Big\rangle + e^{\frac{i}{\hbar}H_0 t}\ i\hbar\ \frac{d}{dt}\Big|\Psi^S(t)\Big\rangle \tag{3.3}$$

wir benutzen 3.1 und erhalten

$$\begin{aligned} i\hbar\frac{d}{dt}|\Psi^I(t)\rangle &= -H_0 e^{\frac{i}{\hbar}H_0 t}\Big|\Psi^S(t)\Big\rangle + e^{\frac{i}{\hbar}H_0 t}H_0\Big|\Psi^S(t)\Big\rangle \\ &+ \underbrace{e^{\frac{i}{\hbar}H_0 t}H_1(t)e^{-\frac{i}{\hbar}H_0 t}}_{:=\mathbf{H_1^I(t)}}\ \underbrace{e^{\frac{i}{\hbar}H_0 t}\Big|\Psi^S(t)\Big\rangle}_{|\Psi^I(t)\rangle} \\ &= H_1^I(t)\Big|\Psi^I(t)\Big\rangle \end{aligned} \tag{3.4}$$

WECHSELWIRKUNGSBILD

$$\begin{gathered} H_1^I(t) = e^{+\frac{i}{\hbar}H_0 t}H_1(t)e^{-\frac{i}{\hbar}H_0 t} \\ i\hbar\frac{d}{dt}|\Psi^I(t)\rangle = H_1^I(t)|\Psi^I(t)\rangle \end{gathered} \tag{3.5}$$

Let us now derive an expansion of $|\Psi^I(t)\rangle$ in powers of H_1^I. This means that we formally replace $H_1^I \to \varepsilon H_1^I$ in 3.5 .[1] Since $|\Psi^I(t)\rangle$ now depends on ε, we can carry out a Taylor expansion.

$$|\Psi^I(t)\rangle = \sum_{\ell=0}^{\infty} \varepsilon^{\ell} |\Psi^{I(\ell)}(t)\rangle \,. \tag{3.6}$$

Inserting this into 3.5 , and collecting same powers of ε^{ℓ} on both sides yields

$$\varepsilon^{(\ell+1)}\ i\hbar \frac{d}{dt} |\Psi^{I(\ell+1)}(t)\rangle = \varepsilon\ H_1^I(t)\ \varepsilon^{\ell}\ |\Psi^{I(\ell)}(t)\rangle \qquad \ell \geq 0\,. \tag{3.7}$$

Assuming that $H_1^I(t)$ vanishes before a certain time t_0 (when the perturbation is switched on), then $\Psi^I(t_0)$ does not depend on $H_1(t)$, and thus on ε, i.e. only the $\ell = 0$ is nonzero. We therefore have the initial conditions

$$|\Psi^{I(\ell)}(t_0)\rangle = \delta_{\ell,0}\ |\Phi\rangle\,, \tag{3.8}$$

where $|\Phi\rangle = |\Phi(t=0)\rangle = |\Psi^{I(\ell=0)}(t)\rangle$ is the unperturbed state evaluated in the interaction representation, which is, by definition, time independent. 3.7 can thus be solved by iteration:

$$\begin{aligned} |\Psi^{I(\ell+1)}(t)\rangle &= -\frac{i}{\hbar}\int_{t_0}^{t} H_1^I(\tau)|\Psi^{I(\ell)}(\tau)\rangle\, d\tau \\ |\Psi^{I(0)}(t)\rangle &= |\Phi\rangle\,. \end{aligned} \tag{3.9}$$

For example, the first-order term reads

$$|\Psi^{I(1)}(t)\rangle = -\frac{i}{\hbar}\int_{t_0}^{t} H_1^I(\tau)d\tau\ |\Phi\rangle \tag{3.10}$$

and the second-order term

$$\begin{aligned} |\Psi^{I(2)}(t)\rangle &= -\frac{i}{\hbar}\int_{t_0}^{t} dt_1\ H_1^I(t_1)|\Psi^{I(1)}(t_1)\rangle = \\ &\left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^{t} dt_1\ H_1^I(t_1) \int_{t_0}^{t_1} dt_2\ H_1^I(t_2)|\Phi\rangle\,. \end{aligned} \tag{3.11}$$

---

[1] This is just a formal way to introduce an expansion for "small" H_1^I. In the end, we will be interested in the case $\varepsilon = 1$

Wir entwickeln nun die $|\Psi^{I(\ell)}(t)\rangle$ nach den Eigenzuständen $|\Phi_n\rangle$ von H_0:

$$|\Psi^{I(\ell)}(t)\rangle = \sum_n c_n^{(\ell)}(t)|\Phi_n\rangle$$

Entsprechend 3.6 sind

$$c_n(t) \equiv \sum_{\ell=0}^{\infty} c_n^{(\ell)}(t) \tag{3.12}$$

die Entwicklungskoeffizienten von $|\Psi^I(t)\rangle$.
Einsetzen in 3.9 und multiplikation von links mit $\langle\Phi_m|$: liefert:

$$c_m^{(\ell+1)}(t) = -\frac{i}{\hbar}\sum_n \int_{t_0}^{t} \underbrace{\langle\Phi_m|H_1^I(\tau)|\Phi_n\rangle}_{e^{+\frac{i}{\hbar}\varepsilon_m\tau}\langle\Phi_m|H_1^S(\tau)|\Phi_n\rangle e^{-\frac{i}{\hbar}\varepsilon_n\tau}} c_n^{(\ell)}(\tau)\, d\tau \tag{3.13}$$

Mit der Definition

$$\omega_{mn} := \frac{\varepsilon_m - \varepsilon_n}{\hbar}$$

lautet die recursive Gleichung 3.13 für die Entwicklungskoeffizienten:

$$\boxed{\begin{aligned} c_m^{(\ell+1)}(t) &= -\frac{i}{\hbar}\sum_n \int_{t_0}^{t} d\tau\, e^{i\omega_{mn}\tau} H_{mn}(\tau)\, c_n^{(\ell)}(\tau) \qquad (3.14) \\ H_{mn}(\tau) &= \langle\Phi_m|H_1^S(\tau)|\Phi_n\rangle \qquad . \end{aligned}}$$

Die $\ell = 0$ Koeffiziente sind die Zeitunabhängige Entwicklungkoeffiziente der Zustandes (in der Wechselwirkungsdarstellung) vor einschalten der Störung

$$c_m^{(\ell=0)}(t_0) = c_m(t_0) \equiv c_m$$

Wir nehmen von nun an zur Vereinfachung $t_0 = 0$. Aus 3.14 lauten die Koeffizienten erster Ordnung

$$c_m^{(1)}(t) \;=\; -\frac{i}{\hbar}\sum_n c_n \int_0^t H_{mn}(\tau)e^{i\omega_{mn}\tau}d\tau$$

Der nächste Iterationsschritt liefert:

$$\begin{aligned} c_m^{(2)}(t) &= -\frac{i}{\hbar}\sum_n \int_0^t d\tau\, H_{mn}(\tau)e^{i\omega_{mn}\tau}c_n^{(1)}(\tau) \qquad (3.15) \\ &= \left(-\frac{i}{\hbar}\right)^2 \sum_n \int_0^t d\tau\, H_{mn}(\tau)e^{i\omega_{mn}\tau} \sum_{n'} c_{n'} \int_0^{\tau} d\tau'\, H_{nn'}(\tau')e^{i\omega_{nn'}\tau'} \end{aligned}$$

Übergangswahrscheinlichkeit

Es interessiert uns folgende Frage: Wenn das System zur Zeit $t = 0$ im Zustand $|\Phi_i\rangle$ ist, wie groß ist die Wahrscheinlichkeit, daß es dann zur Zeit $t > 0$ in dem Zustand $|\Phi_f\rangle$ ist? ($|\Phi_i\rangle, |\Phi_f\rangle$ sind Eigenzustände von H_0)

$$\begin{aligned} P_{i\to f} &= \left|\langle\Phi_f|\Psi(t)\rangle\right|^2 = \left|\langle\Phi_f|\sum_n c_n(t)\Phi_n\rangle\right|^2 = \left|\sum_n c_n(t)\underbrace{\langle\Phi_f|\Phi_n\rangle}_{\delta_{fn}}\right|^2 \\ &= \left|c_f(t)\right|^2 \qquad . \end{aligned} \tag{3.16}$$

Die Anfangsbedingung lautet $c_n(0) = \delta_{n,i}$. Daraus folgt in zweiter Ordnung in H_1 (siehe 3.15)

$$\begin{aligned} c_f(t) = \delta_{f,i} &- \frac{i}{\hbar}\int_0^t H_{fi}(\tau)e^{i\omega_{fi}\tau}d\tau \\ &- \frac{1}{\hbar^2}\sum_n\int_0^t d\tau H_{fn}(\tau)e^{i\omega_{fn}\tau}\int_0^\tau d\tau' H_{ni}(\tau')e^{i\omega_{ni}\tau'} \\ &+ O(H_1^3) \end{aligned} \tag{3.17}$$

3.1.2 Harmonische oder konstante Störung

Eine sehr wichtige Anwendung der zeitabhängigen Störungstheorie sind Probleme, bei denen zur Zeit $t = 0$ eine konstante oder harmonische Störung eingeschaltet wird

$$H_1 = \Theta(t)2V\cos(\omega t)$$

- $\Theta(t)$ schaltet die Störung zur Zeit t=0 ein
- für $\omega = 0$ beschreibt diese Gleichung eine konstante Störung

Es gilt [2]

$$H_1(t) = \Theta(t)\left(Ve^{i\omega t} + V^\dagger e^{-i\omega t}\right)$$

$$H_{mn}(t) = \left(V_{mn}e^{i\omega t} + V_{mn}^* e^{-i\omega t}\right) \qquad = \sum_{s=\pm 1} V_{mn}^s e^{is\omega t}$$

$$\text{mit} \qquad V_{mn}^s = \begin{cases} V_{mn} & \text{für} \quad s = +1 \\ V_{mn}^* & \text{für} \quad s = -1 \end{cases} .$$

---

[2] Für nicht-selbstadjungiertes V ist diese Form allgemeiner und enthält eine Phasenverschiebung

$\Theta(t)$ wird in diesem Zusammenhang nicht mehr benötigt, da die Integrale in 3.17 ohnehin erst bei $t = 0$ beginnen!

Nullte Ordnung

In Nullter Ordnung ist nicht viel zu rechnen. Der Beitrag lautet

$$c_f^{(0)} = \delta_{if}$$

und er kommt nur zum Tragen, wenn Anfangs- und Endzustand gleich sind.

Erste Ordnung

Das erste Integral in 3.17 lautet

$$\begin{aligned} \int_0^t d\tau H_{mn}(\tau) e^{i\omega_{mn}\tau} &= \sum_s V_{mn}^s \int_0^t d\tau e^{i(\omega_{mn}+s\omega)\tau} \\ &= \sum_s V_{mn}^s \frac{e^{i(\omega_{mn}+s\omega)t} - 1}{i(\omega_{mn}+s\omega)} \end{aligned} \tag{3.18}$$

D.h. der Term erster Ordnung liefert:

$$c_f^{(1)}(t) = -\frac{i}{\hbar} \sum_s V_{fi}^s \, e^{i\frac{\omega_{fi}+s\omega}{2}t} \, \frac{\sin\left(\frac{\omega_{fi}+s\omega}{2}t\right)}{\frac{\omega_{fi}+s\omega}{2}} \tag{3.19}$$

Zweite Ordnung

Wir wollen uns zunächst mit der ersten Ordnung begnügen. Den Beitrag zweiter Ordnung werden wir später mit einer leicht modifizierten Methode berechnen, mit der das Ergebnis leichter hergeleitet werden kann.

Konstante Störung

Wir betrachten zunächst eine konstante Störung ($\omega = 0$). Damit vereinfachen sich die Ausdrücke 3.19 bzw. 3.17

$$c_f^{(1)}(t) = -\frac{i}{\hbar} \underbrace{\sum_{s=\pm 1} V_{fi}^s}_{H_{fi}} \, e^{i\frac{\omega_{fi}}{2}t} \, \frac{\sin\left(\frac{\omega_{fi}}{2}t\right)}{\frac{\omega_{fi}}{2}} \tag{3.20}$$

$$\begin{aligned} c_f^{(2)}(t) &= \frac{1}{\hbar^2}\sum_{s,s'=\pm1}\sum_n \frac{V^s_{fn}V^{s'}_{ni}}{\omega_{ni}}\left[\frac{e^{i\omega_{fi}t}-1}{\omega_{fi}}-\frac{e^{i\omega_{fn}t}-1}{\omega_{fn}}\right] \\ &= \frac{1}{\hbar^2}\sum_n \frac{H_{fn}H_{ni}}{\omega_{ni}}\left[\frac{e^{i\omega_{fi}t}-1}{\omega_{fi}}-\frac{e^{i\omega_{fn}t}-1}{\omega_{fn}}\right] \end{aligned} \tag{3.21}$$

Die Wahrscheinlichkeit, dass das System in der Zeit t in den Zustand f übergegangen ist, lautet auf niedrigster Ordnung aus 3.20

$$P_{i\to f} = \left|c_f(t)\right|^2 = \frac{t^2}{\hbar^2}\left|H_{fi}\right|^2 \frac{\sin^2\left(\frac{\omega_{fi}}{2}t\right)}{\left(\frac{\omega_{fi}}{2}t\right)^2} \qquad . \tag{3.22}$$

Falls das Spektrum diskret und ε_i nicht entartet ist, gibt es zwischen der Energie ε_i und der Energie der Endzustände ε_f eine Energielücke $\Delta\varepsilon_f$. Die Übergangswahrscheinlichkeit lautet

$$P_{i\to f} = \frac{4\left|H_{fi}\right|^2}{(\Delta\varepsilon_f)^2}\sin^2\left(\frac{\Delta\varepsilon_f t}{2\hbar}\right) \qquad .$$

Diese Wahrscheinlichkeit oszilliert also mit der Frequenz $\omega = \frac{\Delta\varepsilon}{\hbar}$. Das ist ein charakteristisches Phänomen diskreter Systeme.[3] Die Periode der Oszillationen ist $T = \frac{2\pi\hbar}{\Delta\varepsilon}$ und die Amplitude nimmt proportional zu $\frac{|H_{fi}|^2}{(\Delta\varepsilon_f)^2}$ ab.

Wenn das diskrete Spektrum in ε_i entartet ist, d.h. $\exists f \neq i : \varepsilon_f = \varepsilon_i$, dann liefert 3.22 stattdessen

$$P_{i\to f} = \frac{t^2\left|H_{fi}\right|^2}{\hbar^2}.$$

Die Wahrscheinlichkeit wächst proportional zu t^2 an. Ab einer bestimmten Zeit wird die Wahrscheinlichkeit größer Eins. Das ist natürlich unsinnig und zeigt an, daß in Fall von Entartung

$$t \ll \frac{\hbar}{\left|H_{fi}\right|} \tag{3.23}$$

erfüllt sein muß, damit die Störungstheorie erster Ordnung anwendbar ist.

---

[3] Erst im Fall kontinuierlicher Spektren verschwindet die Periodizität, wie wir gleich sehen werden.

Kontinuierliches Spektrum

Wir wenden uns nun dem Fall zu, daß das Spektrum bei ε_i kontinuierlich ist. Es ist hierbei zweckmäßig, die Übergangsrate (Übergangswahrscheinlichkeit pro Zeiteinheit)

$$W := \frac{P}{t} \tag{3.24}$$

einzuführen, die aus 3.22 folgt

$$W_{i\to f} = \frac{2\pi}{\hbar^2} \left|H_{fi}\right|^2 \frac{t}{2\pi} \left(\frac{\sin(\omega_{fi}t/2)}{\omega_{fi}t/2}\right)^2 \quad .$$

In diesem Ausdruck erscheint die Funktion

$$\Delta_t(\omega) := \frac{t}{2\pi} \left(\frac{\sin(\frac{\omega t}{2})}{\frac{\omega t}{2}}\right)^2 , \tag{3.25}$$

die sich im Limes $t \to \infty$ wie die Delta-Funktion verhält Diskussion hier: Sec. A.21 (siehe Fig. A.1):

$$\lim_{t\to\infty} \Delta_t(\omega) = \delta(\omega) \quad . \tag{3.26}$$

Hiermit wird die Übergangsrate 3.25 für große t zu

FERMI'S GOLDENE REGEL

$$W_{i\to f} = \frac{2\pi}{\hbar} \left|H_{fi}\right|^2 \delta(\varepsilon_f - \varepsilon_i) \quad . \tag{3.27}$$

Diese Darstellung mit der δ-Funktion ist nur dann sinnvoll, wenn in der Nachbarschaft von ε_i ein Kontinuum von Endzuständen vorhanden ist. Das ist in physikalischen Anwendungen oft der Fall. Im Limes $t \to \infty$ beschreibt 3.27 die Energieerhaltung. Für kurze Zeiten ist die Energieerhaltung aufgeweicht, d.h. es hat eine Unschärfe (siehe Fig. A.1) $\Delta E/\hbar \propto 2\pi/t$ also die Heisenberg Unschärfe zwischen Zeit und Energie

$$t\,\Delta E \propto h$$

Wir finden im Fall der Entartung eine zeitlich konstante Übergangsrate, d.h. die Übergangswahrscheinlichkeit wächst linear mit der Zeit und führt zu unphysikalischen Ergebnissen, wenn die Störungstheorie nicht mehr anwendbar ist, d.h. wenn die Ungleichung 3.23 verletzt wird.

Bei einem **kontinuierlichen Spektrum** kann man nicht mehr die Übergangswahrscheinlichkeit in individuelle Zustände angeben. $P = \left|\langle\Phi_f|\Psi(t)\rangle\right|^2$ in 3.16 hat dann vielmehr die Bedeutung einer Wahrscheinlichkeitsdichte. In diesem Fall interessieren wir uns für die Übergangsrate in einem Intervall von Endzustandsenergien ($\varepsilon_n \in \Delta I_f := [\varepsilon_f, \varepsilon_f + \Delta E]$).
Wir führen nun die Zustandsdichte $\rho(E)$ ein . Für ein infinitesimales Energieintervall ΔE ist $\rho(E)$ die Anzahl der Zustände dividiert durch ΔE. Für ein endliches Intervall

$$\int_{\Delta E} \rho(E) dE = \sum_{\substack{n \\ \varepsilon_n \in \Delta E}} 1 \tag{3.28}$$

Man kann auch schreiben

$$\rho(E) = \sum_n \delta(\varepsilon_n - E) \tag{3.29}$$

3.27 wird dann zu:

$$W_{i \to \Delta I_f} = \sum_{\substack{n \\ \varepsilon_n \in \Delta I_f}} \frac{2\pi}{\hbar} |H_{ni}|^2 \, \delta(\varepsilon_n - \varepsilon_i)$$

In der Annahme, dass $|H_{ni}|^2$ I_f nicht wesentlich variiert, kann man diesen durch einem Mittelwert $\overline{\left|H_{fi}\right|^2}$ ersetzen. Wir erhalten

$$W_{i \to \Delta I_f} = \Theta(\varepsilon_i \in \Delta I_f) \, \overline{\left|H_{fi}\right|^2} \, \frac{2\pi}{\hbar} \, \rho(\varepsilon_i) \tag{3.30}$$

Harmonische Störung mit kontinuierlichem Spektrum

Der Fall einer harmonischen Störung läßt sich nun leicht diskutieren. Hier ist $\omega \neq 0$ und es gibt in 3.19 zwei Beiträge: $af(\omega_{fi} + \omega) + bf(\omega_{fi} - \omega)$. Für große t oszillieren diese Terme stark und verschwinden im Durschnitt, es sei denn, der Argument $\omega_{fi} \pm \omega$ ist klein, was nur bei einer der beiden geschehen kann. Die Übergangswahrscheinlichkeit enthält den Term

$$\begin{aligned} \left|af(\omega_{fi} + \omega) + bf(\omega_{fi} - \omega)\right|^2 &= |a|^2 \left|f(\omega_{fi} + \omega)\right|^2 + |b|^2 \left|f(\omega_{fi} - \omega)\right|^2 \\ &\quad + (a^* b + ab^*) f(\omega_{fi} + \omega) \cdot f(\omega_{fi} - \omega) \end{aligned}$$

Der Interferenzterm hat (für $\omega \neq 0$) immer eine stark oszillierende Komponente und kann daher vernachlässigt werden. Die anderen Beiden Termen ergeben eine Übergangsrate in der Form 3.25 mit $\omega_{fi} \to \omega_{fi} \pm \omega$, was letzendlich zur δ-Form 3.27 führen.

Für endliche Frequenzen kann immer einer der beiden Peaks vernachlässigt werden. Voraussetzung hierfür, und auch für die Vernachlässigung des Interferenzterms ist, daß der Abstand 2ω der beiden δ-artigen Peaks groß ist gegen die Peakbreite $2\pi/t$ (siehe Abbildung A.1). Das heißt,

$$t \gg \frac{\pi}{\omega} \approx \frac{\hbar}{|\varepsilon_f - \varepsilon_i|} \qquad .$$

Gleichzeitig muß immer noch 3.23 erfüllt sein, damit die erste Ordnung Störungstheorie gültig ist. Für die Zeit t erhalten wir also die Bedingung

$$\frac{\hbar}{|\varepsilon_f - \varepsilon_i|} \ll t \ll \frac{\hbar}{|H_{fi}|} \qquad .$$

Voraussetzung dafür, daß diese Bedingung für t überhaupt erfüllt werden kann, ist

$$\frac{|H_{fi}|}{|\varepsilon_f - \varepsilon_i|} \ll 1 \qquad .$$

Das ist genau die gleiche Voraussetzung, die für die Gültigkeit der zeitunabhängigen Störungstheorie notwendig ist.
Analog zu 3.27 erhalten wir

$$W_{i\to f} = \frac{2\pi}{\hbar}\left(|W_{fi}|^2 \underbrace{\delta(\varepsilon_f - \varepsilon_i + \hbar\omega)}_{\varepsilon_f=\varepsilon_i-\hbar\omega \Rightarrow \text{Emission}} + |W^*_{fi}|^2 \underbrace{\delta(\varepsilon_f - \varepsilon_i - \hbar\omega)}_{\varepsilon_f=\varepsilon_i+\hbar\omega \Rightarrow \text{Absorption}} \right)$$

Diese Formel ist der Ausgangspunkt zur Beschreibung vieler physikalischer Effekte, wie z.B.: (inverse) Photoemission, Augerspektroskopie, Coulomb-Streuung und Compton-Streuung.

3.1.3 Adiabatisches Einschalten der Störung

Wir multiplizieren den Störterm H_1 mit einem adiabatischen Einschaltfaktor $e^{O^+ t}$. Die Störung wird nun bereits für $t \to -\infty$ eingeschaltet. Jedoch sehr langsam, da O^+ eine infinitesimal kleine positive Größe ist. Die Änderung im Vergleich zum abrupten Einschalten bei $t = 0$ ist, dass die Integrale sich alle bis $t \to -\infty$ erstrecken. Der Einschaltfaktor stellt sicher, dass die Integrale konvergieren. Der einzige Unterschied ist folgender

$$\int_0^t e^{i\omega\tau} d\tau \to \int_{-\infty}^t e^{i(\omega - iO^+)\tau} d\tau$$

$$\frac{e^{i\omega t} - 1}{i\omega} \to \frac{e^{i(\omega - iO^+)t}}{i(\omega - iO^+)} \; .$$

Ganz am Schluss, lassen wir dann $O^+ \to 0$ gehen. Zur Vereinfachung der Schreibarbeit verwenden wir die Abkürzung $\omega^+ := \omega - iO^+$
Für den Term erster Ordnung erhalten wir dann anstelle von 3.18

$$\int_{-\infty}^{t} d\tau H_{mn}(\tau) e^{i\omega_{mn}\tau} \quad = \quad \sum_s V_{mn}^s \frac{e^{i(\omega_{mn}^+ + s\omega)t}}{i(\omega_{mn}^+ + s\omega)} \tag{3.31}$$

Der erste Ordnungsterm in 3.17 liefert somit bei konstanter Störung ($\omega = 0$)

$$\begin{aligned} c_f^{(1)} &= -\frac{i}{\hbar} \sum_s V_{fi}^s \frac{e^{i(\omega_{fi}^+)t}}{i\omega_{fi}^+} \\ &= -\frac{1}{\hbar} H_{fi} \frac{e^{i\omega_{fi}^+ t}}{\omega_{fi}^+} \ . \end{aligned} \tag{3.32}$$

Damit gilt für die Wahrscheinlichkeit

$$P_{i\to f} = \left|c_f\right|^2 = \frac{1}{\hbar^2} \left|H_{ni}\right|^2 \frac{e^{2O^+t}}{\omega_{fi}^2 + O^{+2}}$$

Daraus folgt

$$W_{i\to f} = \frac{dP_{i\to f}}{dt} = \frac{2}{\hbar^2} \left|H_{ni}\right|^2 \frac{O^+ e^{2O^+t}}{\omega_{fi}^2 + O^{+2}} \ .$$

Nun können wir den Grenzübergang $O^+ \to 0$ durchführen und erhalten für die Übergangsrate

$$\text{mit } \lim_{O^+\to 0} \frac{O^+}{\omega^2 + O^{+2}} = \pi\delta(\omega)$$

$$W_{i\to f} = \frac{2\pi}{\hbar} \left|H_{ni}\right|^2 \delta(E_f - E_i) \ .$$

Das ist wieder das bekannte Ergebnis 3.27 . Bestätigt durch dieses Ergebnis berechnen wir nun hiermit die Korrektur zweiter Ordnung für eine $\omega = 0$ Störung.

$$\begin{aligned} c_f^{(2)}(t) &= -\frac{1}{\hbar^2} \sum_n \int_{-\infty}^{t} d\tau H_{fn} e^{i\omega_{fn}^+\tau} \int_{-\infty}^{\tau} d\tau' H_{ni} e^{i\omega_{ni}^+\tau'} \\ &= -\frac{1}{\hbar^2} \sum_n H_{fn} H_{ni} \left[\int_{-\infty}^{t} d\tau e^{i\omega_{fn}^+\tau} \frac{e^{i\omega_{ni}^+\tau}}{i\omega_{ni}^+} \right] \\ &= \frac{1}{\hbar^2} \sum_n \frac{H_{fn} H_{ni}}{\omega_{ni}^+} \frac{e^{i\omega_{fi}^+ t}}{\omega_{fi}^+} \ . \end{aligned}$$

Wir addieren nun die Beiträge erster 3.32 und zweiter Ordnung

$$\begin{aligned} c_f &= -H_{fi}\frac{e^{i\omega_{fi}^{+}t}}{\hbar\omega_{fi}^{+}} + \sum_n \frac{H_{fn}H_{ni}}{\hbar\omega_{ni}^{+}}\frac{e^{i\omega_{fi}^{+}t}}{\hbar\omega_{fi}^{+}} \\ &= -\left(H_{fi} + \sum_n \frac{H_{fn}H_{ni}}{-\hbar\omega_{ni}^{+}}\right)\frac{e^{i\omega_{fi}^{+}t}}{\hbar\omega_{fi}^{+}} \ . \end{aligned}$$

Der erste Nenner lässt sich auch schreiben als $-\hbar\omega_{ni}^{+} = E_i - E_n + iO^{+}$. Der Unterschied zum Ausdruck erster Ordnung 3.32 besteht darin, dass H_{fi} durch

$$H_{fi} \to M_{fi} = H_{fi} + \sum_n \frac{H_{fn}H_{ni}}{E_i - E_n + iO^{+}} \tag{3.33}$$

zu ersetzen ist. Die Übergangsrate ist demnach

$$w_{i\to f} = \frac{2\pi}{\hbar}\left|M_{fi}\right|^2 \ \delta(E_f - E_i)$$

Chapter 4

Charged particle in an electromagnetic field

4.1 Classical Hamilton function of charged particles in an electromagnetic field

Remember from classical mechanics [1]

HAMILTONIAN FOR A CHARGED PARTICLE IN A EM FIELD

$$H = \frac{1}{2m}\left(\mathbf{p} - \frac{q}{c}\mathbf{A}(\mathbf{r},t)\right)^2 + q\phi(\mathbf{r},t) \tag{4.1}$$

We check that it gives the correct equation of motion. First consider that the velocity

$$\mathbf{v} = \frac{d}{dt}\mathbf{r} = \frac{\partial}{\partial \mathbf{p}}H = \cdots\cdots \tag{4.2}$$

is not the usual $\mathbf{p}/m$. Therefore, the Lorentz force ought to be

$$\mathbf{F} = \frac{d}{dt}m\mathbf{v} = \frac{d}{dt}\mathbf{p} - \frac{q}{c}\frac{d}{dt}\mathbf{A} \tag{4.3}$$

---

[1] We use here the *cgs* unit system, so there are here or there *c* factors which are not present in the *SI* system

From the Hamilton equations we have (cf. 4.1

$$\frac{d}{dt} p_i = -\nabla_i H = \cdots\cdots \tag{4.4}$$

Consider that

$$\frac{d}{dt}\mathbf{A}(\mathbf{r}(t),t) = v_j \nabla_j \mathbf{A} + \frac{\partial}{\partial t}\mathbf{A} \tag{4.5}$$

Putting everything (4.3 , 4.4 , 4.5) together, we obtain

$$F_i = \cdots\cdots \tag{4.6}$$

$$= \frac{q}{c}\left(\mathbf{v} \times \underbrace{(\boldsymbol{\nabla} \times \mathbf{A})}_{\mathbf{B}}\right)_i + qE_i \tag{4.7}$$

The correct expression for the Lorentz Force. So indeed 4.1 is the correct Hamilton function.

As usual, the correspondence principle of quantum mechanics tells us that 4.1 is also the quantum mechanical Hamilton operator for a particle in an electromagnetic field. [2]

The Schrödinger equation, thus, becomes

$$i\hbar \frac{\partial}{\partial t}\Psi = \left(\frac{1}{2m}\left(\mathbf{p} - \frac{q}{c}\mathbf{A}(\mathbf{r},t)\right)^2 + q\phi(\mathbf{r},t)\right)\Psi \tag{4.8}$$

We now evaluate the operation of the velocity as the time derivative of the position operator. These operators are understood in the Heisenberg picture [3], although, for simplicity of notation, we omit the ^{H}.

$$\mathbf{v} = \frac{d}{dt}\mathbf{r} = i\,[H,\mathbf{r}] = \cdots\cdots \tag{4.9}$$

has the same expression as the classical one 4.2

For a particle with spin **S** there is an additonal interaction between spin and magnetic field

$$\Delta H = -\mu \mathbf{B}\cdot\mathbf{S} \qquad \mu = g\frac{q}{2m} \tag{4.10}$$

---

[2] We will henceforth be less consistent in indicating operators with the hat-symbol ˆ. We shall only use it in cases where it otherwise might lead to confusion and mixing up.

[3] If you are not happy with this “sloppy” treatment of the operators in the Heisenberg picture, see here: Sec. A.14

4.2 Gauge invariance

Due to the gauge invariance in classical electrodynamics, physical properties should not change under the gauge transformations

$$\mathbf{A}' = \mathbf{A} + \nabla\chi \qquad \phi' = \phi - \frac{1}{c}\frac{\partial}{\partial t}\chi \tag{4.11}$$

The point here is that $\mathbf{A}$ and ϕ are **not observable**. 4.8 seems in contradiction with that, since $\mathbf{A}$ and ϕ enter explicitly in the equation for the wavefunction, in contrast to classical mechanics in which only fields enter the expression for the Lorentz force.
The answer to this issue is that in fact also the wave function is not observable, and it will turn out that any observable quantity does not change under a gauge transformation 4.11 .
To show this let us consider a modified wave function Ψ'

$$\Psi'(\mathbf{r},t) = e^{i\frac{q}{\hbar c}\chi(\mathbf{r},t)}\Psi(\mathbf{r},t) \tag{4.12}$$

Now we show that, if Ψ is a solution of 4.8 , then Ψ' (4.12) is a solution of the Schrödinger equation for the modified potentials 4.11 :

$$i\hbar\frac{\partial}{\partial t}\Psi' = \frac{1}{2m}\left(\mathbf{p} - \frac{q}{c}\mathbf{A}'\right)^2\Psi' + q\phi'\Psi' \tag{4.13}$$

We prove it here : Sec. A.27 . Obviously 4.12 has the same probability density as Ψ. It can be easily shown that all expectation values of observables are equal in the two gauges, as it should be.
For example consider the velocity 4.2 (we use units in which $\hbar = c = 1$ for simplicity), cf 4.11 :

$$\begin{aligned} m\,\mathbf{v}'\,\Psi' &= \cdots\cdots \\ &\quad \cdots\cdots \end{aligned} \tag{4.14}$$

where we have used the product rule

$$-i\nabla e^{i\,q\,\chi}\Psi = -ie^{i\,q\,\chi}\nabla\Psi + qe^{i\,q\,\chi}(\nabla\chi)\Psi$$

so that the two red terms cancel out.
This means that matrix elements of $\mathbf{v}$ are **gauge invariant**:

$$\left\langle \Psi_1' \middle| \mathbf{v}' \middle| \Psi_2' \right\rangle = \langle \Psi_1 | \mathbf{v} | \Psi_2 \rangle$$

(find out why?)
Notice that, in contrast to $\mathbf{v}$, the canonical momentum $\mathbf{p}$ is not a gauge invariant operator. It is, therefore, not an observable (find out why?).

4.3 Landau Levels

The situation of a constant, homogeneous magnetic field is relevant for the quantum Hall effect. Reminder: In classical physics, charged particles in an homogeneous magnetic field move along circular (or spiral) orbits.
Let us consider the case of a constant field in the z direction:

$$\mathbf{B} = B\mathbf{e}_z$$

We have several choices for the vector potential, which are connected by gauge transformations. One possibility is

$$\mathbf{A} = -B\, y\, \mathbf{e}_x \qquad \textbf{check}: \boldsymbol{\nabla} \times \mathbf{A} = \cdots\cdots \tag{4.15}$$

(Other possibilities are $\mathbf{A} = B\, x\, \mathbf{e}_y$, or the symmetric case $\mathbf{A} = \frac{1}{2}\mathbf{r} \times \mathbf{B} = \frac{1}{2}(x\mathbf{e}_y - y\mathbf{e}_x)$).
The Hamiltonian 4.1 thus becomes

$$H = \frac{1}{2m}\left((p_x + \frac{q}{c}By)^2 + p_y^2 + p_z^2\right)$$

The operators p_x and p_z (but not p_y) commute with the hamiltonian. Therefore we can find common eigenfunctions of H, p_x, p_z . The corresponding eigenfunctions will, therefore, have the form:

$$\Psi(\mathbf{r}) = e^{i(k_x x + k_z z)} f(y)$$

Therefore, the time independent Schrödinger equation becomes

$$\begin{aligned} He^{i(k_x x + k_z z)} f(y) &= e^{i(k_x x + k_z z)} \frac{1}{2m}\left((\hbar k_x + \frac{qB}{c}y)^2 + p_y^2 + \hbar^2 k_z^2\right) f(y) \\ &= e^{i(k_x x + k_z z)} E f(y) \end{aligned}$$

and y and p_y are the only operators left. This is the Schrödinger equation for a shifted harmonic oscillator.
To solve it, we introduce the shifted y coordinate:

$$\frac{qB}{c}\bar{y} = \cdots\cdots \tag{4.16}$$

This is allowed because $\bar{y}$ has the correct (canonical) commutation rules with p_y:

$$[\bar{y}, p_y] = i\hbar$$

The Schrödinger equation becomes

$$\left(\frac{p_y^2}{2m}+\frac{q^2B^2}{2mc^2}\,\bar{y}^2\right)\,f(y)=(E-\frac{\hbar^2k_z^2}{2m})\,f(y) \tag{4.17}$$

This describes an harmonic oscillator with frequency

$$\frac{m}{2}\omega_c^2=\frac{q^2B^2}{2mc^2}\qquad \omega_c=\frac{|qB|}{mc} \tag{4.18}$$

which is the well-known cyclotron frequency (in c.g.s. units). The energy eigenvalues are, thus , given by

$$E_{n,k_z}=\cdots\cdots \tag{4.19}$$

There is no dependence of the energies on k_x so there is a **large degeneracy.** Typically, the quantum Hall effect is interesting in two-dimensional systems, where the z coordinate is confined. [4] In that case, there are discrete, highly degenerate energy levels separated by the energy $\hbar\omega_c$, the Landau levels.
The energy separation between the Landau levels depends on the magnetic field and can be estimated as

$$\hbar\omega_c\approx 10^{-4}\;eV\times(B/Tesla)$$

Notice that $10^{-4}\;eV$ corresponds to approximatively 1 Kelvin temperature.
The wave function of the ground state of the harmonic oscillator in 4.17 has the behavior

$$f(\bar{y})\sim\exp\left(-\frac{\bar{y}^2}{2a^2}\right)$$

where

$$a=\sqrt{\frac{\hbar}{m\omega_c}}=\sqrt{\frac{\hbar c}{qB}}\approx 100\overset{\circ}{A}\;(B/Tesla)^{-\frac{1}{2}}$$

---

[4] One could, for example, consider a “box” potential in the z directions

Chapter 5

Extensions and Applications

5.1 Main goals of this chapter (until Sec. 5.4)

- We will consider two simple models for bonding of atoms which often occur in chemistry: the covalent and the van-der-Waals bonding.
- Although the systems are simple, they are complex enough so that they cannot be treated analytically. Therefore, we will have to resort to approximations.
- In the case of covalent bonding we will consider a system of two protons sharing one electron. The first approximation (Born-Oppenheimer approximation) consists in initially neglecting the dynamics (i.e. the momentum) of the two much heavier protons so that one is left with a single-particle problem.
- The remaining problem is still complex, since it is not centrally symmetric. Again one carries out a variational ansatz by choosing a physically motivated form of the wavefunction (see 5.2 with 5.3).
- The distance between the protons is obtained by minimizing the energy.
- The final result is a very good approximation (in comparison to experiment) for the binding energy of the molecule and for the equilibrium distance between the protons.

5.2 Covalent bonding

In molecules and solids we encounter different types of bonding mechanisms. One of them is the covalent bonding, where neighbouring atoms share one or more electrons. This exchange of particles leads to an attractive force between the atoms. This is in contrast to another bonding type, the ionic bonding, where two initially neutral atoms interact in a way that makes it energetically favorable for one atom to give up an electron to the second atom. Thus, differently charged ions are created that electrostatically attract each other. In a covalent bond no electron is transferred, but it is shared by the two atoms involved in the bonding. In order to understand this process quantum mechanically, we will consider the simplest model of an ionized $\mathbf{H}_2^+$ molecule.

5.2.1 The $\mathbf{H}_2^+$ molecule

The $\mathbf{H}_2^+$ molecule consists of two singly-positively-charged nuclei with mass M and one electron with mass m. Even this two-atom molecule represents a fairly complex system and solving it exactely requires considerable effort. For this reason, we will address the problem using approximation procedures, namely the variational method.

Due to the huge mass differences, $\frac{m_e}{m_p} < 10^{-3}$, electrons are moving a lot faster than the nuclei and we can separate the two motions. This means that for the time being we fix the positons $\mathbf{R}_1$ and $\mathbf{R}_2$ of the nuclei and solve the Schrödinger equation for the electron in the potential resulting from the nuclei. We obtain the possible energies of the electronic system $E_n(\mathbf{R})$ as a function of the distance $\mathbf{R} = \mathbf{R}_1 - \mathbf{R}_2$ between the two nuclei. For the dynamics of the nuclei these energies represent the electronical contribution to the potential they move in.

$$V^{\text{eff}}(\mathbf{R}) = V^{\text{Nucl}-\text{Nucl}}(|R_2 - R_1|) + E_n(\mathbf{R}) \qquad .$$

This approximation is called Born-Oppenheimer approximation and is widely applied in solid state physics, as it is extremely reliable. Since the mass of the nuclei is much larger than the mass of the electrons, we can in good approximation treat their motion classically.

$$M\ddot{\mathbf{R}} = -\nabla_R V^{\text{eff}}(\mathbf{R}) \qquad .$$

This approximation is used in quantum chemistry and in solid state physics in order to determine equilibrium configurations of molecules and their vibrations, as well as surface geometries and phonon modes. The approach was originally developed by R. Car und M. Parinello.

In the following we will calculate the ground state and the electronical contribution to the effective nuclear potential for $\mathbf{H}_2^+$. The Hamilton operator takes the

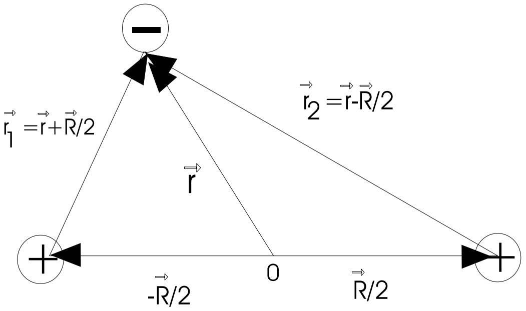

Figure 5.1: *Positioning of the atoms and the electron in the H_2^+ molecule.*

form

$$H = -\frac{\hbar^2}{2m}\left(\frac{d^2}{dx^2}+\frac{d^2}{dy^2}+\frac{d^2}{dz^2}\right)-\frac{e^2}{r_1}-\frac{e^2}{r_2}+\frac{e^2}{R} \qquad ,$$

with r_α and R representing the lengths of the vectors $\mathbf{r}_\alpha$ and $\mathbf{R}$. We will write all lengths in units of a_0, that is $r_\alpha = \tilde{r}_\alpha \cdot a_0$ and $R = \tilde{R} \cdot a_0$. In dimensionless quantities $\tilde{\mathbf{x}}$, $\tilde{\mathbf{R}}$ the Hamilton operator reads

$$\begin{aligned}
&H && = -\frac{\hbar^2}{2m\,a_0^2}\tilde{\nabla}^2 + \frac{e^2}{a_0}\left(-\frac{1}{\tilde{r}_1}-\frac{1}{\tilde{r}_2}+\frac{1}{\tilde{R}}\right)\\
&a_0 && = \frac{\hbar^2}{me^2} \Rightarrow\\
1)\quad &\frac{e^2}{a_0} && = 2\text{Ry} \qquad \ldots\text{Rydberg}\\
2)\quad &\frac{\hbar^2}{2m\,a_0^2} && = \frac{\hbar^2\,m^2e^4}{2m\hbar^4} = \frac{me^4}{2\hbar^2} = 1\text{Ry}
\end{aligned}$$

This leads to

$$H = 2\text{Ry}\left(-\frac{\tilde{\nabla}^2}{2}-\frac{1}{\tilde{r}_1}-\frac{1}{\tilde{r}_2}+\frac{1}{\tilde{R}}\right)$$

In the further course of the calculation we will write the energies in units of 2Ry (Rydberg), $H = \tilde{H}\ 2\text{Ry}$, which results in further simplification of the Hamilton operator. These units are called atomic units.

HAMILTON OPERATOR IN ATOMIC UNITS

$$\tilde{H} = -\frac{\tilde{\nabla}^2}{2} - \frac{1}{\tilde{r}_1} - \frac{1}{\tilde{r}_2} + \frac{1}{\tilde{R}} \qquad . \tag{5.1}$$

In atomic units the numeric values of e, $\hbar$ and m_e are 1, that is the fundamental constants can be left out everywhere. We will in the further course omit the tildes ˜ and assume that all quantities are given in atomic units. This is a very practical approach that is widely used in theoretical physics, since that way all quantities are of order 1.

In order to get an idea of how the variational function could look like, we consider the case where $R >> a_0$. There are two possibilities: Either the electron is near the first nucleus or it is near the second one. The corresponding wavefunctions are simply the ground state functions of the hydrogen atom, 2.31 with $Z = 1$. Since both configurations are possible, we choose the following ansatz:

$$\psi(\mathbf{r}) = c_1 \psi_1(\mathbf{r}) + c_2 \psi_2(\mathbf{r}) \qquad . \tag{5.2}$$

This ansatz, with slight modifications, is also reasonable for smaller distances between the nuclei. Since for $R \to 0$ the exact ground state wavefunction is the one of the H-like atom with $Z = 2$, we use the ansatz 5.2 with [1]

$$\psi_\alpha(r) = \left(\frac{Z^3}{\pi}\right)^{\frac{1}{2}} e^{-Z\, r_\alpha} \tag{5.3}$$

In total, we take

$$\psi(\mathbf{r}) = c_1 \cdot \underbrace{(\frac{Z^3}{\pi})^{\frac{1}{2}} e^{-Z\, r_1}}_{\psi_1(\mathbf{r})} + c_2 \cdot \underbrace{(\frac{Z^3}{\pi})^{\frac{1}{2}} e^{-Z\, r_2}}_{\psi_2(\mathbf{r})}$$

and the variational parameters c_1, c_2 and Z, whose values result from the minimization of energy. To start with we consider

$$\min_{c_1,c_2} E(c_1,c_2,Z) = \min_{c_1,c_2} \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle}$$

for fixed Z. The resulting eigenvalue problem is frequently encountered in quantum mechanics and shall therefore be treated in a more general manner.

---

[1] Remember that in atomic units $a_0 = 1$.

5.3 Optimization of the (variational) wavefunction in a subspace

We expand the desired wave function ψ in an arbitrary "basis". In contrast to the bases used so far, the basis in this case has to be neither complete, nor normalized, nor orthogonal. [2]. However, linearily dependent vectors have to be eliminated beforehand.

$$|\psi\rangle = \sum_{i=1}^{N} c_i |\psi_i\rangle$$

The best possible linear combination for the ground state is obtained by minimizing the energy with respect to the expansion coefficients.

$$E(c) = \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\sum_{i,j} c_i^* \overbrace{\langle\psi_i|\hat{H}|\psi_j\rangle}^{H_{ij}} c_j}{\sum_{i,j} c_i^* \underbrace{\langle\psi_i|\psi_j\rangle}_{S_{ij}} c_j}$$

$$\frac{\partial}{\partial c_i^*} E = \frac{\sum_j H_{ij} c_j}{\langle\psi|\psi\rangle} - \frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle^2} \cdot \sum_j S_{ij} c_j \overset{!}{=} 0$$

Multiplication with $\langle\psi|\psi\rangle$ leads to

$$\sum_j H_{ij} c_j - \underbrace{\frac{\langle\psi|\hat{H}|\psi\rangle}{\langle\psi|\psi\rangle}}_{=E} \cdot \sum_j S_{ij} c_j \overset{!}{=} 0$$

This is a

GENERALIZED EIGENVALUE PROBLEM

$$H\,\mathbf{c} = E\,S\,\mathbf{c} \tag{5.4}$$

---

[2] Up to now, when talking about a basis we've always meant a complete basis. That is indeed a common definition. However, in literature, especially in quantum mechanics, the term "basis" is also used for sets of functions on which series expansions are based that do not necessarily represent a complete basis.

The stationary points of the function $E(c)$ can be obtained from the generalized eigenvalue problem 5.4 . A possible solution is based on the Löwdin-Orthogonalization. Introduce

$$\begin{aligned} \mathbf{x} &:= S^{\frac{1}{2}}\mathbf{c} \\ HS^{-\frac{1}{2}}\mathbf{x} &= ES^{\frac{1}{2}}\mathbf{x} \\ \underbrace{S^{-\frac{1}{2}}HS^{-\frac{1}{2}}}_{\tilde{H}}\mathbf{x} &= E\mathbf{x} \end{aligned} \tag{5.5}$$

See here: Sec. A.15 for more. The matrix $\tilde{H}$ is hermitian as well, which leaves us with an ordinary eigenvalue prolem. The result 5.4 states that the lowest energy in a subspace of the complete Hilbert space can be obtained by solving the eigenvalue problem in this subspace.

5.4 Back to the variational treatment of $\mathbf{H}_2^+$

For the $\mathbf{H}_2^+$ problem the considerations made above indicate that we need to calculate the matrix elements

$$\begin{aligned} \langle\psi_1|H|\psi_1\rangle = \langle\psi_2|H|\psi_2\rangle &=: H_1 \\ \langle\psi_1|H|\psi_2\rangle = \langle\psi_2|H|\psi_1\rangle &=: H_2 \\ S_{11} = S_{22} = \langle\psi_2|\psi_2\rangle &= 1 \\ S_{12} = S_{21} = \langle\psi_1|\psi_2\rangle &=: S \end{aligned}$$

with the symmetry of the problem being exploited. We still have to solve (cf. 5.4):

$$\begin{pmatrix} H_1 & H_2 \\ H_2 & H_1 \end{pmatrix} \cdot \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E \begin{pmatrix} 1 & S \\ S & 1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \tag{5.6}$$

Clearly the Hamilton operator commutes with the parity operator

$$P|\psi_1\rangle = |\psi_2\rangle \qquad P|\psi_2\rangle = |\psi_1\rangle$$

As a consequence, eigenvectors of H 5.6 are also eigenvectors of P, that is they are either even (gerade):

$$\psi_b(\mathbf{r}) = \frac{\psi_1(\mathbf{r}) + \psi_2(\mathbf{r})}{\sqrt{2(1+S)}} \qquad E_b = \frac{H_1 + H_2}{1+S} \tag{5.7}$$

or odd (ungerade).

$$\psi_a(\mathbf{r}) = \frac{\psi_1(\mathbf{r}) - \psi_2(\mathbf{r})}{\sqrt{2(1-S)}} \qquad E_a = \frac{H_1 - H_2}{1-S} \tag{5.8}$$

We can easily check that these states are orthonormal. For reasons that will become clear in a moment, the even state 5.7 is called bonding state and the odd state 5.8 is called antibonding state. The states are depicted in figure 5.2 . The corresponding wavefunctions are also called molecular orbitals.

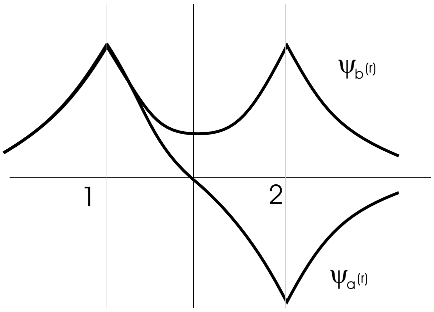

Figure 5.2: *Wavefunctions with even and odd parity.*

Matrix elements of the Hamilton operator 5.1

We know that the exact ground state energy (cf. 2.23) of an H-like atom with the atomic number Z is $-\frac{Z^2}{2}$ (in atomic units). I.e., the stationary Schrödinger equation takes the following form (cf. 5.1):

$$\left(-\frac{\boldsymbol{\nabla}^2}{2}-\frac{Z}{r_1}\right)\psi_1(\mathbf{r})=-\frac{Z^2}{2}\psi_1(\mathbf{r}) \qquad .$$

This fact can be used to simplify the calculation of the matrix elements for the Hamiltonian 5.1 of the ionised $\mathbf{H}_2^+$-molecule by rewriting the Hamiltonian in the following way:

$$H=-\frac{\boldsymbol{\nabla}^2}{2}-\frac{Z}{r_1}+\frac{Z-1}{r_1}-\frac{1}{r_2}+\frac{1}{R}$$

$$H\psi_1(\mathbf{r})=\left(-\frac{Z^2}{2}+\frac{Z-1}{r_1}-\frac{1}{r_2}+\frac{1}{R}\right)\psi_1(\mathbf{r}) \tag{5.9}$$

$$H_1=\langle\psi_1|H|\psi_1\rangle \tag{5.10}$$

$$=(-\frac{Z^2}{2}+\frac{1}{R})\underbrace{\langle\psi_1|\psi_1\rangle}_{=1}+\underbrace{(Z-1)\langle\psi_1|\frac{1}{r_1}|\psi_1\rangle-\langle\psi_1|\frac{1}{r_2}|\psi_1\rangle}_{:=K} \qquad . \tag{5.11}$$

The expectation value

$$\langle\psi_1|\frac{1}{r_2}|\psi_1\rangle = \int |\psi_1(\mathbf{r})|^2 \frac{1}{r_2}\, d^3r$$

with 5.3 corresponds to (minus) the classical Coulomb interaction energy of the electron in the Coulomb field of the **second** nucleus. The result can be obtained using Gauss's law (here: Sec. A.13):

$$\langle\psi_1|\frac{1}{r_2}|\psi_1\rangle = \frac{1}{R}\left(1-(1+ZR)e^{-2ZR}\right)$$

This term decreases with $\frac{1}{R}$.

The second expectation value $\langle\psi_1|\frac{1}{r_1}|\psi_1\rangle$ represents the Coulomb interaction energy of the electron in the Coulomb field of the **first** nucleus. This is formally the previous result with $R \to 0$:

$$\langle\psi_1|\frac{1}{r_1}|\psi_1\rangle = Z\,. \tag{5.12}$$

The two terms can be combined into one quantity K (cf. 5.10)

$$K = Z(Z-1) - \frac{1}{R}(1-(1+ZR)e^{-2ZR})$$

which then leads to the final result for H_1:

$$H_1 = -\frac{Z^2}{2} + \frac{1}{R} + K \tag{5.13}$$

We will next turn to the calculation of H_2 (cf. 5.9)

$$H_2 = \langle\psi_2|H|\psi_1\rangle = (-\frac{Z^2}{2}+\frac{1}{R})\cdot S + \underbrace{(Z-1)\langle\psi_2|\frac{1}{r_1}|\psi_1\rangle - \langle\psi_2|\frac{1}{r_2}|\psi_1\rangle}_{:=A} \tag{5.14}$$

$$\langle\psi_2|\frac{1}{r_1}|\psi_1\rangle = \langle\psi_2|\frac{1}{r_2}|\psi_1\rangle = \int \frac{\psi_1(\mathbf{r})\psi_2(\mathbf{r})}{r_1}\, d^3r = \int \frac{\sqrt{\rho_1(\mathbf{r})\rho_2(\mathbf{r})}}{r_1}\, d^3r \qquad .$$

$\langle\psi_2|\frac{1}{r_2}|\psi_1\rangle$ represents the so-called exchange interaction, an interference effect that does not have a classical equivalent. The exchange interaction is proportional to the overlap of the wavefunctions and therefore falls off with e^{-ZR}. The contributions of the exchange interaction are

$$A = (Z-1)\langle\psi_2|\frac{1}{r_1}|\psi_1\rangle - \langle\psi_2|\frac{1}{r_2}|\psi_1\rangle = (Z-2)\cdot Z(1+RZ)e^{-RZ} \qquad .$$

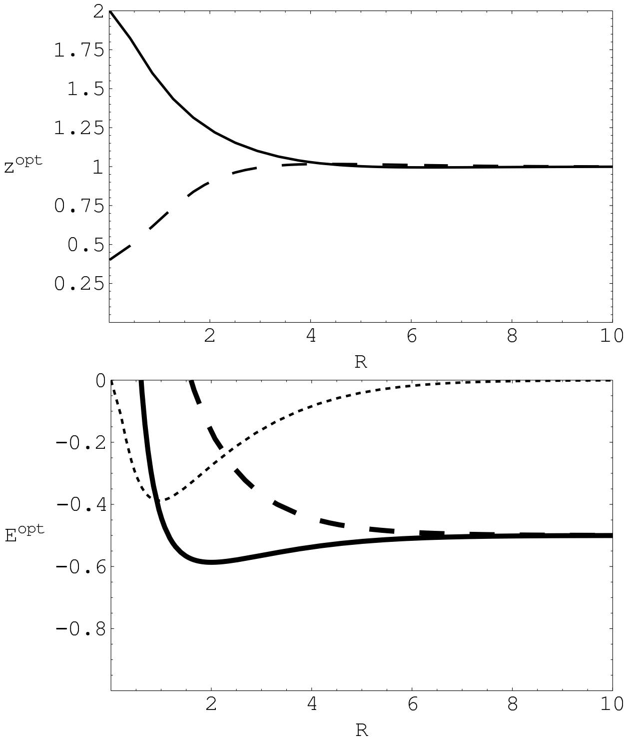

Figure 5.3:

As a last step we need to calculate the overlap integral S.

$$S = \int \psi_1(\mathbf{r})\psi_2(\mathbf{r})\, d^3r = (1+ZR+\frac{1}{3}(ZR)^2)e^{-ZR}$$

We can now insert the expressions for H_1 5.13 and H_2 5.14 into 5.7 and 5.8 and thus obtain the energies for the bonding and the antibonding state for a fixed variational parameter Z and a fixed distance R between the nuclei:

$$E_{b/a}(R,Z) = \frac{H_1 \pm H_2}{1 \pm S} = (-\frac{Z^2}{2} + \frac{1}{R}) + \frac{K \pm A}{1 \pm S}$$

In the upper part of Figure 5.3 $Z^{\text{opt}}(R)$ is depicted for the bonding (continuous line) and the anti-bonding (dashed line) state as a function of R. The lower part shows $E^{\text{opt}}(R, Z^{\text{opt}}(R))$ as a function of R for the binding (continuous line) and the anti-binding (dashed line) state, as well as the exchange interaction term $A(r)$ (thin dashed line)..

- For a fixed R one can determine the optimum $Z^{\text{opt}}(R)$ separately for the two solutions a/b by calculating $\min_Z E_{b/a}$. $Z^{\text{opt}}_{b/a}(R)$ is plotted in figure 5.3 .

The plot shows that only for the binding state the energy approaches the correct value for $R \to 0$.

- In the lower part of figure 5.3 the corresponding energies $E_\alpha(R, Z_\alpha^{\text{opt}}(R))$ are plotted for $\alpha = a$ and $\alpha = b$. Only the bonding state $\psi_b = \frac{\psi_1+\psi_2}{\sqrt{2(1+S)}}$ gives a total energy ($E_{min} = -0.586a.u.$) that is smaller than the energy of the dissociated molecule $E_{\,dis} = E(\mathbf{H} + \mathbf{H}^+) = -1Ry = -\frac{1}{2}a.E..$ The difference between the two energies corresponds to the binding energy

$$\Delta E = E(\mathbf{H}_2^+) - E(\mathbf{H} + \mathbf{H}^+) = 0.086\text{a.u.} = 0.086 \cdot 27.2\ eV = 2.35\ eV$$

  Experimentally one finds a binding energy of 2.8 eV. Since the total energy is $E_{\text{tot}} = -16.95\ eV$, the deviation only amounts to a relative error of $\approx$ 3%, which is a fairly good result for such a rough approximation of the wavefunction.

- The equilibrium distance $R^{\text{opt}} = 2.00a.u. = 2.00 * 0.529\ \overset{\circ}{A} = 1.06\ \overset{\circ}{A}$ is in agreement with the experimentally measured value.

- If one keeps the atomic number fixed at $Z = 1$, one obtains
  - $E_{\text{bind}} = 1.8\ eV$
  - $R^{\text{opt}} = 1.3\ \overset{\circ}{A}$.

  Clearly, taking the atomic number Z as a variational parameter leads to a significantly better result.

- In the case of ψ_b the bonding is caused by an accumulation of electron density in between the nuclei (c.f. 5.2). In this position the the attractive energy between electron charge and nuclei gives the largest contribution.

- The method that we used in order to construct molecular wavefunctions from atomic wavefunctions is called Linear Combination of Atomic Oritals (LCAO) and is widely used in quantum chemistry and solid state physics.

5.4.1 Muon-catalysed fusion

The equilibrium distance between the protons in $\mathbf{H}_2^+$ was determined to be

$$R^* = 2.0a.u. = 2.0\frac{\hbar}{me^2}$$

If, instead of electrons, we had used muons that are 210 times heavier than electrons and, as electrons, have Spin $\frac{1}{2}$ and charge -e, we would have found the equilibrium distance to be

$$R^{\text{opt/Muon}} = \frac{R^{\text{opt/Electron}}}{210}$$

.

This could be exploited to bring nuclei closer to each other. One could think of the following reaction

$$\text{Deuterium}^{+} + \text{Deuterium}^{+} + \mu \overset{\text{Fusion!}}{\longrightarrow} \text{Tritium} + p + 4.0MeV$$

Such reactions have indeed been observed experimentally. Deuterium is available in abundance in the oceans.

In contrast to conventional nuclear fusion, where the Deuterium atoms overcome the Coulomb barrier due to their high kinetic energy (heat), Muon-catalysed fusion constitutes a cold fusion.
However, Muons are not very stable[3] and do not occur naturally (except in cosmic radiation). Therefore, in order to achieve cold fusion the muons first have to be generated in accelerators. So far this type of fusion is not feasible.

5.5 Van der Waals Interaction

- We consider a simple (yet unrealistic) model to understand the van der Waals interaction that consists of two Hydrogen atoms at large distances.
- We use time-independent perturbation theory in order to calculate the Van der Waals interaction.
- For our model the first order energy correction is zero due to the fact that the ground state of the two atoms is spherically symmetric and does not have an electric dipole.
- To find a nonzero result we need to go to second order, which consists in a first order change of the wavefunction leading to the formation of a dipole.

Another interesting application of time-independent perturbation theory is the long range Van der Waals interaction between neutral atoms. This interaction is a consequence of quantum mechanics and results from the fact that the atomic

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[3] Lifetime = 2.2 μsec

states of the two separate atoms begin to correlate upon approaching which leads to mutual polarization. Though Van der Waals interaction is also present between charged particles, it is in that case dominated by the Coulomb interaction.

We now consider the case of two Hydrogen atoms in their ground state. As with the $\mathbf{H}_2^+$ molecule and based on the same reasoning, we use the Born Oppenheimer approximation. The atomic nuclei are positioned at a fixed large distance r along the z-axis (cf. Fig. 5.4). $\mathbf{r}_1$ represents the vector pointing from the first proton to 'its' electron, $\mathbf{r}_2$ likewise represents the vector that points from the second proton to 'its' electron. The Hamilton operator in spatial representation for the two nuclei with electrons (in atomic units) takes the form

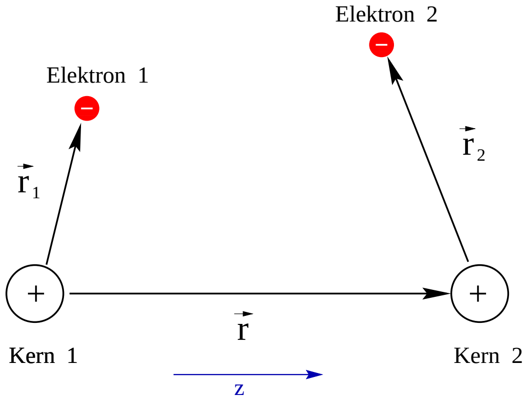

Figure 5.4: *Geometrical arrangement for the calculation of the Van der Waals interaction between two Hydrogen atoms.*

$$\begin{aligned} H = &(-\frac{\nabla_1^2}{2} - \frac{1}{r_1}) + (-\frac{\nabla_2^2}{2} - \frac{1}{r_2}) && =: H_0 \\ &+ \underbrace{\frac{1}{r}}_{\mathscr{K}_1-\mathscr{K}_2} + \underbrace{\frac{1}{|\mathbf{r}+\mathbf{r}_2-\mathbf{r}_1|}}_{\mathscr{E}_1-\mathscr{E}_2} - \underbrace{\frac{1}{|\mathbf{r}+\mathbf{r}_2|}}_{\mathscr{K}_1-\mathscr{E}_2} - \underbrace{\frac{1}{|\mathbf{r}-\mathbf{r}_1|}}_{\mathscr{K}_2-\mathscr{E}_1} && =: H_1(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2) \quad . \end{aligned} \tag{5.15}$$

where $\mathscr{K}_\alpha$ signifies the nucleus α and $\mathscr{E}_\alpha$ signifies the electron α. Since we are only interested in large nuclear distances, H_1 is small and can be treated with perturbation theory . The Schrödinger equation for H_0 can be easily solved, since $H_0 = H_0^1 + H_0^2$ consists of two identical Hamilton operators for the two separated Hydrogen atoms. We obtain the ground state wavefunction of the system described by H_0:

$$\psi_0 = \psi^1(\mathbf{r}_1)\psi^2(\mathbf{r}_2)$$

$$H_0^\alpha \psi^\alpha(\mathbf{r}_\alpha) = E\psi^\alpha(\mathbf{r}_\alpha)$$

$$\psi_0 = (\tfrac{1}{\pi})^{\frac{1}{2}}\, e^{-r_1}\, (\tfrac{1}{\pi})^{\frac{1}{2}}\, e^{-r_2}$$

The superscript indices of the wavefunctions indicate the nucleus around which the function is localized. The first order energy correction $E^1(r) \equiv \langle\psi_0|H_1|\psi_0\rangle$ gives

$$E^1(r) = \int \rho(\mathbf{r}_2)\rho(\mathbf{r}_1)H_1(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2)d^3\mathbf{r}_1\, d^3\mathbf{r}_2$$

In order to calculate $E^1(r)$ we will make use of the integral below 5.16 . This is nothing other than the Coulomb potential of the electron in the ground state of the Hydrogen atom. The solution to this integral, using Gauss's law, has already been derived in : Sec. A.13.

$$\tilde{V}(r) = \int \frac{1}{|\mathbf{r}-\mathbf{r_1}|}\,\rho(r_1)\,d^3r_1 = \frac{1}{r} - e^{-2r}\big(1+\frac{1}{r}\big)\,. \tag{5.16}$$

For large distances 5.16 approaches the Coulomb potential of a point charge. As discussed at the beginning of this section, when dealing with Van der Waals interactions we are only interested in large distances, i.e. distances that are large compared to the dimension of the atoms ($r \gg 1$).[4] We can therefore, up to corrections that are exponentially small in r, approximate the Coulomb potential for the given charge distribution by

$$\tilde{V}(r) \approx \frac{1}{r}$$

The contributions to the first order energy correction that arise from the nucleus-nucleus and the nucleus-electron interaction 5.15 all boil down to integrals of the type $\tilde{V}$ and give, except for an additional sign, the contribution $1/r$.

$$\begin{aligned} E^{(1)}_{K_1,K_2} &= \frac{1}{r} \\ E^{(1)}_{K_1,E_2} &= -\frac{1}{r} \\ E^{(1)}_{K_2,E_1} &= -\frac{1}{r} \end{aligned}$$

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[4] Since we do not take into account the fermionic nature of the electrons in this model, our considerations only make sense as long as the distance between the atoms is large enough so that the overlap of the electron wavefunctions is negligible.

The electron-electron interaction in 5.15 consists of a two-center integral that can be calculated in two steps by again making use of $\tilde{V}$:

$$E^{(1)}_{\mathscr{E}_1\mathscr{E}_2} := \int d^3r_2 \underbrace{\left(\int d^3r_1 \frac{1}{|\mathbf{r}+\mathbf{r}_2-\mathbf{r}_1|}\,\rho(r_1)\right)}_{\tilde{V}(|\mathbf{r}+\mathbf{r}_2|)} \rho(r_2)$$

$$\approx \int d^3r_2 \frac{1}{|\mathbf{r}+\mathbf{r}_2|}\,\rho(r_2) = \tilde{V}(r_2) \approx \frac{1}{r}$$

The calculated contributions to $E^{(1)}(r)$ add up to zero, except for the terms that exponentially (e^{-2r}) decrease with the distance r. This is due to the spherical symmetry of the ground state wavefunction. In order to obtain nonvanishing contributions, or more specifically contributions that do not fall off exponentially, we need to calculate the leading terms of second order perturbation theory . For this purpose we expand $H_1(\mathbf{r},\mathbf{r}_1,\mathbf{r}_2)$ 5.15 in powers of r_i/r . Notice that H_1 describes the interaction of the electron and nucleus "$N2$" in the electric potential φ_1 of the "$N1$" (or vice-versa). To leading order r_1/r (see Electromagnetic Fields, Chap. 1) this is the corresponding **dipole field**, with the dipole $\mathbf{d}_1 = -\mathbf{r}_1$. On the other hand, the potential energy of the system $N2$ in the potential φ_1 to leading order in r_2/r is given by (see Electromagnetic Fields, Chap. 2)

$$H_1 = -\mathbf{E}_1 \cdot \mathbf{d}_2$$

where $\mathbf{E}_1$ is the electric field produced by the charges $N1$, and $\mathbf{d}_2 = -\mathbf{r}_2$ is the dipole of $N2$. Using the well known expression for the electric field of a dipole, one gets (in cgs)

$$H_1 = -\frac{1}{r^3}\left(3(\mathbf{r}_1\cdot\mathbf{r})(\mathbf{r}_2\cdot\mathbf{r})/r^2 - \mathbf{r}_1\cdot\mathbf{r}_2\right) + O(\frac{1}{r^4}) \quad = \frac{x_1x_2+y_1y_2-2z_1z_2}{r^3} + O(\frac{1}{r^4})\,,$$

where in the last term we have taken for definiteness $\mathbf{r} = r\mathbf{e}_z$, i.e. along the z-axis. Second order perturbation theory gives:

$$\Delta E = -\sum_{n_1,n_2}{}' \frac{|\left\langle \psi^1_{n_1}\psi^2_{n_2}\middle| H_1 \left|\psi^1_0\psi^2_0\right\rangle|^2}{E_{n_1}+E_{n_2}-2E_1} =$$

$$= \frac{1}{r^6}\sum_{n_1,n_2}{}' \frac{|\left\langle \psi^1_{n_1}\psi^2_{n_2}\middle| x_1x_2+y_1y_2-2z_1z_2 \left|\psi^1_0\psi^2_0\right\rangle|^2}{E_{n_1}+E_{n_2}-2E_1}$$

The term $n_1 = n_2 = 1$ is excluded from the sum. The second order energy correction is, as was previously shown in general, negative.

VAN DER WAALS INTERACTION

$$E_{\mathrm{vdW}} = -c\frac{1}{r^6} \qquad .$$

The essential properties of Van der Waals interactions are:

- The interaction is attractive $\left(\mathbf{F}(\mathbf{r}) = -\nabla E = -6c\frac{\mathbf{r}}{r^8}\right)$
- The potential falls off with $1/r^6$.
  - It arises from two dipole potentials that each fall off with $1/r^3$.
  - Since the ground state ψ_0 is spherically symmetric, the dipoles are induced by virtual excitations to the excited states.
- The Van der Waals interaction can be observed for neutral atoms.
  It also exists for charged atoms, but is in this case dominated by the monopole term of the Coulomb interaction.

Chapter 6

Several degrees of freedom and the product space

Many physical problems deal with subsystems or multiple degrees of freedom, e.g. atoms are composed of a nucleus and electrons. The electrons in turn are described by spatial coordinates, plus one degree of freedom for spin.
We start with the Hilbert spaces $\mathscr{H}_1, \mathscr{H}_2, \cdots$ of the idividual subsystems/degrees of freedom and construct the Hilbert space of the whole system from them.
example 1:

Electron: $\mathscr{H}_{\mathscr{R}}$ for position (bound state):
set of all functions $f(\mathbf{x})$ with $\int |f(\mathbf{x})|^2\, d^3x < \infty$
$\mathscr{H}_{\mathscr{S}}$ for spin:
Vector space, spanned by the eigenstates of S^z
of the spin operators.

6.1 The Tensor Product

We take two vectors $|\Phi\rangle_1$ and $|\Psi\rangle_2$ from two different Hilbert spaces $\mathscr{H}_1$, $\mathscr{H}_2$ and formally construct a product out of them. (no scalar product and no outer product). The product is written as (different notations may be used):

$$|\Phi,\Psi\rangle := |\Phi\rangle_1 \otimes |\Psi\rangle_2 := |\Phi\rangle \otimes |\Psi\rangle := |\Phi\rangle|\Psi\rangle \qquad . \tag{6.1}$$

Meaning that subsystem 1 is in state $|\Phi\rangle$ and subsystem 2 is in state $|\Psi\rangle$. For the sake of simplicity the indices are eventually left out and remain represented solely by the order of the state vectors. The corresponding "bra" vector is written as

$$\langle\Phi,\Psi| := \langle\Phi| \otimes \langle\Psi| \qquad . \tag{6.2}$$

This product, called tensor product , is supposed to represent a vector from a linear vector space that describes the physics of the combined system. Evidently the vector neither lies in $\mathscr{H}_1$ nor in $\mathscr{H}_2$, but in a so-called product space

$$\mathscr{H} = \mathscr{H}_1 \otimes \mathscr{H}_2 \qquad .$$

$\mathscr{H}$ is spanned by all vectors of the form 6.1 and their linear combinations. From the **distributivity** of $|\Phi\rangle$ it follows that:

$$\begin{aligned} |\Phi\rangle &= a|\Phi_1\rangle + b|\Phi_2\rangle \qquad \Rightarrow \\ |\Phi\rangle \otimes |\Psi\rangle &= a|\Phi_1\rangle \otimes |\Psi\rangle + b|\Phi_2\rangle \otimes |\Psi\rangle \end{aligned}$$

The same applies to $|\Psi\rangle$.

Def. 6.1 (Scalar product in product space)**.** *The scalar product of two product vectors is defined as the product of the scalar products in the two subspaces:*

$$\langle \Phi_A, \Psi_A | \Phi_B, \Psi_B \rangle = \langle \Phi_A | \Phi_B \rangle \, \langle \Psi_A | \Psi_B \rangle \tag{6.3}$$

The **linearity** of Quantum Mechanics also allows for linear combinations of product states 6.1 .

$$a \, |\Phi_A \Psi_A\rangle + b \, |\Phi_B \Psi_B\rangle \tag{6.4}$$

They usually describe **entangled states** that cannot be written as a tensor product of the form $|\Phi\rangle \otimes |\Psi\rangle$.

6.2 Complete basis in the product space

If $\{|\Phi_k\rangle, k = 1, 2, \cdots\}$ is a complete basis of $\{\mathscr{H}_1\}$ and $\{|\Psi_l\rangle, l = 1, 2, \cdots\}$ is a complete basis of $\mathscr{H}_2$, then $\{|\Phi_k\rangle \otimes |\Psi_l\rangle, l = 1, 2, \cdots, k = 1, 2, \cdots\}$ is a complete basis of the product space $\mathscr{H}_1 \otimes \mathscr{H}_2$.
In the product space the index tuples (k,l) consecutively number the basis vectors. If the dimension of $\mathscr{H}_\alpha$ is given by N_α, the dimension of the product space $\mathscr{H}_1 \otimes \mathscr{H}_2$ is equal to $N_1 \cdot N_2$. This concept is also applicable to ∞-dimensional subspaces and it is a straightforward matter to generalize it to any continuous spaces.

6.3 Orthonormalization in product space

Using 6.3 it immediately follows from the orthonormal vectors of the subspaces that

$$\langle \Phi_k, \Psi_l | \Phi_{k'}, \Psi_{l'} \rangle = \langle \Phi_k | \Phi_{k'} \rangle \langle \Psi_l | \Psi_{l'} \rangle = \delta_{k,k'} \delta_{l,l'}$$

If $|\Phi_k\rangle$, $|\Psi_l\rangle$ are two complete orthonormal bases in $\mathscr{H}_1, \mathscr{H}_2$, then

$$\sum\!\!\!\!\!\!\int_k \sum\!\!\!\!\!\!\int_l |\Phi_k, \Psi_l\rangle\langle\Phi_k, \Psi_l| \; dk \, dl = \mathbb{1}$$

$\sum\!\!\!\!\!\!\int_k$ represents either a sum or an integral over the variable k, depending on whether k is a discrete or a continuous quantity.
Any vector $|\Omega\rangle$ in the product space can be expanded as

$$|\Omega\rangle = \sum\!\!\!\!\!\!\int_k \sum\!\!\!\!\!\!\int_l \langle\Phi_k, \Psi_l|\Omega\rangle \;\; |\Phi_k, \Psi_l\rangle \; dk \, dl$$

Examples:

- **Electron with Spin:**
  $|\Psi\rangle$ represents the spatial wave function, i.e. $\langle\mathbf{x}|\Psi\rangle = \Psi(\mathbf{x})$
  $|\chi\rangle$ describes the spin (Basis: S^z-eigenstates $|\sigma\rangle$) [1]
  $|\Psi, \chi\rangle = |\Psi\rangle \otimes |\chi\rangle$ then describes the total state of an electron with a spatial wave fuction $\Psi(\mathbf{x})$ and spin χ.
  In this **product state** the total wave function is

  $$\psi(\mathbf{x}, \sigma) := \langle\mathbf{x}, \sigma|\Psi, \chi\rangle = \langle\mathbf{x}|\Psi\rangle \; \langle\sigma|\chi\rangle = \Psi(\mathbf{x}) \cdot \chi(\sigma)$$

  One possible wave function of the system is an entangled state consisting of a linear combination of product states:

  $$\psi(\mathbf{x}, \sigma) = \Psi_A(\mathbf{x})\chi_A(\sigma) + \Psi_B(\mathbf{x})\chi_B(\sigma) \qquad .$$

- **Two different particles without spin:**
  $|\Psi_1\rangle$ describes the wave function of the first particle.
  $|\Psi_2\rangle$ describes the wave function of the second particle.
  then $|\Psi_1, \Psi_2\rangle$ describes the combined state. (e.g. basis: $|\mathbf{x}_1, \mathbf{x}_2\rangle$)
  The wave function then is

  $$\psi(\mathbf{x}_1, \mathbf{x}_2) = \langle\mathbf{x}_1, \mathbf{x}_2|\Psi_1, \Psi_2\rangle = \Psi_1(\mathbf{x}_1) \cdot \Psi_2(\mathbf{x}_2)$$

  Also in this case we can construct an entangled wave function

  $$\psi_{ENT}(\mathbf{x}_1, \mathbf{x}_2) = \big(\Psi_1(\mathbf{x}_1)\Psi_2(\mathbf{x}_2) + \tilde{\Psi}_1(\mathbf{x}_1)\tilde{\Psi}_2(\mathbf{x}_2)\big)$$

---

[1] For the representation of spin states several equivalent notations exist: $|\pm 1\rangle$, or $|\pm\frac{1}{2}\rangle$, or $|\pm z\rangle$, or $|\uparrow\rangle, |\downarrow\rangle$. They all describe the eigenstates of S^z with eigenvalues $\pm\hbar/2$.

Product states of the type $|\Psi\rangle \otimes |\Phi\rangle$ describe uncorrelated particles. These vectors are also called fundamental tensors. States that cannot be represented in that way are called "entangled" states. They arise from interactions between the particles. For example consider a system of two spins in the state

$$|\Psi\rangle = \Big(|{+z}\rangle \otimes |{-z}\rangle\Big) + \Big(|{-z}\rangle \otimes |{+z}\rangle\Big)$$

None of the two spins is in an eigenstate of the corresponding operators [2] S_1^z, S_2^z:

$$\begin{aligned}
S_1^z|\Psi\rangle &= S_1^z\Big(|{+z}\rangle \otimes |{-z}\rangle + |{-z}\rangle \otimes |{+z}\rangle\Big) \\
&= \frac{\hbar}{2}|{+z}\rangle \otimes |{-z}\rangle + \frac{-\hbar}{2}|{-z}\rangle \otimes |{+z}\rangle \\
&= \frac{\hbar}{2}\Big(|{+z}\rangle \otimes |{-z}\rangle - |{-z}\rangle \otimes |{+z}\rangle\Big) \neq \frac{\hbar}{2}|\Psi\rangle
\end{aligned}$$

The concept of the tensor product can be immediately extended to an arbitrary number of subspaces.

$$|\Psi_1, \Psi_2, \cdots, \Psi_n\rangle = |\Psi_1\rangle \otimes |\Psi_2\rangle \otimes \cdots \otimes |\Psi_n\rangle = \bigotimes_{i=1}^{n} |\Psi_i\rangle$$
$$\mathscr{H} = \mathscr{H}_1 \otimes \mathscr{H}_2 \otimes \cdots \otimes \mathscr{H}_n$$

6.4 Operators in tensor product space

All assumptions previously made about linear operators are also valid for operators in product spaces. Let us consider an operator $\mathscr{L}$ in the basis states

$$\begin{aligned}
|\Phi_k, \Psi_l\rangle &:= |\Phi_k\rangle \otimes |\Psi_l\rangle \\
L(kl;k'l') &:= \langle\Phi_k, \Psi_l|\mathscr{L}|\Phi_{k'}, \Psi_{l'}\rangle
\end{aligned}$$

If $\mathscr{L}$ only acts on $\mathscr{H}_1$, it is represented in $\mathscr{H}_1 \otimes \mathscr{H}_2$ as:

$$\mathscr{L}_1 := \big(\mathscr{L} \otimes \mathbb{1}\big) \;\Rightarrow\; \big(\mathscr{L} \otimes \mathbb{1}\big)|\Phi_k, \Psi_l\rangle = \Big(\mathscr{L}|\Phi_k\rangle\Big) \otimes |\Psi_l\rangle \qquad .$$

In analogy, if the operator $\mathscr{M}$ only acts on vectors in $\mathscr{H}_2$, it is represented in the product space as follows:

$$\mathscr{M}_2 := \big(\mathbb{1} \otimes \mathscr{M}\big) \;\Rightarrow\; \big(\mathbb{1} \otimes \mathscr{M}\big)|\Phi_k, \Psi_l\rangle = |\Phi_k\rangle \otimes \Big(\mathscr{M}|\Psi_l\rangle\Big) \qquad .$$

---

[2] In order to avoid confusion with the indices of the subspaces we will henceforth specify the components of spin and angular momentum as "superscripts", e.g. S^z, J^x, L^+, J^-, etc. The lower index $(1,2)$ indicates to which state the operator applies.

In the basis of the product space the matrix elements of $\mathscr{L}_1$ and $\mathscr{M}_2$ are

$$\begin{aligned} L_1(kl;k'l') &\equiv \langle \Phi_k, \Psi_l|\mathscr{L}_1|\Phi_{k'}, \Psi_{l'}\rangle = & \langle \Phi_k|\mathscr{L}|\Phi_{k'}\rangle \cdot \delta_{ll'} \\ M_2(kl;k'l') &\equiv \langle \Phi_k, \Psi_l|\mathscr{M}_2|\Phi_{k'}, \Psi_{l'}\rangle = & \delta_{kk'} \cdot \langle \Psi_l|\mathscr{M}|\Psi_{l'}\rangle \end{aligned}$$

Operators on different subsystems always commute with each other:

$$[\mathscr{L}_1, \mathscr{M}_2] = 0 \tag{6.5}$$

The product of the two operators $\mathscr{L}_1\mathscr{M}_2$ is represented as a tensor product: $\mathscr{L} \otimes \mathscr{M}$. It means that $\mathscr{L}$ applies to the first state and $\mathscr{M}$ to the second one:

$$\mathscr{L}_1\mathscr{M}_2\,|\Phi_k, \Psi_l\rangle = (\mathscr{L}\,|\Phi_k\rangle) \otimes (\mathscr{M}\,|\Psi_l\rangle)$$

Correspondingly, its matrix elements read:

$$\langle \Phi_k, \Psi_l|\mathscr{L}_1\mathscr{M}_2|\Phi_{k'}, \Psi_{l'}\rangle = \langle \Phi_k|\mathscr{L}|\Phi_{k'}\rangle \cdot \langle \Psi_l|\mathscr{M}|\Psi_{l'}\rangle$$

As an example let us consider the spin-orbit coupling that occurs in the relativistic treatment of the wave function of an atom. The operator describing the coupling is proportional to

$$\mathbf{S} \cdot \mathbf{L} = \sum_{n=1,2,3} S^n L^n$$

the product of spin and angular momentum vector operator. The eigenvectors $|\sigma\rangle$ of S^z can serve as basis states for the spin. For the orbital part one possible choice of basis are the joint eigenvectors $|l,m\rangle$ of L^2 and L^z.

The fundamental tensor products are $|l,m,\sigma\rangle = |l,m\rangle \otimes |\sigma\rangle$. In this basis the matrix elements of the z-component of the spin-orbit coupling take the following form:

$$\begin{aligned} \langle l,m,\sigma|L^z \otimes S^z|l',m',\sigma'\rangle &= \langle l,m|L^z|l',m'\rangle \quad \cdot \quad \langle \sigma|S^z|\sigma'\rangle \\ &= \hbar\, m\, \delta_{m,m'}\delta_{l,l'} \quad \cdot \quad \frac{\hbar}{2}\,\sigma\,\delta_{\sigma,\sigma'} \qquad . \end{aligned}$$

The $\otimes$ between the operators is often omitted, when it is clear to which state each operator acts.

Probabilities

As a further application one may ask what is the probability $P(\Phi_l)$ that a state $|\Psi\rangle$ in $\mathscr{H}$ is found in an eigenstate $|\Phi_l\rangle$ of an operator of, say, the first subspace $\mathscr{H}_1$. This is, as usual given by the square modulus of the projection of $|\Psi\rangle$ onto the space spanned by $|\Phi_l\rangle$. Here, the identity is applied to the second subspace. The corresponding projection operator, thus becomes

$$|\Phi_l\rangle\langle\Phi_l|\otimes \mathbb{1}$$

and the probability

$$P(\Phi_l) = \frac{|(|\Phi_l\rangle\langle\Phi_l|\otimes \mathbb{1})\,|\Psi\rangle|^2}{\langle\Psi|\Psi\rangle}$$

The norm in the denominator can be as usual be omitted if the state is already normalized.

Example

Consider a particle in spin-orbit coupled state

$$|\Psi\rangle = \alpha\,|l,m\rangle\otimes|+z\rangle + \beta\,|l,m+1\rangle\otimes|-z\rangle$$

When measuring the z-component of the spin, the probability $P(s_z = -\frac{\hbar}{2})$ to obtain $-\frac{\hbar}{2}$ if given by

$$P(s_z = -\frac{\hbar}{2}) = \quad \cdots\cdots \tag{6.6}$$

$$\cdots\cdots \tag{6.7}$$

A little more difficult is $P(s_x = +\frac{\hbar}{2})$. One possibility is to expand $|\pm z\rangle$ in the $|\pm x\rangle$ basis. Alternatively (we now take a normalized state $|\alpha|^2 + |\beta|^2 = 1$):

$$\begin{aligned}
P(s_x = +\frac{\hbar}{2}) = \quad & |(\mathbb{1}\otimes|+x\rangle\langle+x|)\,|\Psi\rangle|^2 = \\
& \left|\left(\alpha\,|l,m\rangle\underbrace{\langle+x|+z\rangle}_{1/\sqrt{2}} + \beta\,|l,m+1\rangle\underbrace{\langle+x|-z\rangle}_{1/\sqrt{2}}\right)\otimes|+x\rangle\right|^2 \\
& = \frac{1}{2}\left(|\alpha|^2 + |\beta|^2\right) = \frac{1}{2}
\end{aligned}$$

6.5 Systems with two spin $\frac{1}{2}$ particles

In order to describe the spin state with two particles (i.e., we omit the spatial part) we use the (fundamental) product basis

$$|\sigma_1\rangle\,|\sigma_2\rangle\ .$$

Just a quick reminder:

$$\begin{aligned} S^z_\beta|\sigma\rangle_\beta &= \frac{\hbar}{2}\sigma|\sigma\rangle_\beta \\ S^2_\beta|\sigma\rangle_\beta &= \cdots\cdots \end{aligned}$$

Here, the index β specifies the particle to which the state vector or spin operator refers to. The product basis is complete. All spin information of the two spin-1/2 particles can be expressed using this product basis.
As long as no external B-field is applied the **total spin** of the system

$$\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$$

is conserved, this means that all its 3 components commute with the Hamilton operator. However, the same does not necessarily hold true for the individual spins $\mathbf{S}_1$ and $\mathbf{S}_2$. For example, if we include some interaction between the two particles, $\mathbf{S}_1$ and $\mathbf{S}_2$ do not commute with the Hamilton operator. Therefore, the eigenvalues of the individual z-components S^z_α do not represent suitable quantum numbers (conserved quantities) anymore. The z-component of the **total spin** $S^z \equiv S^z_1 + S^z_2$, however, does remain a suitable quantum number. It is therefore both useful and interesting to solve the eigenvalue problem of the total spin operator. Since $\mathbf{S}_1/\hbar$ ($\mathbf{S}_2/\hbar$) generates the rotations of the spin of the first (second) particle, $\mathbf{S}/\hbar$ is the generator of the rotations of the total spin (in product space) Details: Sec. A.16 . Consequently, the same commutation rules that hold for $\mathbf{S}_1$ and $\mathbf{S}_2$ must apply to $\mathbf{S}$:

$$[S^\alpha, S^\beta] = i\hbar\varepsilon_{\alpha\beta\gamma} S^\gamma \qquad . \tag{6.8}$$

From this it follows that

$$[S^z, \mathbf{S}^2] = 0$$

and that therefore, there must exist a joint basis for these two operators. We are now going to determine the relation between these joint eigenvectors and the product basis states $|\sigma_1\rangle|\sigma_2\rangle$, that is find the transformation between the two bases. At first, we note that, since $\mathbf{S}_1$ and $\mathbf{S}_2$ apply to different particles, i.e. different subsystems (cf. 6.5)

$$[S^\alpha_1, S^\beta_2] = 0$$

As a consequence,

$$[\mathbf{S}^2_1, \mathbf{S}^2_2] = 0$$

furthermore, considering that $\mathbf{S}^2_1$ commutes with all components S^α_1:

$$[\mathbf{S}^2_1, \mathbf{S}^2] = [\mathbf{S}^2_1, \sum_\alpha (S^\alpha_1 + S^\alpha_2)^2] = 0$$

and similarly for $\mathbf{S}_2^2$. In addition, $\mathbf{S}_1^2$ and $\mathbf{S}_2^2$ also commute with $S^z = S_1^z + S_2^z$:

$$[S^z, \mathbf{S}_\alpha^2] = [S_1^z + S_2^z, \mathbf{S}_\alpha^2] = 0 \quad \alpha = 1,2 \,.$$

However, note that

$$[S_\alpha^z, \mathbf{S}^2] = \cdots\cdots \qquad \neq \mathbf{0}$$

We can therefore construct a basis of joint eigenvectors from the operators $\mathbf{S}_1^2, \mathbf{S}_2^2, \mathbf{S}^2$ and S^z, but not from the S_1^z,S_2^z separately.
We will be able to show that this joint eigenbasis spans the whole Hilbert space. We label the vectors of this new basis by $|s_1, s_2, j, m\rangle$, denoting the corresponding quantum numbers of the mutual commuting operators. These obey the following eigenvalue conditions:

$$\begin{aligned}
a)\quad & \mathbf{S}_1^2 |s_1, s_2, j, m\rangle &=& \quad \cdots\cdots \qquad |s_1, s_2, j, m\rangle \\
b)\quad & \mathbf{S}_2^2 |s_1, s_2, j, m\rangle &=& \quad \cdots\cdots \qquad |s_1, s_2, j, m\rangle \\
c)\quad & \mathbf{S}^2 |s_1, s_2, j, m\rangle &=& \quad \cdots\cdots \qquad |s_1, s_2, j, m\rangle \\
d)\quad & S^z |s_1, s_2, j, m\rangle &=& \quad \cdots\cdots \qquad |s_1, s_2, j, m\rangle \quad ,
\end{aligned} \tag{6.9}$$

with $s_1 = s_2 = 1/2$. The transformation between the product basis and the new basis is defined by the expansion coefficients $C_{\sigma_1;\sigma_2}^{(jm)}$ that remain to be calculated.

$$|s_1, s_2, j, m\rangle = \sum_{\sigma_1, \sigma_2 \in \{\pm 1\}} C_{\sigma_1, \sigma_2}^{(jm)} \,|\sigma_1\rangle\, |\sigma_2\rangle$$

6.6 Addition of angular momenta

The above issue can be made more general. Specifically, one can consider, instead of two spin $\frac{1}{2}$ systems, two systems with angular momenta $\mathbf{J}_1$ and $\mathbf{J}_2$.
For example, $\mathbf{J}_1$ can describe the orbital angular momentum of an electron and $\mathbf{J}_2$ its spin. In that case the corresponding quantum numbers will have the possible values $j_1 = 0, 1, \cdots, \infty$, and $j_2 = \frac{1}{2}$. The two angular momenta interact via spin-orbit coupling. This does not commute with $\mathbf{J}_1$ or $\mathbf{J}_2$ separately, but it does commute with $\mathbf{J} \equiv \mathbf{J}_1 + \mathbf{J}_2$. Another example is represented by two interacting atoms, each one with its own angular momentum $\mathbf{J}_i$ ($i = 1, 2$).
The discussion of Sec. 6.5 can be readily taken over, specifically, we have the following set of mutually commuting operators:

$$\mathbf{J}_1^2,\ \mathbf{J}_2^2,\ \mathbf{J}^2,\ \mathbf{J}^z$$

Accordingly, one can derive a **common eigenbasis** specified by the vectors $|j_1,j_2,j,m\rangle$ with the following eigenvalue properties:

$$\begin{array}{lllll} a) & \mathbf{J}_1^2|j_1,j_2,j,m\rangle & = & \hbar^2\, j_1(j_1+1) & |j_1,j_2,j,m\rangle \\ b) & \mathbf{J}_2^2|j_1,j_2,j,m\rangle & = & \hbar^2\, j_2(j_2+1) & |j_1,j_2,j,m\rangle \\ c) & \mathbf{J}^2|j_1,j_2,j,m\rangle & = & \hbar^2\, j(j+1) & |j_1,j_2,j,m\rangle \\ d) & J^z|j_1,j_2,j,m\rangle & = & \hbar m & |j_1,j_2,j,m\rangle \quad , \end{array} \tag{6.10}$$

The basis transformation is given by

$$|j_1,j_2,j,m\rangle = \sum_{m_i=-j_i}^{j_i} C(j_1,m_1;j_2,m_2|j,m)\,|j_1,m_1\rangle\,|j_2,m_2\rangle \tag{6.11a}$$

where the expansion coefficients

$$C(j_1,m_1;j_2,m_2|j,m) = \cdots\cdots \tag{6.11b}$$

are termed **Clebsch-Gordan coefficients** .

6.6.1 Scalar product

The advantage of this classification is that eigenvectors of $\mathbf{J}^2$ are also eigenvectors of an operator which often occurs in physics, namely the scalar product

$$\mathbf{J}_1\cdot\mathbf{J}_2\ .$$

For example, the spin-orbit coupling reads $\mathbf{L}\cdot\mathbf{S}$.
The term is straightforward to evaluate, since

$$\mathbf{J}^2 = \mathbf{J}_1^2+\mathbf{J}_2^2+2\mathbf{J}_1\cdot\mathbf{J}_2\ .$$

Therefore, eigenstates of $\mathbf{J}^2$ are also eigenstates of this operator

$$\mathbf{J}_1\cdot\mathbf{J}_2\,|j_1,j_2,j,m\rangle = \cdots\cdots \qquad |j_1,j_2,j,m\rangle \tag{6.12}$$

6.6.2 Different notations and terming conventions

The notation for the basis states on both sides in 6.11a can quickly become confusing, or overloaded. In order to reduce the number of indices to carry around, different conventions may be used. We start with the states of the **total angular momentum basis** (sometimes referred as **total spin** depending on what one is referring to)

$$|j_1, j_2, j, m\rangle \ .$$

In many situations, j_1 and j_2 are fixed, so it is not necessary to write them explicitly, therefore, one can replace it with the expression

$$|j, m\rangle \ . \tag{6.13}$$

This form will be used in the following.
For states in the (tensor) **product basis**

$$|j_1, m_1\rangle\,|j_2, m_2\rangle \tag{6.14}$$

again in situations in which j_1 and j_2 are fixed, these can be omitted leding to the form

$$|m_1\rangle\,|m_2\rangle \tag{6.15}$$

In this last case it is not advisable to use $|m_1, m_2\rangle$, as we do for tensor products, since this could be confused with 6.13 .
The notation may become confusing when we include concrete numbers. For example, assume I write the state

$$|3, 2\rangle \ .$$

Is this a state in the form 6.13 , or one of the two states in 6.14 ? What quantum numbers do 3 and 2 represent? If there can be such a confusion, it is advisable to write this explicitly in the following form

$$|j = 3, m = 2\rangle$$

Similarly I may have

$$|m_1 = +2\rangle\,|m_2 = -1\rangle$$

so that I know what I am referring to.
Finally, consider the case of a two-spin systems, i.e. two particles for which we just consider their spin degrees of freedom, but no spatial part [3] as in Sec. 6.5. Then for the product states we may have instead of 6.14

$$|s_1, m_1\rangle\,|s_2, m_2\rangle$$

---

[3] This is the case, for example, when the spatial parts of the wave function of the two particles are fixed to belong to a certain orbital or lattice site (a different one for the two particles) because moving them to another orbital would be energetically unfavorable

or σ_i instead of m_i. Notice that while in most cases $s_1 = s_2 = \frac{1}{2}$ there are also particles with larger values of s_i, and in this case the possible values of m_i are not just $\pm\frac{1}{2}$. Then one sometimes uses s for the total spin quantum number instead of j, so 6.13 becomes

$$|s,m\rangle\ .$$

6.6.3 Determining the allowed values of j

For the follwing discussion we work at fixed j_1, j_2 and, thus use 6.13 , i.e. replace $|j_1, j_2, j, m\rangle \to |j, m\rangle$. In this way, the Clebsch-Gordan coefficients may be represented as

$$C(j_1,m_1;j_2,m_2|j,m) = \langle j_1,m_1|\,\langle j_2,m_2|\,|j,m\rangle \tag{6.16}$$

There are some restrictions in the sum 6.11a . First, the z components are additive: $J^z = J_1^z + J_2^z$ so that $m = m_1 + m_2$. This does not hold for j, since $j \neq j_1 + j_2$. However, for given j_1 and j_2, not all values of the total angular momentum quantum number j are allowed: The maximum value m_{max} of m is given by the sum of the maximum values of m_1 and m_2, i.e. $m_{max} = j_1 + j_2$. Since there are no larger values of m, this state must have $j = j_1 + j_2$, and there are no larger values of j. So the first constraint is

$$j \leq j_1 + j_2\ .$$

This discussion clearly identifies (see 6.20 below)

$$|j = j_1 + j_2, m = j_1 + j_2\rangle = |j_1, j_1\rangle\,|j_2, j_2\rangle \tag{6.17}$$

Smaller values of j

Now going to the next smaller value $m = j_1 + j_2 - 1$, there are two states with this m, namely

$$|j_1, j_1 - 1\rangle\,|j_2, j_2\rangle \quad \text{and} \quad |j_1, j_1\rangle\,|j_2, j_2 - 1\rangle \tag{6.18}$$

in this 2 dimensional subspace one vector (a particular linear combination) must have $j = j_1 + j_2$, since if one vector of the multiplet is present, (here $|j = j_1 + j_2, m = j_1 + j_2\rangle$) then all other must be present. The other vector must have $j = j_1 + j_2 - 1$. The expressions of these two vectors $|j = j_1 + j_2, m = j_1 + j_2 - 1\rangle$ and $|j = j_1 + j_2 - 1, m = j_1 + j_2 - 1\rangle$ are nontrivial, since in general, they will be linear combinations of 6.18 .

The following discussion is shown schematically in Tab. 6.20 . One can proceed in the same way for smaller m, noticing that there are three independent vectors with $m = j_1 + j_2 - 2$, and that the subspace with that m will contain the vectors with $j = j_1 + j_2$, $j_1 + j_2 - 1$, and $j_1 + j_2 - 2$ (see 6.20). The

story continues for all $m = j_1 + j_2 - p$ with $p \leq 2j_2$ (for definiteness we assume $j_2 \leq j_1$). The subspace is $p+1$-dimensional, containing the vectors with $j = j_1 + j_2, j_1 + j_2 - 1, \cdots, j_1 + j_2 - p$.
However, the situation changes when $p = 2j_2 + 1$. In that case, there are not enough m_2 to have a total of $p+1$ states. This means that there will be no additional values of j. In summary the

POSSIBLE VALUES OF j ARE

$$j = j_1 + j_2,\ j_1 + j_2 - 1,\ j_1 + j_2 - 2,\ \cdots\ |j_1 - j_2|\,. \tag{6.19}$$

m	product states with that m	combine to j values
$j_1 + j_2$	$\|j_1, j_1\rangle \|j_2, j_2\rangle$	$j_1 + j_2$
$j_1 + j_2 - 1$	$\|j_1, j_1 - 1\rangle \|j_2, j_2\rangle$ $\|j_1, j_1\rangle \|j_2, j_2 - 1\rangle$	$j_1 + j_2$ $j_1 + j_2 - 1$
$j_1 + j_2 - 2$	$\|j_1, j_1 - 2\rangle \|j_2, j_2\rangle$ $\|j_1, j_1 - 1\rangle \|j_2, j_2 - 1\rangle$ $\|j_1, j_1\rangle \|j_2, j_2 - 2\rangle$	$j_1 + j_2$ $j_1 + j_2 - 1$ $j_1 + j_2 - 2$
$\cdots$	$\cdots$	$\cdots$
$j_1 - j_2$	$\|j_1, j_1 - 2 * j_2,\rangle \|j_2, j_2\rangle$ $\cdots$ $\|j_1, j_1\rangle \|j_2, -j_2\rangle$	$j_1 + j_2$ $\cdots$ $j_1 - j_2$
$\cdots$	$\cdots$	$\cdots$

(6.20)

Table 6.1: Schematic structure of the product space of two systems with angular momentum quantum numbers j_1 and j_2

6.6.4 Construction of the eigenstates

We illustrate here how to explicitly construct the eigenstates, i. e., in the end, the coefficients in 6.11a . For practical purposes, these coefficients are available in tables.
As discussed above, the first vector is given by

$$|j = j_1 + j_2, m = j_1 + j_2\rangle = |j_1, j_1\rangle |j_2, j_2\rangle$$

We can now find the next vector with the same j by applying the ladder operator 1.43 :

$$|j = j_1 + j_2, m = j_1 + j_2 - 1\rangle \propto J^- |j_1, j_1\rangle |j_2, j_2\rangle$$

since

$$J^- = J_1^- + J_2^-$$

we thus have (cf 1.43)

$$\begin{aligned} |j = j_1 + j_2, m = j_1 + j_2 - 1\rangle \propto & \cdots\cdots \\ & \cdots\cdots \quad , \end{aligned} \tag{6.21}$$

where the constant is obtained by normalisation. Since the subspace with $m = j_1 + j_2 - 1$ is spanned by the two vectors (see 6.20), the vector with $j = j_1 + j_2 - 1$ is simply the one orthogonal to 6.21 in this subspace.

The procedure goes on recursively like this: one applies the ladder operators to the two vectors $|j = j_1 + j_2, m = j_1 + j_2 - 1\rangle$ and $|j = j_1 + j_2 - 1, m = j_1 + j_2 - 1\rangle$ to obtain the two corresponding vectors with $m = j_1 + j_2 - 2$. The vector orthogonal to both of them in this three dimensional subspace is the one with $j = j_1 + j_2 - 2$. An so on.

6.6.5 Application to the case of two spin $\frac{1}{2}$

The procedure in Sec. 6.6.4 is quite complicated, but relatively easy for two spin $\frac{1}{2}$ systems. Here $j_1 = j_2 = \frac{1}{2}$ do not need to be specified. We have (cf. 6.17):

$$|j = 1, m = +1\rangle = \left|+\frac{1}{2}\right\rangle \left|+\frac{1}{2}\right\rangle \tag{6.22}$$

By applying the ladder operator (cf. 6.21)

$$|j = 1, m = 0\rangle \propto \cdots\cdots \quad , \tag{6.23}$$

and the proportionality (normalization) constant is clearly $\frac{1}{\sqrt{2}}$.

$|j = 0, m = 0\rangle$ is obtained by orthogonalizing to 6.23 :

$$|j = 0, m = 0\rangle \propto \cdots\cdots \quad , \tag{6.24}$$

again with proportionality constant $\frac{1}{\sqrt{2}}$. The sign (or the phase) is of course arbitrary. Finally, we could obtain $|j = 1, m = -1\rangle$ by applying J^- to 6.23 . However, it is easier to observe that $|j = 1, m = -1\rangle$ is the only state having $m = -1$, and thus it is given by

$$|j=1,m=-1\rangle = \left|-\frac{1}{2}\right\rangle \left|-\frac{1}{2}\right\rangle . \tag{6.25}$$

In problems in which the two spins interact with each other, but the Hamiltonian still commutes with the total spin, the four possible states split into the **singlet** $|j=0,m=0\rangle$ and the three degenerate **triplet** $|j=1,m=+1\rangle, |j=1,m=0\rangle, |j=1,m=-1\rangle$ states.

Singlet and triplet states of two spin-1/2 particles

$$\begin{array}{c|c|c|c}
j=0 & m=0 & \frac{1}{\sqrt{2}}\Big(|\uparrow\rangle\,|\downarrow\rangle - |\downarrow\rangle\,|\uparrow\rangle \Big) & \text{singlet} \\
\hline
 & m=+1 & |\uparrow\rangle\,|\uparrow\rangle & \\
j=1 & m=0 & \frac{1}{\sqrt{2}}\Big(|\uparrow\rangle\,|\downarrow\rangle + |\downarrow\rangle\,|\uparrow\rangle \Big) & \text{triplet} \\
 & m=-1 & |\downarrow\rangle\,|\downarrow\rangle\rangle &
\end{array} \tag{6.26}$$

6.6.6 How to use a table of Clebsch-Gordan coefficients

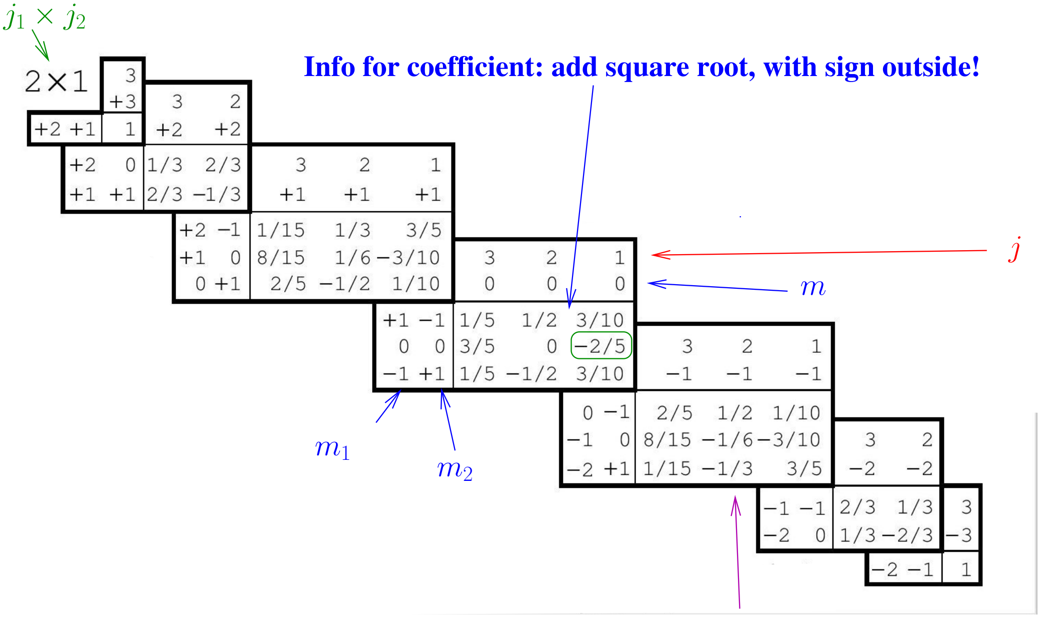
Let us recall the generic expansion 6.11a of a state with given total angular momentum quantum numbers j,m in terms of product states with quantum numbers j_1,m_1 , j_2,m_2.
A table of the coefficient of the expansion (Clebsch-Gordan coefficients) 6.16

$$C(j_1,m_1;j_2,m_2|j,m) = \langle j_1,m_1|\,\langle j_2,m_2|\,|j,m\rangle$$

can be found in http://pdg.lbl.gov/2002/clebrpp.pdf (just for me here) You can also use a SymPy module for example (or mathematica) to produce them.
To understand how to use this table 206 let us look at an example for $j_1 = 2, j_2 = 1$ This table gives information to get the coefficients of the expansion 6.11a

$$\langle j_1=2,m_1|\,\langle j_2=1,m_2|\,|j,m\rangle .$$

The inner rectangle contains, in principle, the coefficients, whereby one has to put a square root in front and pull the sign in front of it. In addition, when exchanging



m_1	m_2	$j=3$, $m=+3$
+2	+1	1

m_1	m_2	$j=3$, $m=+2$	$j=2$, $m=+2$
+2	0	1/3	2/3
+1	+1	2/3	−1/3

m_1	m_2	$j=3$, $m=+1$	$j=2$, $m=+1$	$j=1$, $m=+1$
+2	−1	1/15	1/3	3/5
+1	0	8/15	1/6	−3/10
0	+1	2/5	−1/2	1/10

m_1	m_2	$j=3$, $m=0$	$j=2$, $m=0$	$j=1$, $m=0$
+1	−1	1/5	1/2	3/10
0	0	3/5	0	−2/5
−1	+1	1/5	−1/2	3/10

m_1	m_2	$j=3$, $m=-1$	$j=2$, $m=-1$	$j=1$, $m=-1$
0	−1	2/5	1/2	1/10
−1	0	8/15	−1/6	−3/10
−2	+1	1/15	−1/3	3/5

m_1	m_2	$j=3$, $m=-2$	$j=2$, $m=-2$
−1	−1	2/3	1/3
−2	0	1/3	−2/3

m_1	m_2	$j=3$, $m=-3$
−2	−1	1

Figure 6.1: $j_1 = 2, j_2 = 1$ Clebsch-Gordan coefficients from http://pdg.lbl.gov/2002/clebrpp.pdf.

j_1, m_1 with j_2, m_2 one can use the relation

$$\langle j_1, m_1 | \langle j_2, m_2 | |j, m\rangle = (-1)^{j-j_1-j_2} \langle j_2, m_2 | \langle j_1, m_1 | |j, m\rangle \tag{6.27}$$

For example, the green mark shows a $-2/5$. This means that

$$\langle j_1 = 2, m_1 = 0 | \langle j_2 = 1, m_2 = 0 | |j = 1, m = 0\rangle = -\sqrt{2/5}\,.$$

As another example, let us write a $j = 2, m = -1$ state (see violet arrow):

$$\begin{aligned} &|j = 2, m = -1\rangle \\ &= \frac{1}{\sqrt{2}} |\underset{\substack{\uparrow \\ \mathbf{j_1}}}{2},\ \underset{\substack{\uparrow \\ \mathbf{m_1}}}{0} > |\underset{\substack{\uparrow \\ \mathbf{j_2}}}{1}, \underset{\substack{\uparrow \\ \mathbf{m_2}}}{-1} > -\frac{1}{\sqrt{6}} |2, -1\rangle\, |1, 0\rangle - \frac{1}{\sqrt{3}} |2, -2\rangle\, |1, +1\rangle \end{aligned}$$

6.7 Matrix elements of vector operators (Wigner-Eckart's theorem)

Here, we want to look at the application of the theory of the addition of angular momenta to other problems in atomic and molecular physics (and beyond), whenever we need to calculate matrix elements of vector operators between atomic states. For example, in optics the transition rate between two states contains the dipole matrix element

$$\mathbf{d} = e \langle n, l, m | \hat{\mathbf{r}} \left| n', l', m' \right\rangle \ . \tag{6.28}$$

This is also needed to evaluate the effects of an electric field (Stark effect), and the corresponding lifting of degeneracy of atomic states.
Another application is the Zeeman effect, in which one considers the perturbation due to a magnetic field
Matrix elements of the form 6.28 can involve the calculation of a large number of integrals. For example, for a transition $2p \to 3d$ orbitals one has in 6.28 $l' = 1, l = 2$, i.e. 3×5 combinations of m, m'. In addition, there are 3 components of $\hat{\mathbf{r}}$, for a total of 45 integrals. In addition, many of these integrals are zero due to symmetry, which corresponds to forbidden transitions, i.e. selection rules. It would be a useful information to figure out which one are zero without doing calculations.
Wigner Eckart's Theorem allows to obtain all 45 integrals by just evaluating one of them. The idea is that all those states and integrals can be obtained by symmetry transformations. The generalisation of 6.28 consists of a matrix element of a **vector operator** $\hat{\mathbf{V}}$ between angular momentum eigenstates

$$\langle a, j, m | \hat{\mathbf{V}} | b, j_2, m_2 \rangle$$

Here, a, b are additional quantum numbers, e.g. n, n' for hydrogen atom. j could be just l, or the total angular momentum j, or spin s depending on the problem at hand.
It is convenient to rewrite the vector operator in analogy to the ladder operators 1.22 (there are slightly different factors):

$$\hat{V}_{\pm 1} = \mp(\hat{V}_x \pm i\hat{V}_y)/\sqrt{2} \qquad \hat{V}_0 = \hat{V}_z \tag{6.29}$$

Now the theorem states that Proof here: Sec. A.17

WIGNER-ECKART'S THEOREM FOR VECTORS[1]

$$\begin{aligned} &\langle a, j, m | \hat{V}_M | b, j_2, m_2 \rangle \\ &\qquad = \langle j, m || j_1 = 1, m_1 = M \rangle | j_2, m_2 \rangle \ \ \langle a, j || \hat{\mathbf{V}} || b, j_2 \rangle \ , \end{aligned} \tag{6.30}$$

---

[1] **Important Note:** While there is a symmetry when "turning around" the vectors in $\langle a, j, m | \hat{V}_M | b, j_2, m_2 \rangle$, i.e. $\langle a, j, m | \hat{V}_M^\dagger | b, j_2, m_2 \rangle = \langle b, j_2, m_2 | \hat{V}_M | a, j, m \rangle^*$ **there is no symmetry in the coefficient $\langle a, j || \hat{\mathbf{V}} || b, j_2 \rangle$ i.e. it is $\neq \langle b, j_2 || \hat{\mathbf{V}} || a, j \rangle^*$.** For details see here: Sec. A.19

where $\langle j,m| \, |j_1 = 1, m_1 = M\rangle \, |j_2, m_2\rangle$ are the (complex-conjugates of the) Clebsch-Gordan coefficients 6.16 . The last term $\langle a, j| \, |\hat{\mathbf{V}}| \, |b, j_2\rangle$ is simply a proportionality constant, and can be determined by evaluating just one of the (nonvanishing) matrix elements on the left h.s., i.e. for one set of m, M, m_2. Then one automatically has all of them. 6.30 , compared with 6.16 suggests that $\hat{V}_M$ behaves similarly to a state with angular momentum quantum numbers $j_1 = 1, m_1 = M$.

The more general version of Wigner-Eckart's theorem applies to higher-dimensional tensors such as quadrupoles. A special case is a 0-dimensional tensor, i.e. a scalar operator $\hat{S}$, we already knew that Proof here: Sec. A.18

WIGNER-ECKART'S THEOREM FOR SCALARS

$$\langle a, j, m| \, \hat{S} \, |b, j_2, m_2\rangle = \delta_{j,j_2} \delta_{m,m_2} \, \langle a, j| \, |\hat{S}| \, |b, j\rangle \tag{6.31}$$

Selection rules and parity

6.30 provides an easy rule to determine which matrix elements are allowed. From the rule $j = j_1 + j_2, \cdots, |j_1 - j_2|$, and $m = m_1 + m_2$, we get for the present case $|j - j_2| \leq 1$ and $m = m_2 + M$. The latter observation leads to the selection rules for optical dipole transitions between states of a spherical atom: $l_{final} = l_{initial} \pm 1$.

In principles 6.30 only states $|l_{final} - l_{initial}| \leq 1$ so also $l_{final} = l_{initial}$ would be allowed. This, however, is excluded by the fact that l_{final} and $l_{initial}$ must have different parity, i.e. $l_{final} - l_{initial} =$ odd. To see this, remember that the parity operator $\hat{P}$ transforms $\mathbf{r} \to -\mathbf{r}$:

$$\hat{P}\psi(\mathbf{r}) = \psi(-\mathbf{r})$$

Now, by looking at the spherical harmonics it is easy to see that **states with a given l have a fixed parity $(-1)^l$,** i.e.

$$\hat{P} Y_{lm}(\theta, \varphi) = (-1)^l Y_{lm}(\theta, \varphi) \; .$$

On the other hand, for the position operator, we have

$$\hat{P} \hat{\mathbf{r}} \hat{P} = -\hat{\mathbf{r}}$$

which indicates the transformation of $\hat{\mathbf{r}}$ under $\hat{P}$. We thus have for 6.28

$$\begin{aligned} &\langle n,l,m|\,\hat{\mathbf{r}}\,|n',l',m'\rangle = -\langle n,l,m|\,\hat{P}\hat{\mathbf{r}}\hat{P}\,|n',l',m'\rangle \\ &= (-1)^{l-l'+1}\langle n,l,m|\,\hat{\mathbf{r}}\,|n',l',m'\rangle = \begin{cases} 0 & \text{for } l-l' \text{ even} \\ \neq 0 & \text{for } l-l' \text{ odd} \end{cases} \end{aligned} \tag{6.32}$$

this gives the mentioned condition $l_{final} - l_{initial} = \text{odd}$.

6.7.1 Applications

Stark effect in Hydrogen

As an application we consider the perturbation of the degenerate $n = 2$ Hydrogen states by an homogeneous electric field:

$$\hat{H}_1 = -eE\,\hat{z}\,. \tag{6.33}$$

According to degenerate perturbation theory, we ought to calculate all 16 matrix elements

$$\langle 2,l,m|\,\hat{z}\,|2,l',m'\rangle$$

First of all, due to 6.32 , only matrix elements between $l = 0$ and $l = 1$ are nonzero. Second, since (cf. 6.29) $\hat{z} = \hat{r}_0$, we have from 6.30 $m = m'$. So in the end, the only nonvanishing matrix elements are

$$d \equiv \langle 2,1,0|\,\hat{z}\,|2,0,0\rangle = \langle 2,0,0|\,\hat{z}\,|2,1,0\rangle\ , \tag{6.34}$$

We don't calculate d here. From the 4×4 matrix we are left with a 2×2 between these states:

$$\langle 2,l,0|\,\hat{H}_1\,|2,l',0\rangle = \begin{pmatrix} 0 & -eEd \\ -eEd & 0 \end{pmatrix}$$

so the eigenstates/eigenenergy corrections are (cf. 6.33 , 6.34)

$$\begin{array}{lr} \text{eigenstate} & \text{energy correction} \\ |2,0,0\rangle + |2,1,0\rangle & -eEd \\ |2,1,\pm 1\rangle & 0 \\ |2,0,0\rangle - |2,1,0\rangle & eEd \end{array} \tag{6.35}$$

Further matrix elements Wigner Eckart's theorem can be used to determine matrix elements of all the other components of a vector having evaluated only one. For example, from 6.34 we can evaluate $\langle 2,1,m|\,\hat{x}\,|2,0,0\rangle$.
From 6.29 , we have that for $\hat{\mathbf{V}} = \hat{\mathbf{r}}$,

$$\hat{r}_0 = \hat{z} \qquad \hat{r}_{\pm 1} = \mp(\hat{x} \pm i\,\hat{y})\,/\sqrt{2}$$

and, thus

$$\hat{x} = (\hat{r}_{-1} - \hat{r}_{+1})/\sqrt{2}\,.$$

Using 6.30 and 6.34 we have

$$d = \langle 2,1,0|\,\hat{r}_0\,|2,0,0\rangle = \underbrace{\langle 1,0||j_1 = 1, m_1 = 0\rangle\,|0,0\rangle}_{=1}\langle 2,1|\,|\hat{\mathbf{r}}|\,|2,0\rangle$$

which fixes the constant

$$\langle 2,1|\,|\hat{\mathbf{r}}|\,|2,0\rangle = d\,.$$

Now

$$\begin{aligned}
\langle 2,1,m|\,\hat{x}\,|2,0,0\rangle &= \cdots\cdots \\
&= \cdots\cdots \\
&= \frac{d}{\sqrt{2}}(\delta_{m,-1} - \delta_{m,+1})
\end{aligned}$$

And similarly one can determine $\langle 2,1,m|\,\hat{y}\,|2,0,0\rangle$.
It is instructive to repeat the calculation with the hermitian conjugate (which, of course, should give the same):

$$d = \langle 2,0,0|\,\hat{r}_0\,|2,1,0\rangle = \underbrace{\langle 0,0||j_1 = 1, m_1 = 0\rangle\,|1,0\rangle}_{-1/\sqrt{3}}\langle 2,0|\,|\hat{\mathbf{r}}|\,|2,1\rangle\ .$$

Notice that (cf. footnote on Pag. 97)

$$\langle 2,0|\,|\hat{\mathbf{r}}|\,|2,1\rangle = -\sqrt{3}d \qquad \neq \boldsymbol{\langle 2,1|\,|\hat{\mathbf{r}}|\,|2,0\rangle^*}\,.$$

So these quantities are just constants and do not have the properties of matrix elements.
On the other hand,

$$\begin{aligned}
\langle 2,0,0|\hat{x}\,|2,1,m\rangle &= \frac{1}{\sqrt{2}}(\langle 2,0,0|\,\hat{r}_{-1}\,|2,1,m\rangle - \langle 2,0,0|\,\hat{r}_{+1}\,|2,1,m\rangle) \\
&= \frac{1}{\sqrt{2}}\langle 2,0|\,|\hat{\mathbf{r}}|\,|2,1\rangle\left(\underbrace{\langle 0,0||j_1 = 1, m_1 = -1\rangle\,|1,m\rangle}_{=\delta_{m,+1}/\sqrt{3}} - \underbrace{\langle 0,0||j_1 = 1, m_1 = +1\rangle\,|1,m\rangle}_{=\delta_{m,-1}/\sqrt{3}}\right) \\
&= \frac{d}{\sqrt{2}}(\delta_{m,-1} - \delta_{m,+1})
\end{aligned}$$

the same as 6.36 , as expected.

Land'e g-factor

This deals with the problem of an atom in which electrons have a total orbital angular momentum $\hat{\mathbf{L}}$ and total spin $\hat{\mathbf{S}}$, characterized by corresponding quantum numbers l and s (in the case of one electron, $s = \frac{1}{2}$).
They first couple via spin-orbit coupling

$$H_{SO} = \lambda\, \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \tag{6.37}$$

so that the total angular momentum

$$\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}} \tag{6.38}$$

commutes with the hamiltonian, and eigenenergies depend on the corresponding quantum number j only, with degeneracy $2j+1$ (fine-structure states).
One then studies the influence of an external magnetic field $\mathbf{B} = B\mathbf{e}_z$ which couples as (Zeeman effect)

$$H_B = \hat{\mu} \cdot \mathbf{B} = \mu_B(\hat{\mathbf{L}} + g_s\hat{\mathbf{S}}) \cdot \mathbf{B} \qquad \mu_B = \frac{q}{2m} \tag{6.39}$$

due to the electron's gyromagnetic ratio $g_s = 2$ the term in brackets is not in the same direction as $\hat{\mathbf{J}}$.
Here, the perturbation due to H_B is considered to be smaller than the effect of spin-orbit coupling, so that it is sufficient to consider first-oder perturbation theory, which is, however, degenerate, due to the degeneracy of the j-multiplets. Therefore, we ought to calculate all matrix elements of H_B, i.e. of L_z and S_z between the degenerate states $\left|n, j, m_j\right\rangle$ for all m_j.
But again, Wigner-Eckart's theorem gives us an easier solution. From the proportionality 6.30 , it is clear that within a fixed set of $(a, j), (b, j_2)$ (here $(n, j), (n, j)$) all matrix elements of a vectors are proportional to each other, so in our case for an arbitrary vector $\mathbf{V}$

$$\left\langle n, j, m_j \right| \hat{\mathbf{V}} \left| n, j, m'_j \right\rangle = \gamma(n, j) \left\langle n, j, m_j \right| \hat{\mathbf{J}} \left| n, j, m'_j \right\rangle \; . \tag{6.40}$$

Here we prove : Sec. A.20 that the ($\mathbf{V}$-dependent) constant $\gamma(n, j)$ is given by

$$\gamma(n, j) = \frac{\left\langle n, j, m_j \right| \hat{\mathbf{V}} \cdot \hat{\mathbf{J}} \left| n, j, m_j \right\rangle}{\hbar^2\; j(j+1)} \tag{6.41}$$

and is independent of m_j (projection theorem).
6.39 with 6.40 gives

$$\left\langle n, j, m_j \right| \hat{\mu} \left| n, j, m'_j \right\rangle = g_{nj}\; \mu_B \left\langle n, j, m_j \right| \hat{\mathbf{J}} \left| n, j, m'_j \right\rangle \tag{6.42}$$

with the Landé factor (cf. 6.41

$$g_{nj} \equiv \frac{\left\langle n, j, m_j \right| (\hat{\mathbf{L}} + g_s \hat{\mathbf{S}}) \cdot \hat{\mathbf{J}} \left| n, j, m_j \right\rangle}{\hbar^2 \; j(j+1)} \tag{6.43}$$

To determine this factor we consider that

$$\hat{\mathbf{L}} \cdot \hat{\mathbf{J}} = \hat{\mathbf{L}} \cdot (\hat{\mathbf{L}} + \hat{\mathbf{S}}) = \hat{\mathbf{L}}^2 + \frac{1}{2}(\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2)$$

and similarly

$$\hat{\mathbf{S}} \cdot \hat{\mathbf{J}} = \hat{\mathbf{S}}^2 + \frac{1}{2}(\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2)$$

So that 6.43

$$g_j = \frac{j(j+1)(1+g_s) + l(l+1)(2-1-g_s) + s(s+1)(-1+g_s)}{2j(j+1)} \tag{6.44}$$

Therefore, the Hamiltonian 6.39 can be written within these fixed-j states

$$H_B = \mu_B \, g_{nj} \, \mathbf{B} \cdot \hat{\mathbf{J}} \; .$$

Taking, without restriction of generality the magnetic field in the z-direction, we have for the energies

$$E_{m_j} = \mu_B \, g_{nj} \, B \, \hbar m_j$$

Chapter 7

Identical particles

In many-body systems (e.g. atoms with more than one electron, molecules) we deal with a system of identical particles. In classical mechanics, identical particles are always distinguishable in the sense that their trajectories can be traced. However, in quantum mechanics, identical particles are truly indistinguishable, because due to the uncertainty relation, we cannot follow their trajectory. A paradigmatic example is here the double-slit experiment The fact that particles are indistinguishable has a number of important consequences. We consider a system of N identical particles. We initially assume that the particles do not interact with each other.

$$H = H_1 + H_2 + \cdots + H_N \qquad .$$

Particle α must satisfy the eigenvalue equation

$$H_\alpha |\varphi_\nu\rangle_\alpha = \varepsilon_\nu |\varphi_\nu\rangle_\alpha \qquad .$$

An eigenstate of H is therefore the product of the eigenstates of the subsystems

$$|\Psi\rangle = \bigotimes_{\alpha=1}^{N} |\varphi_{\nu_\alpha}\rangle_\alpha = \left|\varphi_{\nu_1}, \varphi_{\nu_2}, \cdots, \varphi_{\nu_N}\right\rangle = \left|\varphi_{\nu_1}\right\rangle \otimes \left|\varphi_{\nu_2}\right\rangle \otimes \cdots \otimes \left|\varphi_{\nu_N}\right\rangle$$

$$H\,|\Psi\rangle = E\,|\Psi\rangle \quad \text{mit} \quad E = \sum_{\alpha=1}^{N} \varepsilon_{\nu_\alpha}$$

[**Note:** We have to distinguish between many-particle states, such as $|\Psi\rangle$, and single-particle states such as the $|\varphi_i\rangle$. In many-body physics, the former are often simply refereed to as "states" and the latter as "orbitals" or "levels", although they must not necessarily refer to atomic orbitals.]

Example

$$\begin{aligned} N &= 2 \\ |\Psi\rangle &= \left|\varphi_\nu, \varphi_\mu\right\rangle \\ E &= \varepsilon_\nu + \varepsilon_\mu \qquad . \end{aligned}$$

The point is that also the state vector $\left|\varphi_\mu, \varphi_\nu\right\rangle$ with interchanged particles is an eigenstate with energy $E = \varepsilon_\mu + \varepsilon_\nu$. Hence, the two states are degenerate. Therefore, a state consisting of N particles with different energies has a very high degeneracy of $N!$. This is termed exchange degeneracy.

We now consider, independently of the Hamilton-operator, the consequences of the indistinguishability of particles. If the interchange of two particles should not lead to measurable consequence, initial and final states can differ only by a phase.

$$P_{ij}|\Psi\rangle = e^{i\alpha}|\Psi\rangle$$

def.**Exchange operator**

P_{ij} is the exchange operator, which interchanges particles i and j.

$$P_{ij}|\varphi_1, \varphi_2, \cdots, \varphi_i, \cdots, \varphi_j, \cdots, \varphi_n\rangle = |\varphi_1, \varphi_2, \cdots, \varphi_j, \cdots, \varphi_i, \cdots, \varphi_n\rangle \tag{7.1}$$

Applying P_{ij} twice to an N-particle state obviously leads back to the initial state.

As a consequence

$$\begin{aligned} P_{ij}^2 &= 1\!\!1 \\ \Rightarrow \quad P_{ij}^2|\Psi\rangle &= e^{2i\alpha}|\Psi\rangle = |\Psi\rangle \\ e^{2i\alpha} = 1 \quad &\Leftrightarrow \quad \alpha = 0, \pi \\ \Rightarrow \quad P_{ij}|\Psi\rangle &= \pm|\Psi\rangle \end{aligned}$$

This holds for arbitrary indices i, j. Thus, $|\Psi\rangle$ has to by symmetric / antisymmetric with respect to all pairs i, j. Only two of the $N!$ possibilities are physically distinguishable.

PARTICLE STATISTICS

$$\begin{aligned} &\text{When } P_{ij}|\Psi\rangle = +|\Psi\rangle \text{ one refers to as bosons.} \\ &\text{When } P_{ij}|\Psi\rangle = -|\Psi\rangle \text{ one refers to as fermions.} \end{aligned} \tag{7.2}$$

From relativistic quantum theory, particles with integer spin are bosons and particles with half integer spin are fermions. Two combined fermions form a boson (e.g. superconductivity).
In general one can carry out an arbitrary permutation which is produced by the Permutation operator P, that has the following effect on an arbitrary N-particle wave function.

$$P|\varphi_1, \varphi_2, \cdots, \varphi_n\rangle = |\varphi_{P_1}, \varphi_{P_2}, \cdots, \varphi_{P_n}\rangle$$

We can now combine all possible permutations of a n particle system in a symmetric way via the Symmetrisation operator

$$S := \frac{1}{\sqrt{N!}} \sum_P P$$

Or for the case of antisymmetric wave functions the Antisymmetrisation operator

$$A := \frac{1}{\sqrt{N!}} \sum_P \mathrm{sign}(P) P$$

Starting from an arbitrary N-particle tensor product state vector $|\Psi\rangle$, which does not fullfill 7.2 in general bosonic and fermionic states satisfying 7.2 can be produced by applying S resp. A :

$$\begin{array}{lrcl} \text{Bosons:} & |\Psi_B\rangle & = & S\,|\Psi\rangle \\ \text{Fermions:} & |\Psi_F\rangle & = & A\,|\Psi\rangle \end{array}$$

Example for $N = 2$

$$|\Psi_{Bos}\rangle = \cdots\cdots \tag{7.3}$$

$$|\Psi_F\rangle = \cdots\cdots \tag{7.4}$$

For a tensor product state $|\varphi_1, \varphi_2, \cdots\rangle = |\varphi_1\rangle_1 \otimes |\varphi_2\rangle_2 \cdots$, then $|\Psi_F\rangle$ is a so-called **Slater determinant**

$$|\Psi_F\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} |\varphi_1\rangle_1 & |\varphi_2\rangle_1 & \cdots & |\varphi_N\rangle_1 \\ |\varphi_1\rangle_2 & |\varphi_2\rangle_2 & \cdots & |\varphi_N\rangle_2 \\ \cdots & \cdots & \cdots & \cdots \\ |\varphi_1\rangle_N & |\varphi_2\rangle_N & \cdots & |\varphi_N\rangle_N \end{vmatrix}$$

in coordinate representation

$$\begin{aligned} \langle \mathbf{x}_1, \cdots, \mathbf{x}_N | \Psi_F \rangle &= \Psi_F(\mathbf{x}_1, \cdots, \mathbf{x}_N) \\ &= \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(\mathbf{x}_1) & \varphi_2(\mathbf{x}_1) & \cdots & \varphi_N(\mathbf{x}_1) \\ \varphi_1(\mathbf{x}_2) & \varphi_2(\mathbf{x}_2) & \cdots & \varphi_N(\mathbf{x}_2) \\ \cdots & \cdots & \cdots & \cdots \\ \varphi_1(\mathbf{x}_N) & \varphi_2(\mathbf{x}_N) & \cdots & \varphi_N(\mathbf{x}_N) \end{vmatrix} \end{aligned}$$

Example for $N = 2$

$$
\begin{aligned}
|\Psi_F\rangle &= \frac{1}{\sqrt{2}} \begin{vmatrix} |\varphi_A\rangle_1 & |\varphi_B\rangle_1 \\ |\varphi_A\rangle_2 & |\varphi_B\rangle_2 \end{vmatrix} \\
&= \cdots\cdots \\
&= \cdots\cdots
\end{aligned}
$$

in coordinate representation

$$\Psi_F(\mathbf{x}_1, \mathbf{x}_2) = \cdots\cdots$$

Example for $N = 3$

$$
\begin{aligned}
|\Psi_F\rangle &= \frac{1}{\sqrt{3!}} \begin{vmatrix} |\varphi_A\rangle_1 & |\varphi_B\rangle_1 & |\varphi_C\rangle_1 \\ |\varphi_A\rangle_2 & |\varphi_B\rangle_2 & |\varphi_C\rangle_2 \\ |\varphi_A\rangle_3 & |\varphi_B\rangle_3 & |\varphi_C\rangle_3 \end{vmatrix} \\
&= \frac{1}{\sqrt{6}} \Big(|\varphi_A\rangle_1 \otimes |\varphi_B\rangle_2 \otimes |\varphi_C\rangle_3 + |\varphi_B\rangle_1 \otimes |\varphi_C\rangle_2 \otimes |\varphi_A\rangle_3 \\
&\quad + |\varphi_C\rangle_1 \otimes |\varphi_A\rangle_2 \otimes |\varphi_B\rangle_3 - |\varphi_C\rangle_1 \otimes |\varphi_B\rangle_2 \otimes |\varphi_A\rangle_3 \\
&\quad - |\varphi_B\rangle_1 \otimes |\varphi_A\rangle_2 \otimes |\varphi_C\rangle_3 - |\varphi_A\rangle_1 \otimes |\varphi_C\rangle_2 \otimes |\varphi_B\rangle_3 \Big) .
\end{aligned} \tag{7.5}
$$

7.1 Pauli exclusion principle

An immediate consequence of antisymmetry is that the electron must satisfy the **Pauli exclusion principle:**: Two identical fermions cannot occupy the same state. If $|\varphi_i\rangle = |\varphi_j\rangle$ where $i \neq j$, the exchange 7.1 results in the same state, but because of 7.2 with a negative sign, so it gives the zero state. Analogously, in this case two columns in the Slater determinant are identical, thus the determinant vanishes.

Example: He atom, two electrons

Quantum numbers: $n; l; m_l; m_s$

Two electrons may not have the same set of quantum numbers.

The ground state has the quantum numbers: $n = 1; l = 0; m_l = 0; m_s = \pm\frac{1}{2}$

Two electrons with opposite spin can be in the ground state. (Therefore, all states are pairwise occupied.)

Adding more electrons, they have to occupy the next shell:

$n = 2$:
$l = 0; m_l = 0$=> 2 electrons
$l = 1; m_l = -1, 0, +1$ => 6 electrons
In this way, the *Aufbau* of the periodic table is explained.

7.2 Anyons (optional)

$P_{ij}^2 = \mathbb{1}$ is not valid in two dimensions because of the special topology. Exchanging two particles in $\mathbb{R}^2$ twice, the way in which the particles are exchanged matters. The two ways to swap the particles back cannot be distorted into each other. Either particle I goes once around particle II or it goes down and up again on the same side. (Abb. 7.1).
A very demonstrative example is given in fig. 7.2. Two laces are fixed at one end, the loose end is 'exchanged'. In three dimensions, the two ways (fig. 7.1) are identical, because they can be distorted into each other without touching the second particle. In two dimensions, $P_{ij}^2 = \mathbb{1}$ is not valid. Thus they can have any phase upon particle exchange rather than just ±1. Particles which get an arbitrary phase upon exhange are called **Anyons**. These play an important role in the theory of fractional quantum hall effect (FQH).

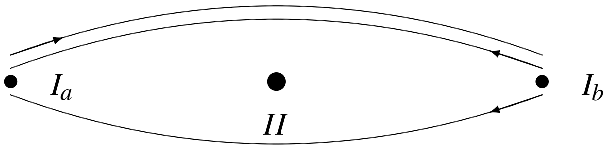


Figure 7.1: *Double exchange of two particles (I and II) in* $\mathbb{R}^2$.

7.3 Occupation number representation

As discussed above, a basis vector for a Hilbert space $\mathscr{H}_N$ describing N identical particles consists of a symmetrized (Bosons) or antisymmetrized (Fermions) tensor product of single-particle basis states ("orbitals") $|\varphi_m\rangle$:

$$S_{\pm} \left|\varphi_{m_1}\right\rangle \otimes \left|\varphi_{m_2}\right\rangle \cdots \otimes \left|\varphi_{m_N}\right\rangle$$

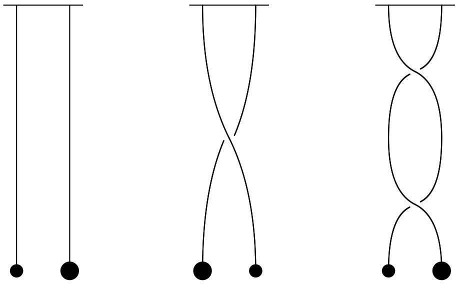


Figure 7.2: *double exchange of two particles in* $\mathbb{R}^2$.

where we have denoted $S_+ = S$ (symmetrisation) for bosons, and $S_- = A$ (antisymmetrisation) for fermions. The wave function is

$$\Psi(x_1,\cdots,x_N) = S_\pm \ \varphi_{m_1}(x_1)\varphi_{m_2}(x_2)\cdots\varphi_{m_N}(x_N) \ .$$

For simplicity, we have consider here a discrete basis for a single particle system, and taken, $m_i = 1,2,\cdots,\infty$. In general, m can describe a set of quantum number (e.g. $m \equiv (n,l,m)$), or be continuous.

Each basis element is, therefore, specified by the set of positive integers $\{m_1,\cdots,m_N\}$. This provides the information: in which orbital each particle is. However, due to the indistinguishability of the particles, this is a redundant information, since any permutation describes the same many body-state, up to a constant.

A more appropriate specification of a many-body basis state is the so-called **“occupation number representation” (Besetzungszahldarstellung)**. Here one specifies for each orbital $|\varphi_m\rangle$, the number of particles N_m which are present in (occupy) that orbital.:

$$|N_1,N_2,N_3,\cdots\rangle \tag{7.6}$$

Obviously, for bosons each N_m can be any integer from 0 to ∞, for fermions just 0 or 1 due to the Pauli principle. Notice that, especially for fermions, this specifies the many-body state only up to $\pm$ sign which depends on the order in which the orbitals are occupied. However, one can fix a convention according to which, for example, single-particle states are sorted in order of increasing m from left to right.

7.3.1 Fock Space

For a Hilbert space $\mathscr{H}_N$ with a given particle number N, the N_m are constrained to be $\sum_m N_m = N$
However, one can consider the space obtained as the direct sum of all the $\mathscr{H}_N$ for $N = 0, \cdots, \infty$. This space with variable particle number is called **Fock space**. Clearly, a possible basis for the Fock space is given by the set of states 7.6 with $N_m = 0, 1$ for fermions or $N_m = 0, \cdots, \infty$ for bosons but otherwise no restriction on the sum of the N_m.
The state $|0\rangle$ with no particles is called the **vacuum state**. This state is normalized $\langle 0|0\rangle = 1$ and should not be confused with the 0 "vector" which has norm 0.
The scalar product in the Fock space is naturally defined as

$$\left\langle N_1', N_2', N_3', \cdots | N_1, N_2, N_3, \cdots \right\rangle = \delta_{N_1',N_1} \delta_{N_2',N_2} \delta_{N_3',N_3} \cdots \tag{7.7}$$

A particular useful formalism to describe a Fock space of bosons or fermions is given by **second quantisation** which will be introduced in Sec. 9.

7.4 Electron and spin

Electrons have an intrinsic degree of freedom (spin). The complete state of an electron consists of a orbital part φ_i and a spin part $|\chi_\alpha\rangle$ (for example, $|\chi_\alpha\rangle = |+z\rangle$ or $|-z\rangle$, but also linear combinations) . The general form of the state vector of **one** electron can be written as

$$|\Psi\rangle = \sum_{i,\alpha} c_{i,\alpha} \; |\varphi_i \chi_\alpha\rangle$$

The corresponding wave function

$$\Psi(\mathbf{x}, \sigma) := \langle \mathbf{x}, \sigma | \Psi \rangle = \sum_{i,\alpha} c_{i,\alpha} \varphi_i(\mathbf{x}) \chi_\alpha(\sigma) \quad \sigma = \pm z \qquad .$$

Two electrons What states can **two** electrons occupy? An elementary tensor product reads

$$|\Psi\rangle \quad = \quad \left| \varphi_i \chi_\alpha, \varphi_j \chi_\beta \right\rangle = |\varphi_i\rangle_1 \otimes |\varphi_j\rangle_2 \otimes |\chi_\alpha\rangle_1 \otimes |\chi_\beta\rangle_2 \qquad ,$$

Notice that we have grouped together the spatial part and the spin part of the state vector. This vector still has to be antisymmetrized, as discussed above. Two situations can be distinguished:

1. **Identical orbital parts ($i = j$):** Due to the Pauli exclusion principle, we must have $\alpha \neq \beta$. The antisymmetrisation of the state yields (without normalization):

$$\begin{aligned}
&\Big|\varphi_i\chi_\alpha, \varphi_i\chi_\beta\Big\rangle - \Big|\varphi_i\chi_\beta, \varphi_i\chi_\alpha\Big\rangle \\
= \quad & |\varphi_i\rangle_1 \otimes |\varphi_i\rangle_2 \otimes \underbrace{\frac{1}{\sqrt{2}}\Big(|\chi_\alpha\rangle_1 \otimes |\chi_\beta\rangle_2 - |\chi_\beta\rangle_1 \otimes |\chi_\alpha\rangle_2\Big)}_{\text{Singlet}} \qquad .
\end{aligned}$$

Taking the $|\pm z\rangle$ basis, we get the singlet ($s = 0$) state, cf. 6.26 .[1]

SINGLET STATE OF TWO SPINS

$$|\text{Singlet}\rangle = \frac{1}{\sqrt{2}}\Big(|+z, -z\rangle - |-z, +z\rangle\Big) \tag{7.8}$$

1. **Different orbital parts ($i \neq j$):** Taking the $|\pm z\rangle$ basis, there are four possibilities for spins

   I) $\alpha = \beta = +z$
   II) $\alpha = \beta = -z$
   III) $\alpha = -\beta = +z$
   IV) $\alpha = -\beta = -z$

   The resulting **globally** antisymmetrized states can be combined in antisymmetric in spin and symmetric in space; or symmetric in spin and antisymmetric in space. The triplet states in 6.26 are all symmetric in spin. Therefore, we have as possible two-electron states:

---

[1] In fact notice that the singlet term 7.8 has the same form in any quantisation direction $\hat{n}$ for the spin (for basis states $|\pm\hat{n}\rangle$), i.e.
$|\text{Singlet}\rangle = \frac{1}{\sqrt{2}}(|+\hat{n}, -\hat{n}\rangle - |-\hat{n}, +\hat{n}\rangle)$. A simple way to see this is by considering that this state has angular momentum of zero and is therefore invariant under rotations and, thus, independent of the quantisation direction.

SINGLET AND TRIPLET STATES OF TWO ELECTRONS

$$\begin{aligned} &\tfrac{1}{\sqrt{2}}\Big(\big|\varphi_i,\varphi_j\big\rangle + \big|\varphi_j,\varphi_i\big\rangle\Big)\otimes|S=0,m_s=0\rangle && \text{spin-singlet} \\ &\tfrac{1}{\sqrt{2}}\Big(\big|\varphi_i,\varphi_j\big\rangle - \big|\varphi_j,\varphi_i\big\rangle\Big)\otimes|S=1,m_s\in\{0,\pm1\}\rangle && \text{spin-triplet} \end{aligned} \tag{7.9}$$

7.5 The Helium atom

As an application, let us consider the example of two electrons in the Helium atom. As shown in figure 7.3 , Helium consists of a nucleus (Z = 2) and two electrons. The Hamiltonian for He is given by (atomic units)

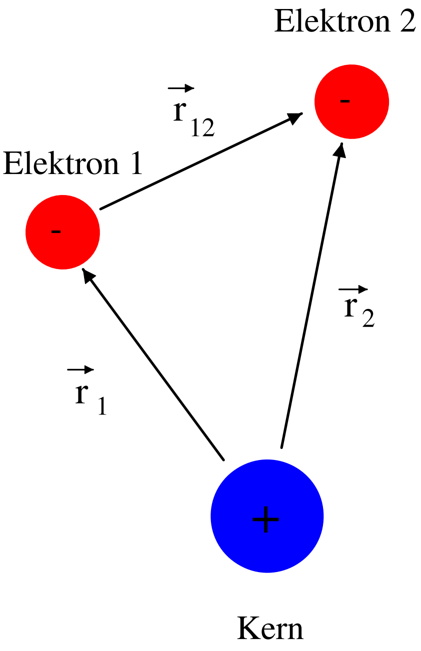


Figure 7.3: *Schematic sketch of an Helium atom*

$$H = \underbrace{\overbrace{\frac{\mathbf{p}_1^2}{2} - \frac{Z}{r_1}}^{H_{0,1}} + \overbrace{\frac{\mathbf{p}_2^2}{2} - \frac{Z}{r_2}}^{H_{0,2}}}_{H_0} + \underbrace{\frac{1}{r_{12}}}_{H_1} \tag{7.10}$$

We first focus on H_0. The two terms $H_{0,1}$ and $H_{0,2}$ are identical, except that they act on different particles. Each separate Hamilton operator describes a H-like atom with $Z = 2$. The lowest energy is obtained when both electrons are in ground state. Due to 7.9 the spin part has to be in a singlet state.

$$\begin{aligned} |\psi_{orb}\rangle &= |n=1, l=0, m_l=0\rangle_1 \otimes |n=1, l=0, m_l=0\rangle_2 \\ &= |1,0,0\rangle_1 \otimes |1,0,0\rangle_2 \equiv |\varphi_0\rangle_1 \otimes |\varphi_0\rangle_2 \\ |\psi_{spin}\rangle &= |s=0, m_s=0\rangle \end{aligned}$$

The corresponding energy is

$$E = -2\left(\frac{Z^2}{2}\right) = -4 \overset{\wedge}{=} -4 \cdot 27,2\text{eV} = -108.8\text{eV}$$

Now, we take the interaction term $H_1 = H_1^{orb} \otimes 1\!\!1^{spin}$ into account within first-order perturbation theory details: Sec. A.22 :

$$\begin{aligned} \Delta E^{(1)} &= \langle \Psi^{orb}|H_1^{orb}|\Psi^{orb}\rangle \langle \Psi^{spin}|1\!\!1^{spin}|\Psi^{spin}\rangle \\ &= \langle \Psi^{orb}|H_1^{orb}|\Psi^{orb}\rangle \\ &= \iint |\langle \mathbf{r}_1|1,0,0\rangle_1|^2 \, |\langle \mathbf{r}_2|1,0,0\rangle_2|^2 \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} d^3r_1 d^3r_2 \\ &= \iint \rho(\mathbf{r}_1) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \rho(\mathbf{r}_2) \, d^3r_1 \, d^3r_2 \end{aligned}$$

It describes the electrostatic interaction of two identical charge distributions $\rho(\mathbf{r})$. The electron density for the ground state is

$$\rho(\mathbf{r}) = \left|\varphi_0(Z,\mathbf{r})\right|^2 = \left|\frac{1}{\sqrt{\pi}} Z^{3/2} \, e^{-Zr}\right|^2 = \frac{1}{\pi} Z^3 \, e^{-2Zr} \tag{7.11}$$

The energy correction, thus, reads

$$\Delta E^{(1)} = \left(\frac{Z^3}{\pi}\right)^2 \iint e^{-2Zr_1} \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} e^{-2Zr_2} \, d^3r_1 \, d^3r_2$$

We substitue $2Z\mathbf{r}_\alpha = \mathbf{x}_\alpha$ and get

$$\Delta E^{(1)} = \underbrace{\left(\frac{Z^3}{\pi}\right)^2 (2Z)^{-5}}_{=\frac{Z}{2^5\pi^2}} \iint e^{-x_1} \frac{1}{|\mathbf{x}_1 - \mathbf{x}_2|} e^{-x_2} \, d^3x_1 \, d^3x_2 \tag{7.12}$$

The integral is not dependent on Z. The calculation (details : Sec. A.23) gives

$$\Delta E^{(1)} = \frac{5}{8} Z \overset{\wedge}{=} \frac{5}{4} \cdot 27,2\mathrm{eV} = 34.0\mathrm{eV} \qquad . \tag{7.13}$$

Thus, the ground state energy at this order is $E \cong -74.8\mathrm{eV}$. The experimental value is $E_{\mathrm{Exp}} = -78.8\mathrm{eV}$. The calculated value does not yet agree very well with the experimental results due to the crude approximation we made. An improvement consists in adopting the variational method. We consider the atomic number $Z \to \mathscr{Z}$ of the wave function $|n=1, l=0, m_l=0\rangle$ (cf. 7.11) of the unperturbed problem as a variational parameter. We find the minimum of the expectation value of the energy

$$E^{(1)} = \frac{\langle \varphi_0(\mathscr{Z}) | H_0 + H_1 | \varphi_0(\mathscr{Z}) \rangle}{\langle \varphi_0(\mathscr{Z}) | \varphi_0(\mathscr{Z}) \rangle}$$

as a function of $\mathscr{Z}$. The result can only improve by finding a better $\mathscr{Z}$ with respect to $\mathscr{Z} = 2$ we just evaluated. This choice also has a physical interpretation. The effective charge $\mathscr{Z}$ seen by each electrons is smaller than the true $Z = 2$, because the positive charge is partially screened by the negatively charged cloud of the other electron. By replacing $Z \to \mathscr{Z}$ we take this effect into account.
We rewrite the Hamiltonian (which has the correct $Z = 2$) as

$$H = \overbrace{\frac{\mathbf{p}_1^2}{2} - \frac{\mathscr{Z}}{r_1}}^{H_{0,1}(\mathscr{Z})} + \frac{\mathscr{Z} - Z}{r_1} + \overbrace{\frac{\mathbf{p}_2^2}{2} - \frac{\mathscr{Z}}{r_2}}^{H_{0,2}(\mathscr{Z})} + \frac{\mathscr{Z} - Z}{r_2} + \frac{1}{r_{12}}$$

The contributions from $H_{0,1}(\mathscr{Z})$ and $H_{0,2}(\mathscr{Z})$ result in

$${}_1\langle \varphi_0(\mathscr{Z}) | H_{0,1}(\mathscr{Z}) | \varphi_0(\mathscr{Z}) \rangle_1 \quad + \quad {}_2\langle \varphi_0(\mathscr{Z}) | H_{0,2}(\mathscr{Z}) | \varphi_0(\mathscr{Z}) \rangle_2 = -2 \frac{\mathscr{Z}^2}{2} \; ,$$

where $|\Psi\rangle = |\varphi_0(\mathscr{Z})\rangle_1 \, |\varphi_0(\mathscr{Z})\rangle_2$ has been taken as a product of ground state wave functions of the two electrons. For this calculation, we used the fact that the hamiltonian as well as the wave function describe an atom with atomic number $\mathscr{Z}$ similar to hydrogen.
The contribution from the modified potential was already calculated in 5.12 .

$${}_1\langle \varphi_0(\mathscr{Z}) | \frac{1}{r_1} | \varphi_0(\mathscr{Z}) \rangle_1 + {}_2\langle \varphi_0(\mathscr{Z}) | \frac{1}{r_2} | \varphi_0(\mathscr{Z}) \rangle_2 = 2\, \mathscr{Z} \qquad .$$

The remaining term was already evaluated in 7.13 .

$$\langle \Psi | \frac{1}{r_{12}} | \Psi \rangle = \frac{5}{8} \mathscr{Z} \qquad .$$

The total variational energy, thus, becomes

$$E(\mathscr{Z}) = -\mathscr{Z}^2 + 2(\mathscr{Z}-Z)\mathscr{Z} + \frac{5}{8}\mathscr{Z} = \mathscr{Z}^2 - (2Z - \frac{5}{8})\mathscr{Z} \qquad .$$

Minimisation with respect to $\mathscr{Z}$ yields

$$\begin{aligned}
\frac{\partial E(\mathscr{Z})}{\partial \mathscr{Z}} &= 2(\mathscr{Z} - Z + \frac{5}{16}) \overset{!}{=} 0 \qquad \Rightarrow \\
\mathscr{Z}^* &= Z - \frac{5}{16} = 1.69 \\
E(\mathscr{Z}^*) &= \underbrace{-Z^2 + \frac{5}{8}Z}_{E^{(1)}} - (\frac{5}{16})^2 \mathrel{\hat{=}} -2.848 \cdot 27.21\ \text{eV} = -77.5\ \text{eV} \qquad .
\end{aligned}$$

The first two terms coincide with the results of perturbation theory. The result is already very close to the experimental value (-78.8 eV).

7.6 Excited states of helium

Finally, we consider the lowest excited states of helium, to show interesting effects of the symmetry of the wave function.

For an excited state, one particle stays in the ground state $n = 1, l = 0, m_l = 0$, whereas the second particle is in $n = 2, l, m_l$. According to 7.9 , there are four combinations

$$\begin{array}{lll}
\underbrace{\frac{1}{\sqrt{2}}(|100\rangle_1 \otimes |2lm\rangle_2 + |2lm\rangle_1 \otimes |100\rangle_2)}_{\Psi^+_{Orb}} & |s=0, m_s=0\rangle & \text{Singlet} \\
\underbrace{\frac{1}{\sqrt{2}}(|100\rangle_1 \otimes |2lm\rangle_2 - |2lm\rangle_1 \otimes |100\rangle_2)}_{\Psi^-_{Orb}} & |s=1, m_s \in \{0, \pm 1\}\rangle & \text{Triplet}
\end{array} \tag{7.14}$$

These states are degenerate, if we do not take electron electron interaction into account, and have the following energy (in zeroth order)

$$E_0 = \left(-\frac{Z^2}{2\cdot 1^2} - \frac{Z^2}{2\cdot 2^2}\right) = -\frac{Z^2}{2}\left(1 + \frac{1}{4}\right) = -\frac{5}{2} \mathrel{\hat{=}} -68.0\text{eV}$$

The energy does not dependend neither on the spin state (singlet, triplet) nor on the angular momentum quantum numbers (l, m). There are four spin states and for $n = 2$ there are four angular momentum quantum numbers $(l = 0, m = 0)$

and ($l = 1, m = 0, \pm 1$). Thus, there is a sixteenth-fold degeneracy. To estimate the energy correction in first order, we have to diagonalize H_1 in this subspace. However, we will see that the perturbation hamiltonian is already diagonal in the states 7.14 . H_1 does not act on spin, therefore matrix elements of H_1

$$\Big(\langle \psi_{Orb}| \otimes \langle \psi_S|\Big) H_1 \Big(|\psi'_{Orb}\rangle \otimes |\psi'_S\rangle\Big) = \langle \psi_{Orb}|H_1|\psi'_{Orb}\rangle\langle\, \psi_S|\psi'_S\rangle$$

are proportional to the overlap of spin states. The spin states are orthonormal, thus the perturbation term is diagonal in the spin quantum numbers.
Similar considerations apply to the orbital part: First observe that the states in 7.14 are eigenstates of $\mathbf{J}^2$ and J^z, where

$$\mathbf{J} = \mathbf{L_1} + \mathbf{L_2}$$

is the **total angular momentum-** Indeed, the product state

$$|100\rangle_1 \otimes |2lm\rangle_2 \tag{7.15}$$

corresponds to the first particle having $l_1 = 0, m_1 = 0$ and the second $l_2 = l, m_2 = m$. Thus, since the first particle has no angular momentum at all, the total angular momentum is determined by the second particle. Therefore, 7.15 is a state with total angular momentum quantum numbers $j = l, j_z = m$. The same discussion holds for the state $|2lm\rangle_1 |100\rangle_2$, and, consequently, for the linear combinations in 7.14 .
Now, observe that H_1 is invariant under rotations of the coordinate system (see 7.10), i.e. a scalar. Therefore (see also 6.31), we deduce that (i) it is diagonal in the states 7.14 and (ii) its expectation value depends on l **but not on** m. In other words, the states are already adapted to the symmetry of the perturbation and we only need to evaluate the diagonal terms (cf. 7.14):

$$\begin{aligned}
&\langle \Psi^{\pm}_{Orb}|H_1|\Psi^{\pm}_{Orb}\rangle\langle \Psi^{S/T}_S|\Psi^{S/T}_S\rangle = \langle \Psi^{\pm}_{Orb}|H_1|\Psi^{\pm}_{Orb}\rangle \\
= \;& \frac{1}{2}\Big(\langle 100|_1 \otimes \langle 2lm|_2\Big) H_1 \Big(|100\rangle_1 \otimes |2lm\rangle_2\Big) \\
+ \;& \frac{1}{2}\Big(\langle 2lm|_1 \otimes \langle 100|_2\Big) H_1 \Big(|2lm\rangle_1 \otimes |100\rangle_2\Big) \\
\pm \;& 2 \cdot \frac{1}{2}\Big(\langle 2lm|_1 \otimes \langle 100|_2\Big) H_1 \Big(|100\rangle_1 \otimes |2lm\rangle_2\Big)
\end{aligned} \tag{7.16}$$

which will not depend on m. The first two terms are equal, the factor 2 occuring in the third term is due to the equality of the mixed terms. We obtain, for details see here : Sec. A.24 :

$$
\begin{aligned}
&= \underbrace{\int |\varphi_{100}(\mathbf{r}_1)|^2 \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|} |\varphi_{2lm}(\mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2}_{\text{classical Coulomb interaction}} \\
&\pm \underbrace{\int \varphi^*_{2lm}(\mathbf{r}_1)\varphi_{100}(\mathbf{r}_1)\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\varphi^*_{100}(\mathbf{r}_2)\varphi_{2lm}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2}_{\text{Exchange interaction}} \qquad (7.17) \\
&=: C_l \pm A_l
\end{aligned}
$$

C_l originates from the electrostatic Coulomb interaction and corresponds to the term causing a first l-dependent energy shift. The exchange term A_l describes another quantum phenomenon. It is caused by the interference of the different involved orbital states. The integral in 7.17 gives $A_l > 0$. Therefore, **the spin singlet state (symmetric orbital part) is raised energetically, whereas the spin triplet state (antisymmetric orbital part) is lowered by A_l.** This can be qualitatively understood: For an antisymmetric orbital state, the probability to find both electrons very close to each other is strongly reduced. Thus, the Coulomb repulsion is small. For a symmetric orbital state, the opposite is true. Contrary to the ground state, the lowest excited state is a spin triplet, since it is energetically favorable to have an antisymmetric orbital part. Even though there is no spin interaction in H, the spin-dependent splitting comes into play due to Fermi statistics.

This **exchange interaction** is in many case responsible for **collective magnetism** in some ferromagnetic materials. A similar mechanism leads to **Hund's rules.** By calculating the integrals in 7.17 , we get

$$
\begin{aligned}
E^{(1)}_{1s,2s} &= C_s \pm A_s &&= 11.4eV \pm 1.2eV && (7.18a)\\
E^{(1)}_{1s,2p} &= C_p \pm A_p &&= 13.2eV \pm 0.9eV \quad . && (7.18b)
\end{aligned}
$$

By adding the zero-order energy (-68.0eV), we get the total energy

$$
\begin{aligned}
E_{1s,2s} &= -56.6eV \pm 1.2eV && \text{Exp: } -58.8eV \pm 0.4eV && (7.19a)\\
E_{1s,2p} &= -54.8eV \pm 0.9eV && \text{Exp: } -57.9eV \pm 0.1eV \quad . && (7.19b)
\end{aligned}
$$

The degeneracy is lifted for the spin s (singlet-triplet) as well as for the angular momentum quantum number l (s-,p-Orbitals). Only the degeneracy for m_s and m survives due to the rotation invariance in spin and position space. The quantitative agreement between experiments and first-order perturbation theory is not perfect.

Nevertheless, two important effects can be qualitatively explained: (i) singlet-triplet splitting of the energy levels (ii) The splitting for the $2s$ state is larger than for the $2p$ state.
The energy levels are outlined in figure 7.4.

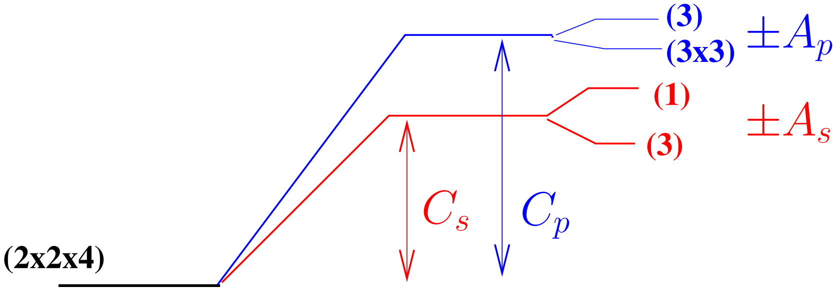


Figure 7.4: Energy splitting of excited states for helium. In parentheses the degeneracies.

Chapter 8

Field quantisation

optional (no compulsory material for the exam)

8.1 Continuum systems: classical treatment

On the way to the concept of photons, we have to figure out how to quantize fields, i.e. continuum variables of position x and time t. As a first example, we consider a vibrating string. We start by summarizing some of the classical results. See e.g. the lecture "Theoretische Mechanik" by E. Arrigoni with lecture notes here. The notation here may be slightly different.
The vertical displacement $u(x,t)$ of an infinitesimal string segment at horizontal position x along the string ($0 < x < L$) obeys the equations of motion EOM

$$\cdots\cdots \tag{8.1}$$

This equation can be obtained from the corresponding **Lagrange functional**

$$\mathscr{L}[\dot{u},u,t] = \int_0^L \ell(u(x,t),u'(x,t),\dot{u}(x,t),x,t)\,dx \tag{8.2}$$

with the **Lagrange density**

$$\ell(u(x,t),u'(x,t),\dot{u}(x,t),x,t) = \frac{\rho}{2}\left(\dot{u}^2 - c^2\,u'^2\right)\ . \tag{8.3}$$

Here, ρ is the mass density of the string, and

$$\dot{u} \equiv \frac{\partial u}{\partial t} \qquad u' \equiv \frac{\partial u}{\partial x}\ .$$

The Hamilton (minimal action) principle leads to the continuum Euler equations of motion[1]

$$\frac{d}{dt}\frac{\partial \ell}{\partial \dot{u}} + \frac{d}{dx}\frac{\partial \ell}{\partial u'} = \frac{\partial \ell}{\partial u} \tag{8.4}$$

which can be easily shown to give the EOM 8.1 .
Equation 8.4 can be obtained by discretising the values of x to x_i, with spacing Δx. Then $\mathscr{L}$ can be seen as a function of the $u_i \equiv u(x_i)$ and $\dot{u}_i$. In the continuum ($\Delta x \to 0$) limit, the usual (discrete) Lagrange II equation

$$\frac{d}{dt}\frac{\partial \mathscr{L}}{\partial \dot{u}_i} = \frac{\partial \mathscr{L}}{\partial u_i} \tag{8.5}$$

can be shown to go over to 8.4 . One way to prove this ((proof here): Sec. A.25) is to start from a discrete version of 8.2 :

$$\mathscr{L} = \Delta x \sum_i \ell(u_i, u_i', \dot{u}_i, x_i, t) \tag{8.6}$$

8.2 Quantisation

The starting point for quantising a set of independent discrete variables u_i is to identify their canonical momenta p_i, and assuming commutation rules between the variables and their momenta

$$[\hat{u}_i, \hat{p}_j] = i\hbar\ \delta_{ij}\ . \tag{8.7}$$

We thus need the canonical momenta. Once we have the Lagrange function, we know from classical mechanics that the p_i are given by

$$p_i = \cdots\cdots$$

Thus, for the present case 8.6

$$p_i = \Delta x\ \frac{\partial \ell}{\partial \dot{u}_i}$$

Introducing the **momentum field**

$$\pi(x_i) = \frac{p_i}{\Delta x} = \frac{\partial \ell}{\partial \dot{u}(x_i)}\ , \tag{8.8}$$

---

[1] Here the "total derivatives" $\frac{d}{dt}$ and $\frac{d}{dx}$ are meant in the sense that one takes into account the dependence of u on x and t.

which in this case 8.3 equals $\rho\dot{u}$, the commutation rules 8.7 become

$$\begin{aligned}[\hat{u}_i,\hat{\pi}_j] &= i\hbar\frac{\delta_{ij}}{\Delta x} \underset{\Delta x\to 0}{\Rightarrow} \\ [\hat{u}(x),\hat{\pi}(x')] &= i\hbar\,\delta(x-x')\,. \end{aligned} \tag{8.9}$$

The commutation rules between the u and the π are zero:

$$[\hat{u}(x),\hat{u}(x')] = [\hat{\pi}(x),\hat{\pi}(x')] = 0\,. \tag{8.10}$$

8.8 with 8.9 and 8.10 determine the quantisation of the field u.
The Hamilton function is obtained as usual from the Legendre transformation. Replacing classical fields with their operators yields the Hamilton operator

$$\begin{aligned}\hat{H} &= \int \dot{u}(x)\hat{\pi}(x)\,dx - \mathscr{L} \equiv \int \hat{h}\left(\hat{\pi}(x),\hat{u}(x)\right)\,dx \\ &= \frac{1}{2}\int_0^L \left[\frac{1}{\rho}\left(\hat{\pi}(x)\right)^2 + c^2\,\rho\left(\frac{d\hat{u}(x)}{dx}\right)^2\right]\,dx \end{aligned} \tag{8.11}$$

with the Hamiltonian density $\hat{h}$.
This example summarizes the **generic procedure** (which we will use later for other cases) **to quantize a field**

- Determine the Lagrange density (here 8.3) which gives the correct classical wave equation
- With 8.8 determine the canonical momenta $\pi(x)$
- Postulate the commutation rules 8.9 (which correspond to the classical Poisson brackets)
- Write the Hamilonian in terms of the $\hat{\pi}$ and $\hat{u}$. This will determine the quantum mechanical time evolution in the usual way.

After quantising the field, we have to solve the problem i.e. first put the

8.2.1 Hamiltonian 8.11 in diagonal form

In order to carry out calculations it is convenient to bring the Hamiltonian 8.11 in diagonal form. This is achieved by starting from the set of classical solutions of the homogeneous wave equation

$$u(x,t) = U_n(x)\,\cos(\omega_n t)$$

In the present case, $U_n(x) = \sqrt{\frac{2}{L}}\sin(k_n x)$ and $\omega_n = ck_n$ with $k_n = \pi n/L$. The important point is the $U_n(x)$ build a complete orthonormal basis with the usual properties

$$\int_0^L U_n(x)\, U_m(x)\, dx = \delta_{n,m} \tag{8.12}$$
$$\sum_{n=1}^{\infty} U_n(x) U_n(x') = \delta(x-x') \,.$$

One can use these relation to introduce new operators

$$\hat{q}_m = \int_0^L U_m(x)\, \hat{u}(x)\, dx \tag{8.13}$$
$$\hat{p}_m = \int_0^L U_m(x)\, \hat{\pi}(x)\, dx \,. \tag{8.14}$$

The inverse relations read

$$\hat{u}(x) = \sum_{n=1}^{\infty} U_n(x) \hat{q}_n$$
$$\hat{\pi}(x) = \sum_{n=1}^{\infty} U_n(x)\, \hat{p}_n \tag{8.15}$$

It is straightforward to show (see here): Sec. A.25 that the $\hat{q}_m$ and $\hat{p}_m$ obey canonical commutation rules

$$[\hat{q}_m, \hat{p}_{m'}] = i\hbar\delta_{m,m'} \qquad [\hat{q}_m, \hat{q}_{m'}] = [\hat{p}_m, \hat{p}_{m'}] = 0 \tag{8.16}$$

The Hamiltonian in terms of these operators has a particularly simple form (see here): Sec. A.25:

$$\hat{H} = \frac{1}{2}\sum_n \left(\frac{1}{\rho}\hat{p}_n^2 + \rho\ \omega_n^2\ \hat{q}_n^2\right) \,. \tag{8.17}$$

with $\omega_n = ck_n$.
This is the Hamilton operator of a set of uncoupled harmonic oscillators with mass ρ and frequencies ω_n. The solution goes via the usual ladder operators:

$$\hat{b}_n^\dagger = \frac{1}{\sqrt{2}}\left(\sqrt{\frac{\rho\,\omega_n}{\hbar}}\ \hat{q}_n - i\frac{1}{\sqrt{\hbar\rho\,\omega_n}}\ \hat{p}_n\right) \tag{8.18}$$
$$\hat{b}_n = \frac{1}{\sqrt{2}}\left(\sqrt{\frac{\rho\,\omega_n}{\hbar}}\ \hat{q}_n + i\frac{1}{\sqrt{\hbar\rho\,\omega_n}}\ \hat{p}_n\right) \,.$$

with the known commutation relations

$$[\hat{b}_n, \hat{b}_m] = 0 \tag{8.19}$$
$$[\hat{b}_n^\dagger, \hat{b}_m^\dagger] = 0$$
$$[\hat{b}_n, \hat{b}_m^\dagger] = \delta_{nm} \ .$$

It is customary to omit the ˆ from these ladder operators, which we are going to do in the following.
The hamiltonian finally becomes

$$\hat{H} = \sum_{n=1}^{\infty} \hbar\omega_n \left(b_n^\dagger b_n + \frac{1}{2} \right) .$$

Its eigenstates can be written in terms of the set of quantum numbers $\{N_n, n = 1, 2, \cdots\}$ of each one of the harmonic oscillators as

$$|N_1, N_2, \cdots\rangle \ . \tag{8.20}$$

where each N_n can be $0, 1, \cdots, \infty$.
These states have the same structure as the states of the many-particle Fock space 9.43 . The scalar product is the same as 7.7 .
The interesting aspect of this result is that we started from a field, whose excitations are **waves**, and we come out with a description in which the wave modes are similar to **particles**. This is an important characteristic of quantum mechanics in which, on the one hand, particles are described by waves but also the opposite waves are described by particles.

8.2.2 Creation and destruction operators

From the Bachelor Quantum Mechanics course, we already know the properties of the ladder operators b_n and $b_n^\dagger$. Acting on the basis states they have the properties of increasing or decreasing the excitations:

$$b_n^\dagger \ |N_1, N_2, \cdots N_n, \cdots\rangle = \sqrt{N_n + 1}\, |N_1, N_2, \cdots (N_n + 1), \cdots\rangle \ ,$$
$$b_n \ |N_1, N_2, \cdots N_n, \cdots\rangle = \sqrt{N_n}\, |N_1, N_2, \cdots (N_n - 1), \cdots\rangle \ . \tag{8.21}$$

Obviously the same operators with the same properties can be formally introduced for a bosonic Fock space. They are completely defined by their commutation rules 8.19 and, due to their properties 8.21 to create and destroy particles are termed **creation and destruction (or annihilation) operators**.
One important composite operator is the **number operator** $b_n^\dagger b_n$ which counts the number of particles in level n:

$$b_n^\dagger b_n \ |N_1, N_2, \cdots N_n, \cdots\rangle = N_n\, |N_1, N_2, \cdots N_n, \cdots\rangle \tag{8.22}$$

Chapter 9

Second quantisation

9.1 Quantisation of the Schrödinger field

We could now consider the wave function in the Schrödinger equation, also known as SCHRÖDINGER FIELD, as a classical field, and adopt the procedure described in Chap. 8) to quantise it. Since the system is somewhat quantised twice, this is referred to as **Second Quantisation**. A more correct term is **Field Quantisation**.

The goal is to introduce a formalism to treat states with many identical particles in a more compact way.
(i) As in Sec. 8 we will introduce creation and destruction operators which change the number of bosonic or fermionic particles.
(ii) Operators, such as the Hamilton operator, but also other operators (observables) will be written in terms of these operators.
(iii) Many-body states will be constructed by creating particles on top of a state without particles, the vacuum state.
(iv) The second quantisation formalism provides an alternative to the one of Sec. 7, whereby many-body states are written as symmetrized/antisymmetrized wave functions. Of course physical quantities, i.e. the expectation values of operators will be the same when evaluated with the two formalisms. We will not derive an exact proof but illustrate it for some examples.

To achieve this we need to carry out the same procedure described in Sec. 8.2 but for another wave equation. Instead of the wave equation for an elastic string 8.1 , we will consider the Schrödinger equation and quantize the corresponing field.

9.1.1 Lagrangian of the Schrödinger field

Starting from the Schrödinger equation of a single particle in a potential $V(x)$,

$$-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2\Psi + V(\mathbf{x})\Psi = i\hbar\dot{\Psi}\,.$$

we can consider the real and the imaginary part as independent fields since Ψ and Ψ^* are complex functions of $\mathbf{x}$ and t. Another possibility is to take Ψ and Ψ^* as indepenent fields.
We are looking for a Lagrangian, which produces the Schrödinger equation via the Lagrange II equations. A possible form satisfying this is easily seen to be

$$\mathscr{L} = \int \Psi^* \left[i\hbar\dot{\Psi} + \frac{\hbar^2}{2m}\boldsymbol{\nabla}^2\Psi - V(\mathbf{x})\Psi \right] d^3x\,. \tag{9.1}$$

The Lagrange II equations are now evaluated with respect to Ψ^*. The canonical momentum for Ψ^* vanishes, due to

$$\tilde{\pi} := \frac{\delta\mathscr{L}}{\delta\dot{\Psi}^*} = 0\,. \tag{9.2}$$

Therefore we have

$$\begin{aligned} 0 = \frac{\delta\mathscr{L}}{\delta\Psi^*} &= i\hbar\dot{\Psi} + \frac{\hbar^2}{2m}\boldsymbol{\nabla}^2\Psi - V(\mathbf{x})\Psi \\ \text{i.e.}\quad i\hbar\dot{\Psi} &= -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2\Psi + V(\mathbf{x})\Psi\,. \end{aligned}$$

This is indeed the Schrödinger equation. We now derive the Lagrangian II equation with respect to the second independent variable Ψ. The canonical momentum is (see 9.1)

$$\ldots\ldots \tag{9.3}$$

and the Lagrangian II equation gives the complex conjugate Schrödinger equation.((proof here): Sec. A.26). As usual, we obtain the Hamilton function by a Legendre transformation. With 9.1 , we get

$$\begin{aligned} H &= \int \left(\overbrace{\frac{\delta\mathscr{L}}{\delta\dot{\Psi}^*}}^{\overset{9.2}{=}\;0} \dot{\Psi}^* + \overbrace{\frac{\delta\mathscr{L}}{\delta\dot{\Psi}}}^{\overset{9.3}{=}\;i\hbar\Psi^*} \dot{\Psi} - \overbrace{\mathscr{L}}^{9.1} \right) d^3x \\ &= \int \left(i\hbar\Psi^*\dot{\Psi} - i\hbar\Psi^*\dot{\Psi} - \Psi^* \left[\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 - V(\mathbf{x}) \right] \Psi \right) d^3x\,. \end{aligned}$$

The first two terms cancel out and therefore we get the Hamilton function

$$H = \int \Psi^* \left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{x}) \right] \Psi \, d^3x \, . \tag{9.4}$$

Despite of the fact that the Lagrangian is not symmetric between Ψ and Ψ^*, we obtained a symmetric form of the Hamilton function. We recognize this as the expectation value of the Hamiltonian for a single particle.

$$H = \langle \Psi | \hat{H}_{\mathrm{FQ1}} | \Psi \rangle \tag{9.5}$$

Here the subscript $_{\mathrm{FQ1}}$ has been introduced in order to label an operator for a particle in first quantisation, in contrast to operators in second quantisation, labeled below by $_{\mathrm{SQ}}$
Up to now, Ψ and Ψ^* were classical fields. As next step, we are going to quantise them.

9.1.2 Quantisation

We use the relation 9.3 $\pi = i\hbar\Psi^*$ to find the canonical momentum to Ψ. We replace both fields with field operators and we require as before

$$[\hat{\Psi}(\mathbf{x}), \hat{\pi}(\mathbf{x}')] = i\hbar\delta(\mathbf{x} - \mathbf{x}') \, . \tag{9.6}$$

This results in

$$[\hat{\Psi}(\mathbf{x}), \hat{\Psi}^\dagger(\mathbf{x}')] = \delta(\mathbf{x} - \mathbf{x}') \, . \tag{9.7}$$

Additionally we require that $\hat{\Psi}(\mathbf{x})$ and $\hat{\Psi}^\dagger(\mathbf{x})$ commute with each other.

$$[\hat{\Psi}(\mathbf{x}), \hat{\Psi}(\mathbf{x}')] = 0 \tag{9.8a}$$

$$[\hat{\Psi}^\dagger(\mathbf{x}), \hat{\Psi}^\dagger(\mathbf{x}')] = 0 \, . \tag{9.8b}$$

Similarly to Chapter 8 we expand the field operators in terms of the stationary solutions of the field equation, i.e. the eigenfunctions of the Schrödinger equation $\varphi_n(\mathbf{x})$ with operator coefficients $\hat{b}_n$.

$$\hat{\Psi}(\mathbf{x}) = \sum_n \hat{b}_n \varphi_n(\mathbf{x}) \tag{9.9}$$

$$\hat{\Psi}^\dagger(\mathbf{x}) = \sum_n \hat{b}_n^\dagger \varphi_n^*(\mathbf{x}) \, .$$

The canonical commutation rules for the fields 9.6 and 9.7), become for the operators b_n (we will omit the ˆ for b_n) proof here: Sec. A.28 :

$$[b_n, b_m^\dagger] = \delta_{n,m} \tag{9.10a}$$
$$[b_n, b_m] = 0 \tag{9.10b}$$
$$[b_n^\dagger, b_m^\dagger] = 0\,. \tag{9.10c}$$

Since we quantised the wave functions, the Hamilton function becomes the Hamiltonian operator proof here: Sec. A.28

HAMILTON OPERATOR IN SECOND QUANTISATION
IN ITS EIGENBASIS

$$\hat{H}_{\text{SQ}} = \int \hat{\Psi}^\dagger(\mathbf{x}) \underbrace{\left[-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V(x)\right]}_{\hat{H}_{\text{FQ1}}} \hat{\Psi}(\mathbf{x})\; d^3x_1 \tag{9.11a}$$

$$= \sum_n E_n b_n^\dagger b_n\,. \tag{9.11b}$$

As in Sec. 8 these kinds of “ harmonic oscillator” operators $b_n^\dagger$ describe the creation of a particle in the eigenstate of the Hamiltonian (“level”) with single-particle wave function $\varphi_n(\mathbf{x})$. The advantage of 9.11a is, that one can create many (identical) particles with different wave functions. In first quantisation, this is only possible with a symmetrized function with more than one variable $\Psi(\mathbf{x}_1, \cdots, \mathbf{x}_n)$.

It is thus convenient to use the one-to-one correspondence with a quantum-mechanical system consisting of a set of harmonic oscillators. Its (unnormalized) eigenstates are

$$|\psi\rangle = \prod_n (b_n^\dagger)^{N_n} |0\rangle\,, \tag{9.12}$$

where N_n is the occupation of the level n.

Here, $|0\rangle$ is **vacuum state** with the following properties:

$$b_n|0\rangle = 0 \qquad \text{for all } n \tag{9.13}$$

and, due to 9.9

$$\hat{\Psi}(\mathbf{x})|0\rangle = 0 \qquad \text{for all } \mathbf{x} \tag{9.14}$$

Alternatively to 9.9 one can expand the field operators in terms of an alternative set of orthonormal basis functions χ_n.

$$\hat{\Psi}(\mathbf{x}) = \sum_n \hat{c}_n \, \chi_n(\mathbf{x}) \qquad \hat{\Psi}^\dagger(\mathbf{x}) = \sum_n \hat{c}_n^\dagger \, \chi_n^*(\mathbf{x}) \; . \tag{9.15}$$

One can transform directly from the operators b to c:

$$b_n = \sum_m U_{nm} \hat{c}_m \qquad b_n^\dagger = \sum_m U_{nm}^* \hat{c}_m^\dagger \; , \tag{9.16}$$

using the unitary matrix $U_{nm} = \int \varphi_n^*(\mathbf{x}) \chi_m(\mathbf{x}) \; d^3x$. This follows from 9.9 by multiplying from the left with φ_n and integrating (Exercise).
The creation and destruction (or annihilation) operators $c_n^\dagger$ (c_n) (as for the operators b we will omit the ˆ from now on) obey the same commutation rules as the operators b due to the orthonormality of the basis. proof here: Sec. A.28 The Hamiltonian is no longer diagonal in the c operators. Instead, we get for the

HAMILTONIAN IN SECOND QUANTISATION
FOR AN ARBITRARY ORTHONORMAL BASIS

$$\hat{H}_{\text{SQ}} = \sum_{n,m} h_{n,m} c_n^\dagger c_m \tag{9.17}$$

with matrix elements

$$\begin{aligned} h_{n,m} &= \int \chi_n^*(\mathbf{x}) \left[-\frac{\hbar^2}{2m} \boldsymbol{\nabla}^2 + V(x) \right] \chi_m(\mathbf{x}) \; d^3x \\ &= \langle \chi_n | \hat{H}_{\text{FQ1}} | \chi_m \rangle \;\; : \end{aligned} \tag{9.18}$$

One could think, that the second quantisation leads to different physical results. This is not the case. Both formalisms are completely equivalent. However, second quantisation has several practical advantages, especially when dealing with many-particle systems. Moreover, second quantisation is more flexible for phenomena without a constant number of particles (e.g. annihilation and creation of photons).

9.2 Second quantisation for fermions

The form discussed in the previous section reproduces the **symmetry** of the wave function (particle statistics), which is valid for bosons. To describe fermions, which have an **antisymmetric** wave function we have to use different creation and destruction operators. As an example, we consider a state with two fermionic particles in two levels $|\varphi_{\mathbf{q}}\rangle$ and $|\varphi_{\mathbf{q}'}\rangle$

$$|\Psi\rangle = \frac{1}{\sqrt{2}}\Big(|\varphi_{\mathbf{q}}\rangle \otimes |\varphi_{\mathbf{q}'}\rangle - |\varphi_{\mathbf{q}'}\rangle \otimes |\varphi_{\mathbf{q}}\rangle\Big) \, .$$

In second quantisation, this state has the form

$$|\Psi\rangle = c^\dagger_{\mathbf{q}} c^\dagger_{\mathbf{q}'} |0\rangle \, .$$

To assure the correct antisymmetry, we clearly require

$$\begin{aligned} c^\dagger_{\mathbf{q}} c^\dagger_{\mathbf{q}'} &= -c^\dagger_{\mathbf{q}'} c^\dagger_{\mathbf{q}} \\ \text{i.e.} \quad \{c^\dagger_{\mathbf{q}}, c^\dagger_{\mathbf{q}'}\} &= 0 \\ \text{with} \quad \{A,B\} &:= AB + BA \quad \text{(Anti-commutator)} \, . \end{aligned}$$

For fermions we often have to consider spin $(\sigma = \pm 1$ this means the sign of one component, e.g. of $z)$. Therefore, in the above equations the level $|\varphi_{\mathbf{q}}\rangle$ describes both the spatial as well as the spin part of the wave function. In other words, we can use a convention whereby $\mathbf{q} \equiv (n,\sigma)$ describes both the orbital (n) quantum numbers as well as the spin projection.
Summarizing, for fermions the following anti commutation guarantee the description of a properly antisymmetrized wave function (we won't prove it)

$$\begin{aligned} \{c^\dagger_{\mathbf{q}}, c^\dagger_{\mathbf{q}'}\} &= \{c_{\mathbf{q}}, c_{\mathbf{q}'}\} = 0 \\ \{c^\dagger_{\mathbf{q}}, c_{\mathbf{q}'}\} &= \delta_{\mathbf{q},\mathbf{q}'} \, . \end{aligned}$$

If we consider spin explicitly, we note that the delta splits to $\delta_{\mathbf{q},\mathbf{q}'} = \delta_{n,n'}\delta_{\sigma,\sigma'}$ leading to

ANTI-COMMUTATION RELATIONS FOR FERMIONS

$$\{c^\dagger_{n,\sigma}, c^\dagger_{m,\sigma'}\} = 0 \tag{9.19}$$

$$\{c_{n,\sigma}, c_{m,\sigma'}\} = 0 \tag{9.20}$$

$$\{c_{n,\sigma}, c^\dagger_{m,\sigma'}\} = \delta_{n,m}\delta_{\sigma,\sigma'} \, . \tag{9.21}$$

The Pauli principle is accounted for, since $(c^{\dagger}_{n,\sigma})^2 |0\rangle = 0$, i.e. I cannot have two fermions with the same n and σ.
The **Hamiltonian in second quantisation for fermions** is analogous as for bosons. In the eigenbasis (cf . 9.11a):

$$\hat{H} = \sum_{n,\sigma} E_{n\sigma}\, c^{\dagger}_{n,\sigma}\, c_{n,\sigma}$$

where $E_{n\sigma}$ is often independent of spin σ. Or for an arbitrary basis [1]

$$\hat{H} = \sum_{n,m,\sigma} h_{n,m}\, a^{\dagger}_{n,\sigma}\, a_{m,\sigma}\ ,$$

where $a^{\dagger}_{n,\sigma}$,$a_{n,\sigma}$ have the same anticommutation rules 9.21 , and the matrix elements $h_{n,m}$ have the same expression as in 9.17 . As one can see, the difference is just the introduction of spin to label the single-particle state.
Also the many-particle eigenstates have the same form 9.12 as for bosons

$$|\psi\rangle = \prod_{n,\sigma} (c^{\dagger}_{n\sigma})^{N_{n\sigma}} |0\rangle\ , \tag{9.22}$$

where $N_{n\sigma}$ is the occupation of the level n with spin σ, which, in contrast to bosons, can only take the values 0 or 1. The **vacuum state** $|0\rangle$ has the same properties as 9.13

$$c_{n\sigma}|0\rangle = 0 \qquad \text{for all } n,\sigma \tag{9.23}$$

The anticommutation rules guarantee that these fermionic states are automatically antisymmetrised.

9.3 Operators in second quantisation

The procedure to quantise fields described above consisted in starting from the Lagrange and Hamilton function (total energy), quantise the fields Ψ, and to expand them in terms of orthonormal solutions of the field equation with the coefficients (amplitudes) being operators. Based on this approach, arbitrary operators/observables can be translated into second quantisation.

9.3.1 Single particle operators

In first quantisation the Hamiltonian $\hat{H}_{\mathrm{FQ}}$ of N identical, non interacting particles is the sum of the Hamiltonians $\hat{H}_{\mathrm{FQ}i}$ of each particle i

$$\hat{H}_{\mathrm{FQ}} = \sum_{i=1}^{N} \hat{H}_{\mathrm{FQ}i} = \sum_{i=1}^{N} H(\hat{\mathbf{r}}_i, \hat{\mathbf{p}}_i) \tag{9.24}$$

---

[1] we take a spin-independent Hamiltonian for simplicity

In second quantisation, this is replaced by the quantized Hamiltonian of the Schrödinger field. As discussed in 9.5 , the latter is composed of the Expectation value of the first-quantisation Hamiltonian (for one particle)

$$H_{\mathrm{SQ}} = \langle\Psi|\hat{H}_{\mathrm{FQ1}}|\Psi\rangle \,,$$

where the wave function Ψ is quantized according to 9.7 and 9.8a for bosons, or the corresponding anticommutator expression including spin for fermions

$$\begin{aligned} \{\hat{\Psi}_\sigma(\mathbf{x}), \hat{\Psi}^\dagger_{\sigma'}(\mathbf{x}')\} &= \delta(\mathbf{x}-\mathbf{x}')\;\delta_{\sigma,\sigma'} \\ \{\hat{\Psi}_\sigma(\mathbf{x}), \hat{\Psi}_{\sigma'}(\mathbf{x}')\} &= 0 \\ \{\hat{\Psi}^\dagger_\sigma(\mathbf{x}), \hat{\Psi}^\dagger_{\sigma'}(\mathbf{x}')\} &= 0\,. \end{aligned}$$

This procedure can be applied in the same way to arbitrary, so-called single-particle operators.

A single-particle operator is one, which has the form 9.24 in first quantisation, i.e. it is composed of an independent sum over all particles of the same operator acting on just one of the particles.

$$\hat{O}_{\mathrm{FQ}} = \sum_{i=1}^{N} \hat{O}_{\mathrm{FQ}i} \tag{9.25}$$

Terms describing interactions between the particles cannot be described by single-particle operators, and will be discussed below.

We apply the procedure of Sec. 9.1 to an arbitrary operator $\hat{O}_{\mathrm{FQ}}$ in first quantisation generically expressed in the form 9.25 The single operators $\hat{O}_{\mathrm{FQ}i}$ can be, for example, expressed as functions of $\hat{\mathbf{x}}_i$ and $\hat{\mathbf{p}}_i = -i\hbar\boldsymbol{\nabla}_i$. e.g. $\hat{O}_{\mathrm{FQ}i} = \hat{\mathbf{r}}_i$.

As discussed in Sec. 9.1, we need the expectation value

$$\langle\Psi|\,\hat{O}_{\mathrm{FQ1}}\,|\Psi\rangle = \int \Psi^*(\mathbf{x})\;\hat{O}_{\mathrm{FQ1}}\;\Psi(\mathbf{x})\;d^3x\,.$$

Using the same procedure as for $\hat{H}$ this leads to

$$\hat{O}_{\mathrm{SQ}} = \int \hat{\Psi}^\dagger(\mathbf{x})\;\hat{O}_{\mathrm{FQ1}}\;\hat{\Psi}(\mathbf{x})\;d^3x\,. \tag{9.26}$$

As in 9.9 , we can expand the field operator into eigenfunctions $\varphi_n(\mathbf{x})$ of $\hat{H}$ (or in arbitrary orthogonal functions $\chi_n(\mathbf{x})$, as in 9.15) and get

$$\begin{aligned} \hat{\Psi}(\mathbf{x}) &= \sum_n \varphi_n(\mathbf{x})\hat{b}_n \\ \hat{O}_{\mathrm{SQ}} &= \sum_{n,m}\left(\int \varphi_n^*(\mathbf{x})\;\hat{O}_{\mathrm{FQ1}}\;\varphi_m(\mathbf{x})\;d^3x\right) b_n^\dagger b_m \\ &= \sum_{n,m}\langle\varphi_n|\,\hat{O}_{\mathrm{FQ1}}\,|\varphi_m\rangle\; b_n^\dagger b_m \end{aligned}$$

i.e

$$\hat{O}_{\mathrm{SQ}} = \sum_{n,m} O_{n,m}\, b_n^\dagger b_m \tag{9.27}$$
$$O_{n,m} = \langle \varphi_n | \hat{O}_{\mathrm{FQ1}} | \varphi_m \rangle$$

9.27 provides the expression for an arbitrary (single-particle) operators in second quantisation in terms of creation and destruction operators.

Summary: single-particle operators

In general, for a system with N identical particles a single-particle operator $\hat{O}$ has the form[2]

SINGLE-PARTICLE OPERATORS

$$\text{for} \quad \hat{O}_{\mathrm{FQ}} = \sum_{i=1}^{N} O_{\mathrm{FQ}i} = \sum_{i=1}^{N} O(\hat{\mathbf{x}}_i, \hat{\mathbf{p}}_i) \qquad \text{in first quantisation}$$
$$\hat{O}_{\mathrm{SQ}} = \sum_{n,n'} O_{n,n'}\, b_n^\dagger b_{n'} \qquad \text{in second quantisation} \tag{9.28}$$
$$\text{with} \quad O_{n,n'} = \langle \varphi_n | \hat{O}_{\mathrm{FQ1}} | \varphi_{n'} \rangle = \int \varphi_n^*(\mathbf{x}) O(\mathbf{x}, -i\hbar\boldsymbol{\nabla}) \varphi_{n'}(\mathbf{x}) d^3\mathbf{x}\,.$$

The many-body basis states are given in 9.12 . These bosonic states are automatically symmetrised.
For fermions we have in complete analogy, the only difference being spin

SINGLE PARTICLE OPERATORS FOR FERMIONS IN SQ

$$\hat{O} = \sum_{n,n',\sigma} O_{n,n'}\, c_{n,\sigma}^\dagger c_{n',\sigma}$$
$$O_{n,n'} = \langle \varphi_n | \hat{O}_{\mathrm{FQ1}} | \varphi_{n'} \rangle = \int \varphi_n^*(\mathbf{x}) O(\mathbf{x}, -i\hbar\boldsymbol{\nabla}) \varphi_{n'}(\mathbf{x}) d^3\mathbf{x}\,. \tag{9.29}$$

---

[2] Again: $\hat{O}_{\mathrm{FQ}i}$ is the first quantisation operator for just particle i, while $\hat{O}_{\mathrm{FQ}}$ is the sum over all particles of that operator

With many-body states 9.22 .

Useful rules for (anti) commutators

When working in second quantisation one often has to carry out commutators or anticommutators between operators consisting of product of creation and destruction operators. In this case, the (possibly repeated) application of these relation can be useful. The proof is here: Sec. A.30

$$\begin{aligned}[a\,b,c] &= \\ &= a[b,c]+[a,c]b \\ &= a\{b,c\}-\{a,c\}b\end{aligned} \tag{9.30}$$

$$\begin{aligned}[c,a\,b] &= \\ &= [c,a]b+a[c,b] \\ &= \{c,a\}b-a\{c,b\}\end{aligned} \tag{9.31}$$

Equivalence between FQ and SQ for single-particle operators

As discussed above, second quantisation is just an alternative formalism to deal with many-particle systems in an efficient way. Of course, the requirement is that first (FQ) and second (SQ) quantisation should give the same physical results. In other words, expectation values of corresponding operators must coincide in the two formalisms.

To evaluate expectation values of operators in FQ one has first to symmetrize (or antisymmetrize) the wave function, as discussed in Chap. 7, which for more than two or three particles becomes quite laborious.

In second quantisation (anti)-symmetrisation is not necessary, as it is automatically taken care by states of the form 9.12 .

We will not prove systematically the equivalence of FQ and SQ here. This would be a lengthy procedure. We refer to the abundant literature. However, we will illustrate this for simple examples. This gives us the opportunity to exercise a bit with creation and destruction operators.

We consider an arbitrary single-particle operator $\hat{O}$, e.g. the position operator $\hat{\mathbf{x}}$. For a particle with wave function $\varphi_\nu(\mathbf{x})$, the expectation value of $\hat{O}$ in first quantisation is given by

$$\langle \hat{O}_{\mathrm{FQ1}} \rangle = \int \varphi_\nu^*(\mathbf{x})\ \hat{O}_{\mathrm{FQ1}}\ \varphi_\nu(\mathbf{x})\ d\mathbf{x}\,.$$

In second quantisation, the state has the following form [3]

$$|\varphi_\nu\rangle = b_\nu^\dagger |0\rangle$$

and the expectation value of the operator 9.27 becomes

$$\langle \hat{O}_{\text{SQ}} \rangle = \sum_{n,m} O_{n,m} \langle 0| b_\nu b_n^\dagger b_m b_\nu^\dagger \,|0\rangle \tag{9.32}$$

To evaluate this, we first deal with the right hand side of 9.32 :

$$\underbrace{b_m b_\nu^\dagger}\,|0\rangle = \cdots\cdots$$

Here and below, the upper sign is for bosons and the lower for fermions. Moreover, we have defined $[A,B]_\mp \equiv AB \mp BA$ as the commutator/anticommutator. Another way to obtain to this result is to interpret the state $b_\nu^\dagger\,|0\rangle$ as a "single particle in level ν". b_m destroys a particle in level m: if $m \neq \nu$ this results in "nothing" (0), otherwise, if $m = \nu$, we arrive at the vacuum state (state without particles).

The left hand side is evaluated by using the hermitian conjugate, which results in a similar expression as above (see 9.47):

$$\langle 0|\, b_\nu b_n^\dagger = \left(b_n b_\nu^\dagger \,|0\rangle \right)^\dagger = (\delta_{n,\nu}\,|0\rangle)^\dagger = \delta_{n,\nu}\,\langle 0|$$

In total, 9.32 results in

$$\langle \hat{O}_{\text{SQ}} \rangle = \sum_{n,m} O_{n,m} \delta_{n,\nu} \delta_{m,\nu}\,\langle 0|0\rangle = O_{\nu,\nu} = \int \varphi_\nu^*\; \hat{O}_{\text{FQ1}}\; \varphi_\nu(\mathbf{x})\; d\mathbf{x}\,.$$

This is also what is expected in first quantisation. First and second quantisation lead to the same result.

More interesting is the case of a state with more than one particle in second quantisation. Here, several levels are occupied, e.g. for two particles:

$$|\varphi_\nu, \varphi_\mu\rangle = \frac{1}{Z_{\nu\mu}}\, b_\nu^\dagger b_\mu^\dagger |0\rangle\,.$$

The normalisation constant $Z_{\nu\mu}$ can be determined by analogy with a system of harmonic oscillators. For $\nu = \mu$ (only possible for bosons), we have $Z_{\nu\nu} = \sqrt{2}$. For $\nu \neq \mu$ the state corresponds to having two "oscillators" in the first excited state. Here the normalisation constant is[4] $Z_{\nu\mu} = 1 \cdot 1 = 1$.

---

[3] Also valid for fermions, whereby spin is included in the index ν.

[4] The normalisation constant can be also determined explicitly by carry out the scalar product of the state with itself. (see here for bosons): Sec. A.29

The expectation value of an arbitrary single-particle operator (cf. 9.27) in this state becomes

$$\langle \hat{O}_{\mathrm{SQ}} \rangle = \cdots\cdots \tag{9.33}$$

As before, we first consider the right-hand side of the expectation value. We want to end up having the annihilation operator b_m on the right, in order to destroy the vacuum state.

$$\begin{aligned} \underbracket{b_m b_\nu^\dagger} b_\mu^\dagger |0\rangle &= \pm b_\nu^\dagger \underbracket{b_m b_\mu^\dagger} |0\rangle + \delta_{m,\nu} b_\mu^\dagger |0\rangle \\ &= \cdots\cdots \\ &= \pm \delta_{m,\mu} b_\nu^\dagger |0\rangle + \delta_{m,\nu} b_\mu^\dagger |0\rangle \ . \end{aligned} \tag{9.34}$$

This result can be understood in the following way: b_m should destroy a particle in level m. If there is no particle in m, the result is 0, otherwise the other particle in the initial state remains. In the case of fermions there is an additional minus sign depending on which of the two particles has been destroyed.

The left-hand side is again evaluated by using the hermitian conjugate of the right-hand side:

$$\langle 0| b_\mu b_\nu b_n^\dagger = \langle 0| b_\mu \delta_{n,\nu} \pm \langle 0| b_\nu \delta_{n,\mu} \ .$$

We now distinguish the cases $\nu = \mu$ and $\nu \neq \mu$. For $\nu = \mu$ 9.34 becomes [5]

$$b_m b_\nu^{\dagger\,2} |0\rangle = 2\delta_{m,\nu} b_\nu^\dagger |0\rangle$$

using $\langle 0| b_\nu \, b_\nu^\dagger |0\rangle = 1$ this results in

$$\langle 0| b_\nu^2 b_n^\dagger \, b_m b_\nu^{\dagger\,2} |0\rangle = 4\delta_{n,\nu} \delta_{m,\nu}$$

so that 9.33 becomes

$$\langle \hat{O}_{\mathrm{SQ}} \rangle = \frac{4}{2} O_{\nu,\nu} = 2\, O_{\nu,\nu} \ .$$

For $\nu \neq \mu$ using 9.34 and its hermitian conjugate as well as $\langle 0| b_\nu b_\mu^\dagger |0\rangle = \delta_{\nu\mu}$

$$\langle 0| b_\mu b_\nu b_n^\dagger \, b_m b_\nu^\dagger b_\mu^\dagger |0\rangle = \delta_{n,\nu} \delta_{m,\nu} + \delta_{n,\mu} \delta_{m,\mu}$$

---

[5] This is valid for bosons only. For fermions this becomes zero, which is understandable since $\nu = \mu$ is not allowed by Pauli principle

(notice that the fermionic sign cancels out), and 9.33 becomes

$$\langle \hat{O}_{\mathrm{SQ}} \rangle = O_{\nu,\nu} + O_{\mu,\mu}$$

These are results we would obtain in first quantisation for two particles in the (anti-)symmetrized states

$$|\Psi\rangle = |\varphi_\nu\rangle \otimes |\varphi_\nu\rangle \qquad \text{for bosons only}$$

or

$$|\Psi\rangle = \frac{1}{\sqrt{2}} \Big(|\varphi_\nu\rangle \otimes |\varphi_\mu\rangle \pm |\varphi_\mu\rangle \otimes |\varphi_\nu\rangle \Big)$$

To evaluate this in first quantisation, we should have used the respective operators in first quantisation for two particles

$$\hat{O} = \hat{O}_{\mathrm{FQ1}} + \hat{O}_{\mathrm{FQ2}} \ .$$

Physical meaning of the field operator $\hat{\Psi}$

The probability density $\rho(\mathbf{x})$ at the position $\mathbf{x}$ in first quantisation becomes the **particle density operator** in second quantisation.

$$\hat{\rho}(\mathbf{x}) \equiv \hat{\Psi}^\dagger(\mathbf{x}) \hat{\Psi}(\mathbf{x}) \tag{9.35}$$

In this way, one can show that the **operator $\hat{\Psi}^\dagger(\mathbf{x})$ creates a particle at the position $\mathbf{x}$**. This means that

$$|\mathbf{x}\rangle \equiv \hat{\Psi}^\dagger(\mathbf{x}) |0\rangle \tag{9.36}$$

becomes a state with one particle in $\mathbf{x}$ (with a delta-wave function). In order to proof this, we show that $|\mathbf{x}\rangle$ is an eigenstate of the density 9.35

Proof:

$$\begin{aligned} \hat{\rho}(\mathbf{y}) |\mathbf{x}\rangle &= \cdots\cdots \\ &= \cdots\cdots \\ &= \cdots\cdots \end{aligned}$$

Similarly, including spin for fermions it is straightforward to show that

$$\hat{\Psi}^\dagger_{\sigma'}(\mathbf{x}) |0\rangle$$

is an eigenstate of the density for one spin direction

$$\hat{\rho}_\sigma(\mathbf{y}) \equiv \hat{\Psi}^\dagger_\sigma(\mathbf{y}) \hat{\Psi}_\sigma(\mathbf{y})$$

with eigenvalue $\delta_{\sigma,\sigma'} \delta(\mathbf{x} - \mathbf{y})$. In this case the **total density operator** is obtained by summing over spin:

$$\hat{\rho}(\mathbf{y}) \equiv \sum_\sigma \hat{\Psi}^\dagger_\sigma(\mathbf{y}) \hat{\Psi}_\sigma(\mathbf{y})$$

we'll need it later.

9.3.2 Two-particle operators

In addition to the single-particle operators that describe, in an Hamiltonian, the kinetic energy and the interaction with external potentials, two-particle operators also play an important role. Two-particle operators describe the interaction between particles expressed as a sum of interactions between pairs of particles.
One of the most important examples is the Coulomb interaction. To determine its second quantisation expression, we start from the classical form of the interaction between two charge densities $\rho_1(\mathbf{x})$ and $\rho_2(\mathbf{x}')$

$$\begin{aligned} H_{int} &= \int\int \rho_1(\mathbf{x})V(\mathbf{x},\mathbf{x}')\rho_2(\mathbf{x}')d^3\mathbf{x}d^3\mathbf{x}' \\ &= \frac{1}{2}\int\int \rho(\mathbf{x})V(\mathbf{x},\mathbf{x}')\rho(\mathbf{x}')d^3\mathbf{x}d^3\mathbf{x}' - self.energy\,, \end{aligned} \tag{9.37}$$

where we use the total charge density $\rho(\mathbf{x}) = \rho_1(\mathbf{x}) + \rho_2(\mathbf{x})$, as the two charges are indistinguishable. The factor $1/2$ compentsates for the double counting and the *self.energy* term subtracts the interaction energy $\rho_1(\mathbf{x})\rho_1(\mathbf{x}')$ of a charge with itself. We now replace the particle density with the corresponding operator in second quantisation (we don't consider spin for the moment).

$$\hat{\rho}(\mathbf{x}) = \hat{\Psi}^\dagger(\mathbf{x})\hat{\Psi}(\mathbf{x}) \tag{9.38}$$

and get [6]

$$\hat{H}_{int} = \frac{1}{2}\int\int \hat{\Psi}^\dagger(\mathbf{x})\hat{\Psi}(\mathbf{x})V(\mathbf{x},\mathbf{x}')\hat{\Psi}^\dagger(\mathbf{x}')\hat{\Psi}(\mathbf{x}')d^3\mathbf{x}d^3\mathbf{x}' - self.energy\,,\,. \tag{9.39}$$

The subtraction of the self energy term can be taken into account by requiring that the interaction vanishes if less than two particles are present, i.e.

$$\begin{aligned} \hat{H}_{int}|0\rangle &= 0 \\ \hat{H}_{int}\, b_l^\dagger|0\rangle &= 0\,. \end{aligned}$$

In second quantisation this requirement is naturally achieved by "normal ordering" creation and destruction operator. This means that all destruction operators are moved to the right and all creation operators to the left. We obtain:

---

[6] From now on, for simplicity we will omit the explicit subscript $_{\mathrm{SQ}}$. So all operators will be understood to be in second quantisation, unless specified with the $_{\mathrm{FQ}}$ subscript.

INTERACTION PART OF THE HAMILTONIAN IN SECOND QUANTISATION
IN TERMS OF FIELD OPERATORS (CF. 9.39)

$$\text{for}\quad \hat{H}_{int\,\mathrm{FQ}} = \frac{1}{2}\sum_{i\neq j=1}^{N} V(\hat{\mathbf{x}}_i,\hat{\mathbf{x}}_j) \qquad \text{in FQ} \tag{9.40}$$

$$\hat{H}_{int} = \frac{1}{2}\int\int \hat{\Psi}^{\dagger}(\mathbf{x})\hat{\Psi}^{\dagger}(\mathbf{x}')V(\mathbf{x},\mathbf{x}')\hat{\Psi}(\mathbf{x}')\hat{\Psi}(\mathbf{x})d^3\mathbf{x}d^3\mathbf{x}' \qquad \text{in SQ}\,.$$

By introducing an arbitrary single-particle basis $\varphi_n(\mathbf{x})$ as in 9.9 and by using 9.40 we obtain

INTERACTION PART OF THE HAMILTONIAN IN SECOND QUANTISATION
IN ARBITRARY SINGLE-PARTICLE BASIS

$$\hat{H}_{int} = \frac{1}{2}\sum_{n_1,n_2,n_3,n_4} V_{\underline{n}}\, b^{\dagger}_{n_1} b^{\dagger}_{n_2} b_{n_3} b_{n_4} \tag{9.41}$$

$$\begin{aligned} V_{\underline{n}} &= \int\int \varphi^*_{n_1}(\mathbf{x})\varphi^*_{n_2}(\mathbf{x}')V(\mathbf{x},\mathbf{x}')\varphi_{n_3}(\mathbf{x}')\varphi_{n_4}(\mathbf{x})\; d^3\mathbf{x}\; d^3\mathbf{x}' \\ &= {}_1\langle\varphi_{n_1}|\;{}_2\langle\varphi_{n_2}|V(\hat{\mathbf{x}}_1,\hat{\mathbf{x}}_2)|\varphi_{n_4}\rangle_1\,|\varphi_{n_3}\rangle_2\;. \end{aligned}$$

9.3.3 Two-particle operators for fermions

The expressions above are in principle also valid for fermions, if spin can be omitted. The form of the interaction is the same as for bosons, 9.39 . Taking into account spin the density is given by

$$\hat{\rho}(\mathbf{x}) = \sum_{\sigma}\Psi^{\dagger}_{\sigma}(\mathbf{x})\Psi_{\sigma}(x)$$

This means that in the two densities in 9.37 one has to sum independently over spin. Therefore, 9.40 becomes for fermions (see also Fig. 9.1)

$$\hat{H}_{int} = \frac{1}{2}\sum_{\sigma_A,\sigma_B}\int\int \hat{\Psi}^{\dagger}_{\sigma_A}(\mathbf{x})\;\hat{\Psi}^{\dagger}_{\sigma_B}(\mathbf{x}')\;V(\mathbf{x},\mathbf{x}')\;\hat{\Psi}_{\sigma_B}(\mathbf{x}')\;\hat{\Psi}_{\sigma_A}(\mathbf{x})\;d^3\mathbf{x}\;d^3\mathbf{x}'$$

And the interacting hamiltonian 9.41 acquires a similar form, including spin

INTERACTION PART OF THE HAMILTONIAN FOR FERMIONS WITH SPIN

$$H_{int} = \frac{1}{2} \sum_{n_1,n_2,n_3,n_4} \sum_{\sigma_A,\sigma_B} V_{\underline{n}}\, c^{\dagger}_{n_1,\sigma_A}\, c^{\dagger}_{n_2,\sigma_B}\, c_{n_3,\sigma_B}\, c_{n_4,\sigma_A} \tag{9.42}$$

$$V_{n_1,n_2,n_3,n_4} = \int\int \varphi^*_{n_1}(\mathbf{x})\varphi^*_{n_2}(\mathbf{x}')V(\mathbf{x},\mathbf{x}')\varphi_{n_3}(\mathbf{x}')\varphi_{n_4}(\mathbf{x})\; d^3\mathbf{x}\; d^3\mathbf{x}'$$
$$= {}_1\langle\varphi_{n_1}\big|\; {}_2\langle\varphi_{n_2}\big|V(\hat{\mathbf{x}}_1,\hat{\mathbf{x}}_2)\big|\varphi_{n_4}\rangle_1\big|\varphi_{n_3}\rangle_2$$

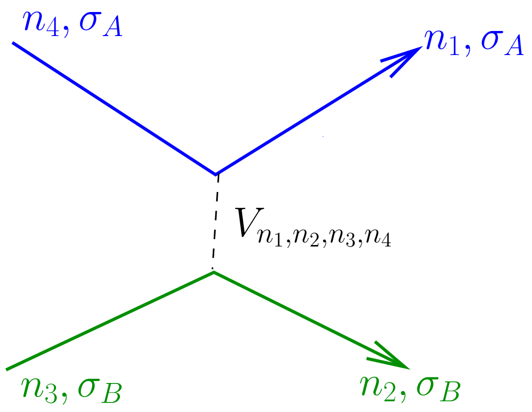


Figure 9.1: Intepretation of the interaction term in 9.42 . Two particles in the initial levels n_3 and n_4 are scattered $n_4 \to n_1$ and $n_3 \to n_2$. Spin is not changed by scattering, which explains the spin structure. In SQ scattering is described by first destroying the particles and then creating them in different levels. Also the matrix element in 9.42 (last line) can be understood by this picture

9.4 Summary: creation and destruction operators and Fock space

A Fock space (see Sec. 7.3.1) describes a system with different particle numbers. A natural set of basis states is given by the occupation-number representation.

$$|N_1, N_2, \cdots, N_n, \cdots\rangle \tag{9.43}$$

The subscript indices represent a single-particle state or level. E.g.:

$$\begin{array}{ll} 1 \to (n=1, l=0, m=0, \sigma=\uparrow) & 2 \to (n=1, l=0, m=0, \sigma=\downarrow) \\ 3 \to (n=2, l=0, m=0, \sigma=\uparrow) & 4 \to (n=2, l=0, m=0, \sigma=\downarrow) \\ 5 \to (n=2, l=1, m=-1, \sigma=\uparrow) & 6 \to (n=2, l=1, m=-1, \sigma=\downarrow) \\ 7 \to (n=2, l=1, m=0, \sigma=\uparrow) & 8 \to (n=2, l=1, m=0, \sigma=\downarrow) \\ 9 \to (n=2, l=1, m=+1, \sigma=\uparrow) & 10 \to (n=2, l=1, m=+1, \sigma=\downarrow) \quad \cdots \end{array}$$

The capital N_n indicates how many particles there are in level n. Clearly $N_n = 0, 1$ for fermions, due to Pauli principle, and $N_n = 0, 1, 2, \cdots$ for bosons.
An arbitrary state of the Fock space is a linear combination of 9.43

$$|\Psi\rangle = \sum_{N_1, N_2, \cdots, N_n, \cdots} C_{N_1, N_2, \cdots, N_n, \cdots} |N_1, N_2, \cdots, N_n, \cdots\rangle \ . \tag{9.44}$$

Second quantisation allows us to express these states with the help of creation and annihiltaion operators:

$$\begin{aligned} &|N_1, N_2, \cdots, N_n, \cdots\rangle \\ &= \frac{1}{\sqrt{N_1! N_2! \cdots N_n!}} \cdots \left(b_1^\dagger\right)^{N_1} \left(b_2^\dagger\right)^{N_2} \cdots \left(b_n^\dagger\right)^{N_n} \cdots |0\rangle \end{aligned} \tag{9.45}$$

The **vacuum** $|0\rangle$ is the state without particles and has the property 9.13 , and the operators b_i obey the commutation 9.10a for bosons or anticommutation rules 9.21 for fermions. [7] Moreover, they are the hermitian conjugate of each other:

$$(b_n)^\dagger = b_n^\dagger \tag{9.46}$$

Single-and two-particle operators can be written in both case in the form 9.28 and 9.41 .
Corresponding "bra" states can be obtained by a useful rule of hermitian conjugation:

$$\langle\Psi|\hat{A} = \left(\hat{A}^\dagger |\Psi\rangle\right)^\dagger \tag{9.47}$$

so that from 9.45

$$\begin{aligned} &\langle N_1, N_2, \cdots, N_n, \cdots| = (|N_1, N_2, \cdots, N_n, \cdots\rangle)^\dagger \\ &= \frac{1}{\sqrt{N_1!}} \frac{1}{\sqrt{N_2!}} \cdots \frac{1}{\sqrt{N_n!}} \cdots \langle 0| \cdots (b_n)^{N_n} \cdots (b_2)^{N_2} (b_1)^{N_1} \end{aligned} \tag{9.48}$$

9.47 together wit 9.13 implies that the "left vacuum" is annihilated by creation operators:

$$\langle 0| b_n^\dagger = 0 \qquad \forall n \tag{9.49}$$

---

[7] Note that the index n may include spin in this case, see above.

9.5 Unitary transformations

optional (no compulsory material for the exam)

It may sometimes be convenient to carry out a transformation from a set of operators $\left(b_n, b_n^\dagger\right)$ to another set $\left(c_n, c_n^\dagger\right)$. This is allowed as long as the $c_n, c_n^\dagger$ obey the same commutation or anticommutation relation as the $b_n, b_n^\dagger$. It can be shown that this is the case if the transformation is done with the help of a unitary matrix U:

$$c_k = \sum_n U_{k,n}\, b_n \tag{9.50}$$

Using its unitarity ($U^{-1} = U^\dagger$) the inverse reads

$$b_n = \sum_k U^*_{k,n} c_k \tag{9.51}$$

Due to 9.46 , the † operators are transformed as

$$c_k^\dagger = \sum_n U^*_{k,n} b_n^\dagger \tag{9.52}$$

As already discussed in Sec. 9.1.2 the transformation 9.51 corresponds to replacing operators ($b_n^\dagger$) creating particle on one basis set of orbitals ($\varphi_n(\mathbf{x})$) to new operators ($c_k^\dagger$) creating particle on another basis set (say $\chi_k(\mathbf{x})$).
From 9.50 , we easily get the (anti)commutation rules:

$$[c_k, c_p^\dagger]_\pm = \cdots\cdots \tag{9.53}$$

i.e. the correct ones. Here, we used a common notation $[\cdots]_\pm$ where the $+$ stays for anticommutators and $-$ for commutators.

9.5.1 Application: tight-binding hamiltonian

optional (no compulsory material for the exam)

Consider a chain of L lattice sites $n = 0, 1, \cdots, L-1$ with periodic boundary conditions $n + L \equiv n$ (for example, these could be points on a ring, e.g. Benzene, or a very long chain, for which boundary conditions don't matter). $b_n^\dagger$ creates a particle (fermion or boson) on the lattice site n (this could be, for example, an orbital on that site). The **tight-binding hamiltonian** reads

$$\hat{H} = \varepsilon \sum_n b_n^\dagger b_n - t \sum_n \left(b_{n+1}^\dagger b_n + b_n^\dagger b_{n+1} \right) . \tag{9.54}$$

and describes particles on orbitals with energies ε, and an amplitude t for each particle for moving to the left or to the right orbital ("hopping").

This model is easily solved by discrete Fourier transformation 9.50 with

$$U_{k,n} = \frac{1}{\sqrt{L}} e^{2\pi\ i\ k\ n/L} \tag{9.55}$$

Notice that also the indices $k = 0, \cdots, L-1$ have periodic boundary conditions: $U_{k+L,n} = U_{k,n}$. In this way, it can be seen that U is indeed unitary:

$$(UU^\dagger)_{k,p} = \sum_n U_{k,n} U^*_{p,n} = \frac{1}{L} \sum_n e^{2\pi\ i\ (k-p)\ n/L} = \delta_{k,p} \tag{9.56}$$

All indices have to be understood from 0 to $L-1$.
In this way, 9.54 becomes (we use 9.51)

$$\hat{H} = \varepsilon \sum_{p,k} \underbrace{\sum_n U_{p,n} U^*_{k,n}}_{\delta_{p,k}} c^\dagger_p c_k - t \sum_{n,p,k} \left(U_{p,n+1} U^*_{k,n} + U_{p,n} U^*_{k,n+1} \right) c^\dagger_p c_k \,. \tag{9.57}$$

Now

$$\sum_n U_{p,n+1} U^*_{k,n} = \cdots\cdots$$

similarly

$$\sum_n U_{p,n} U^*_{k,n+1} = e^{-2\pi\ i\ p/L}\ \delta_{k,p}$$

So that 9.57 becomes

$$\hat{H} = \sum_k (\varepsilon - 2t\cos(2\pi k/L))\ c^\dagger_k c_k \tag{9.58}$$

which is in diagonal form.
The operators $c^\dagger_k$ create particles with (crystal) momentum $P_k = 2\pi k/L$ and energy $\varepsilon_k \equiv (\varepsilon - 2t\cos(2\pi k/L))$. The mode with lowest energy is the one with $k = 0$, so the bosonic ground state with N particles is simply

$$\left| G^B_N \right\rangle = \frac{1}{\sqrt{N!}} \left(c^\dagger_0 \right)^N |0\rangle$$

all particles are in the lowest level: it is a Bose-Einstein condensate. Its energy is $N(\varepsilon - 2t)$.
For fermions one has to start filling levels according to Pauli principle. This is discussed in the context of the Fermi sphere in Sec. 9.6.1

9.6 Momentum space

For translation invariant systems it may be convenient to carry out the transformation 9.15 where the ortonormal basis set consists of eigenfunction of momentum, i.e. plane waves. The basis is, in principle, continuous, so that the sum in 9.15 should be replaced by an integral. However, it is often common practice to restrict the space to a cubic box of edge L with periodic boundary condition. In the end, physical results are obtained by letting $L \to \infty$.
In a periodic box, the normalized eigenfunction of the momentum operator $\hat{p}$ are

$$\varphi_{\mathbf{k}} = \frac{1}{\sqrt{\Omega}} e^{i\,\mathbf{k}\cdot\mathbf{x}} \qquad \Omega = L^3 = \text{volume} \tag{9.59}$$

with

$$\mathbf{k} = \frac{2\pi}{L}(n_1, n_2, n_3) \quad n_i = -\infty, \cdots, +\infty \tag{9.60}$$

Then 9.17 becomes [8]

$$\begin{aligned} \hat{H} &= \sum_{\mathbf{k},\mathbf{k}'} h_{\mathbf{k}',\mathbf{k}} c^\dagger_{\mathbf{k}'} c_{\mathbf{k}} \\ h_{\mathbf{k}',\mathbf{k}} &= \frac{1}{\Omega}\int d^3\mathbf{x}\; e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{x}} \left(\frac{\hbar^2\mathbf{k}^2}{2m} + U(\mathbf{x})\right) = \frac{\hbar^2\mathbf{k}^2}{2m}\delta_{\mathbf{k},\mathbf{k}'} + \frac{U(\mathbf{k}-\mathbf{k}')}{\Omega} \end{aligned} \tag{9.61}$$

where we have used two useful formulas

$$\frac{1}{\Omega}\int d^3\mathbf{x} e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{x}} = \delta_{\mathbf{k},\mathbf{k}'} \tag{9.62}$$

$$\int d^3\mathbf{x} e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{x}}\, U(\mathbf{x}) = U(\mathbf{k}-\mathbf{k}') \tag{9.63}$$

which is the Fourier transform of $U(\mathbf{x})$ (with abuse of notation).
The interacting term 9.41 can be obtained by first carrying out the integral. We consider the case of a potential which depends on distance only:

$$\begin{aligned} &\int\int \varphi^*_{\mathbf{k}_1}(\mathbf{x})\varphi^*_{\mathbf{k}_2}(\mathbf{x}')V(\mathbf{x}-\mathbf{x}')\varphi_{\mathbf{k}_3}(\mathbf{x}')\varphi_{\mathbf{k}_4}(\mathbf{x})\; d^3\mathbf{x} d^3\mathbf{x}' \\ &= \cdots\cdots \\ &= \cdots\cdots \end{aligned} \tag{9.64}$$

---

[8] We use $U(\mathbf{x})$ for the external potential instead of $V(\mathbf{x})$, in order to distinguish it from the electron-electron interaction

where we have transformed $\mathbf{x}' = \mathbf{x} - \mathbf{r}$, used 9.62 and again introduced the Fourier transform of V, analogously to 9.63 .
In this way, by taking $\mathbf{k}_3 = \mathbf{k}_2 - \mathbf{q}$ and exploiting the δ leading to $\mathbf{k}_4 = \mathbf{k}_1 + \mathbf{q}$ it is convenient to write 9.41 (or 9.42) as

$$\hat{H}_{int} = \frac{1}{2\Omega} \sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{q}} \sum_{\sigma,\sigma'} V(\mathbf{q})\ c^\dagger_{\mathbf{k}_1,\sigma}\ c^\dagger_{\mathbf{k}_2,\sigma'}\ c_{\mathbf{k}_2-\mathbf{q},\sigma'}\ c_{\mathbf{k}_1+\mathbf{q},\sigma}\ , \tag{9.65}$$

where for convenience we have introduced spin (for the case of Fermions, otherwise the expression is the same for bosons). The interaction term describes a process in which two particles with momenta $\mathbf{k}_2 - \mathbf{q}$ and $\mathbf{k}_1 + \mathbf{q}$ come together and exchange momentum $\mathbf{q}$ so that total momentum is conserved.

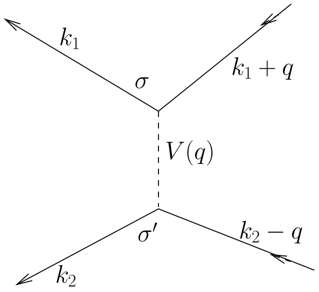


Figure 9.2: Schematic representation of an interacting process

The amplitude for the process is given by the Fourier transform of the interaction evaluated at the transferred momentum $\mathbf{q}$. On the other hand, the external potential given by U in 9.61 can be written as (again with spin, when we have Fermions)

$$\hat{H}_U = \frac{1}{\Omega} \sum_{k,q} \sum_{\sigma} U(\mathbf{q})\ c^\dagger_{k-q,\sigma} c_{k,\sigma} \tag{9.66}$$

and describe a transfer of momentum $\mathbf{q}$ from the potential center, so momentum is not conserved.

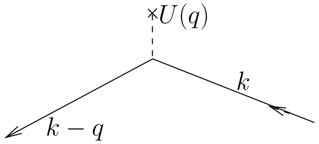


Figure 9.3: Scattering by a potential

9.6.1 Free fermions

For free fermions we have 9.61 with $U = 0$:

$$\hat{H} = \sum_{\mathbf{k}} \sum_{\sigma} \varepsilon_{\mathbf{k}} \hat{n}_{\mathbf{k},\sigma} \tag{9.67}$$

$$\varepsilon_{\mathbf{k}} \equiv \frac{\hbar^2 \mathbf{k}^2}{2m} \qquad \hat{n}_{\mathbf{k},\sigma} \equiv c^\dagger_{\mathbf{k},\sigma} c_{\mathbf{k},\sigma}$$

The ground state $|F\rangle$ (state with minimal energy) is the one in which all levels **k** up to a certain energy ε_F (Fermi energy), or, equivalently with $|\mathbf{k}|$ smaller than the Fermi momentum k_F with $\varepsilon_F = \frac{\hbar^2 k_F^2}{2m}$ are occupied ($\hat{n}_{\mathbf{k},\sigma} = 1$) and the other ones are empty ($\hat{n}_{\mathbf{k},\sigma} = 0$): [9]

$$|F\rangle = \prod_{|\mathbf{k}| \leq k_F} \prod_{\sigma} c^\dagger_{\mathbf{k},\sigma} |0\rangle \ . \tag{9.68}$$

These states can be represented by a filled sphere, the **Fermi sphere**. The total number of particles is given by the sum of the **k** points within the sphere times 2 for spin:

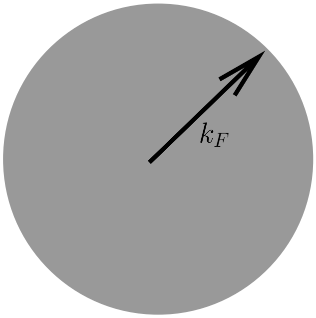


Figure 9.4: Fermi sphere

$$N_p = 2 \sum_{|\mathbf{k}| \leq k_F} 1 = 2\Omega \int_{|\mathbf{k}| \leq k_F} \frac{d^3\mathbf{k}}{(2\pi)^3} = \frac{2\Omega}{(2\pi)^3} \frac{4\pi}{3} k_F^3 \tag{9.69}$$

where we have used $\sum_{\mathbf{k}} \cdots = \Omega \int \frac{d^3\mathbf{k}}{(2\pi)^3} \cdots$ cf. here: Sec. A.32. We, thus have the relation between k_F and the particle density n_p:

$$k_F^3 = 3\pi^2 n_p \tag{9.70}$$

---

[9] Note that in the expression below one has to specify the order of the operators in the product.

Similarly, the total ground-state energy is given by

$$\mathcal{E}_{\mathcal{F}} = 2 \sum_{|\mathbf{k}| \leq k_F} \varepsilon_{\mathbf{k}} = 2\Omega \int_{|\mathbf{k}| \leq k_F} \frac{d^3\mathbf{k}}{(2\pi)^3} \frac{\hbar^2 \mathbf{k}^2}{2m} = \frac{3}{5} \varepsilon_F N_p$$

Excited states are obtained by removing a particle from within the Fermi sphere (i.e., creating a hole) and putting it outside: particle-hole excitations:

$$c^\dagger_{\mathbf{k}_1,\sigma} c_{\mathbf{k}_2,\sigma'} |F\rangle \qquad |\mathbf{k}_1| > k_F , |\mathbf{k}_2| \leq k_F \tag{9.71}$$

the corresponding excitation energy is

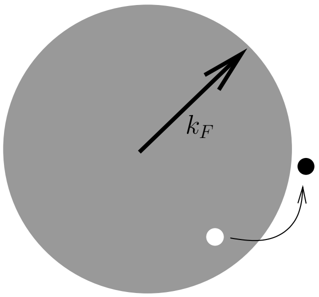


Figure 9.5: Particle-hole excitation.

$$E_{ex,\mathbf{k}_1\sigma,\mathbf{k}_2\sigma} = E_{\mathbf{k}_1\sigma,\mathbf{k}_2\sigma} - E_F = \varepsilon_{\mathbf{k}_1} - \varepsilon_{\mathbf{k}_2} \tag{9.72}$$

These excitations play an important role in solid state physics. For example, at finite temperature particle-hole excitations are created up to an energy $E_{ex,\mathbf{k}_1\sigma,\mathbf{k}_2\sigma} \approx k_B T$.

9.7 Field operators

The transformation 9.15 , whose inverse is given in A.48 is a continuous version of 9.50 . While operators such as $b^\dagger_n$, $c^\dagger_k$ create particles on discrete levels, field operators $\Psi^\dagger(\mathbf{x})$ create particles on continuous single-particle states, in this case on an eigenstate of the position operator $\hat{\mathbf{x}}$, as discussed around 9.36 . The concept of field operators can be extended to an arbitrary continuous basis. Let us consider a basis labeled by a continuous variable k (the momentum basis, but also the real-space basis are one possible example). Let us denote the corresponding single particle state vectors “levels” by $|\varphi_k\rangle$ with wave functions $\langle x|\varphi_k\rangle = \varphi_k(x)$ (e.g. $\varphi_k(x) = \frac{1}{\sqrt{2\pi}} e^{ikx}$)

As is known from QMI, these states are not normalizable in the usual way: one has to use a "delta-function" normalisation:

$$\langle \varphi_{k'} | \varphi_k \rangle = \delta(k - k') \tag{9.73}$$

Then one can introduce creation $\hat{\Upsilon}^\dagger(k)$ and destruction $\hat{\Upsilon}(k)$ operators, who have the property to create or annihilate particles in the corresponding "level" $|\varphi_k\rangle$.
According to the different normalisation 9.73 , the (anti-)commutation rules have, instead of 9.10a , the delta-form[10]

$$[\hat{\Upsilon}(k), \hat{\Upsilon}^\dagger(k')] = \delta(k - k') \tag{9.74}$$

The expressions for single and two-particle operators operators in second quantisation, 9.28 and 9.41 , respectively, remain the same except that one replaces $n_i \to k_i$ and one integrates over the k_i.
Notice that the $\hat{\Psi}^\dagger(\mathbf{x})$ (resp. $\hat{\Psi}(\mathbf{x})$) (cf. 9.7) are a special case, as they create (resp. destroy) a particle in a orbital localized in $\mathbf{x}$ (delta function).

9.8 Heisenberg time dependence for operators

Creation and annihilation, as well as field operators discussed above can be assigned a time dependence according to the usual Heisenberg representation , which for an arbitrary operator (in both first or second quantisation) reads:

$$i\hbar \frac{d}{dt} \hat{O}(t) = [\hat{O}(t), \hat{H}] + i\hbar \frac{\partial}{\partial t} \hat{O}(t) \tag{9.75}$$

For time-independent Hamiltonians and operators, the formal solution reads, as usual

$$\hat{O}(t) = e^{i\,\hat{H}\,t/\hbar}\,\hat{O}\,e^{-i\,\hat{H}\,t/\hbar}\,. \tag{9.76}$$

Since operators can be quite generally expressed as polynomials in the $b, b^\dagger$ and/or $\hat{\Psi}, \hat{\Psi}^\dagger$ operators, it is easy to show that the time dependence can be pulled over to these operators. For example, take the interaction operator 9.40 (we

---

[10] Depending on the convention there might be a coefficient, like 2π or so in front of the δ, as well as in fromt of 9.73

omit the subscript $_{SQ}$):

$$
\begin{aligned}
&\hat{H}_{int}(t) = e^{i\,\hat{H}\,t/\hbar}\,\frac{1}{2}\int\int \hat{\Psi}^{\dagger}(\mathbf{x})\hat{\Psi}^{\dagger}(\mathbf{x}')V(\mathbf{x},\mathbf{x}')\hat{\Psi}(\mathbf{x}')\hat{\Psi}(\mathbf{x})d^3\mathbf{x}d^3\mathbf{x}'\ e^{-i\,\hat{H}\,t/\hbar} = \\
&\frac{1}{2}\int\int e^{i\,\hat{H}\,t/\hbar}\,\hat{\Psi}^{\dagger}(\mathbf{x})\underbrace{e^{-i\,\hat{H}\,t/\hbar}\ e^{i\,\hat{H}\,t/\hbar}}_{\mathbf{1}}\hat{\Psi}^{\dagger}(\mathbf{x}')e^{-i\,\hat{H}\,t/\hbar}\,V(\mathbf{x},\mathbf{x}') \\
&\times e^{i\,\hat{H}\,t/\hbar}\,\hat{\Psi}(\mathbf{x}')e^{-i\,\hat{H}\,t/\hbar}\underbrace{e^{i\,\hat{H}\,t/\hbar}\,\hat{\Psi}(\mathbf{x})e^{-i\,\hat{H}\,t/\hbar}}_{\hat{\Psi}(\mathbf{x},t)}d^3\mathbf{x}d^3\mathbf{x}' \\
&= \frac{1}{2}\int\int \hat{\Psi}^{\dagger}(\mathbf{x},t)\hat{\Psi}^{\dagger}(\mathbf{x}',t)V(\mathbf{x},\mathbf{x}')\hat{\Psi}(\mathbf{x}',t)\hat{\Psi}(\mathbf{x},t)d^3\mathbf{x}d^3\mathbf{x}'\,, \qquad (9.77)
\end{aligned}
$$

i.e. the time dependence of $\hat{H}_{int}(t)$ is obtained by inserting the time dependence in the constituent field operators.

9.8.1 Time dependence of field operators

For a noninteracting Hamiltonian 9.11a (we use $U(\mathbf{x})$ instead of $V(\mathbf{x})$ for the potential:

$$
\begin{aligned}
i\hbar\frac{d}{dt}\hat{\Psi}(\mathbf{x}) &= \int d^3\mathbf{x}'\ \Big(\hat{\Psi}(\mathbf{x})\hat{\Psi}^{\dagger}(\mathbf{x}')\left[-\frac{\hbar^2}{2m}\boldsymbol{\nabla}'^2+U(\mathbf{x}')\right]\hat{\Psi}(\mathbf{x}') \\
&\quad -\hat{\Psi}^{\dagger}(\mathbf{x}')\left[-\frac{\hbar^2}{2m}\boldsymbol{\nabla}'^2+U(\mathbf{x}')\right]\hat{\Psi}(\mathbf{x}')\hat{\Psi}(\mathbf{x})\Big) \\
&= \int d^3\mathbf{x}'\ \underbrace{\Big(\hat{\Psi}(\mathbf{x})\hat{\Psi}^{\dagger}(\mathbf{x}')\mp\hat{\Psi}^{\dagger}(\mathbf{x}')\hat{\Psi}(\mathbf{x})\Big)}_{\delta(\mathbf{x}-\mathbf{x}')}\left[-\frac{\hbar^2}{2m}\boldsymbol{\nabla}'^2+U(\mathbf{x}')\right]\hat{\Psi}(\mathbf{x}') \\
&= \left[-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2+U(\mathbf{x})\right]\hat{\Psi}(\mathbf{x})\,, \qquad (9.78)
\end{aligned}
$$

where the $-$ sign is for bosons and $+$ for fermions. We now include also the interaction, 9.40 so that the total Hamiltonian is $\hat{H}_{SQ}+\big(\hat{H}_{int}\big)_{SQ}$. One obtains (without proof)

$$
i\hbar\frac{d}{dt}\hat{\Psi}(\mathbf{x}) = \left[-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2+U(\mathbf{x})\right]\hat{\Psi}(\mathbf{x})+\int d^3\mathbf{x}'\ \hat{\rho}(\mathbf{x}')V(\mathbf{x},\mathbf{x}')\hat{\Psi}(\mathbf{x}) \qquad (9.79)
$$

Both expressions are formally analogous to the Schödinger equation in first quantisation.

9.8.2 Time dependence of creation and annihilation operators

The Heisenberg time dependence for $c, c^\dagger$ operators described by the noninteracting Hamiltonian is given by 9.17

$$i\hbar \frac{d}{dt} c_n(t) = \sum_{k,m} h_{k,m} \underbrace{[c_n(t), c_k^\dagger(t) c_m(t)]}_{\delta_{n,k}\; c_m(t)} = \sum_m h_{n,m} c_m(t) \tag{9.80}$$

For the case of a diagonal hamiltonian 9.11a , for which $h_{n,m} \to \delta_{n,m} E_n$ $c_n \to b_n$ the solution is simple

$$b_n(t) = e^{-iE_n\, t/\hbar}\, b_n(0) \tag{9.81}$$

For the more general case 9.80 the solution can be formally obtained by introducing a column vector

$$\mathbf{c} \equiv \begin{pmatrix} c_1 \\ \vdots \\ c_n \end{pmatrix}$$

together with the matrix $\mathbf{h} = \{h_{n,m}\}$. Then 9.80 becomes a matrix equation

$$i\hbar \frac{d}{dt}\, \mathbf{c}(t) = \mathbf{h} \cdot \mathbf{c}(t)$$

with formal solution

$$\mathbf{c}(t) = e^{-i\mathbf{h}\, t/\hbar}\, \mathbf{c}(0)$$

These expressions are used for Green's functions in many-body solid state physics.

9.8.3 Single-particle correlation function

One quantity of interest is the single-particle correlation function

$$G(\mathbf{x}, t; \mathbf{x}', t') \equiv \langle F | \hat{\Psi}_\sigma(\mathbf{x}, t) \hat{\Psi}^\dagger_\sigma(\mathbf{x}', t') | F \rangle \ . \tag{9.82}$$

Physically, this describes the amplitude that after creating a particle at $\mathbf{x}'$ at time t', this is found at time t in $\mathbf{x}$. It thus describes particle transport from $\mathbf{x}'$ to $\mathbf{x}$.
We evaluate this quantity for the case of free fermions. First, we transform the field operators according to 9.9 with the φ_n replaced by the eigenfunctions 9.59 and the b by c.

$$\hat{\Psi}_\sigma(\mathbf{x}) = \sum_k c_{\mathbf{k},\sigma} \frac{1}{\sqrt{\Omega}} e^{i\mathbf{k}\cdot\mathbf{x}} \tag{9.83}$$

Then

$$\hat{\Psi}_\sigma(\mathbf{x},t)\hat{\Psi}^\dagger_\sigma(\mathbf{x}',t') = \frac{1}{\Omega}\sum_{\mathbf{k},\mathbf{k}'} e^{i\mathbf{k}\cdot\mathbf{x}} e^{-i\mathbf{k}'\cdot\mathbf{x}'} c_{\mathbf{k},\sigma}(t)c^\dagger_{\mathbf{k}',\sigma}(t') \tag{9.84}$$

Since the Hamiltonian 9.67 is diagonal in the c, their Heisenberg time dependence is given by the same form as in 9.81

$$c_{\mathbf{k},\sigma}(t) = e^{-i\varepsilon_{\mathbf{k}}\,t/\hbar} c_{\mathbf{k},\sigma}\ . \tag{9.85}$$

We are left with the evaluation of expectation values of operators in 9.82 (cf. 9.84)

$$\langle F|\, c_{\mathbf{k},\sigma} c^\dagger_{\mathbf{k}',\sigma}\, |F\rangle$$

clearly, if one creates a particle at $\mathbf{k}'$, this same particle has to be annihilated again in order to get the same state, therefore $\mathbf{k} = \mathbf{k}'$. Moreover, $\mathbf{k}'$ must be outside of the Fermi sphere: $|\mathbf{k}'| > k_F$. This gives for the above expectation value

$$\langle F|\, c_{\mathbf{k},\sigma} c^\dagger_{\mathbf{k}',\sigma}\, |F\rangle = \delta_{\mathbf{k},\mathbf{k}'}\theta(|\mathbf{k}| - k_F) \tag{9.86}$$

Using 9.84 , 9.85 , and 9.86 we obtain for 9.82

$$\begin{aligned}
G(\mathbf{x},t;\mathbf{x}',t') = G(\underbrace{|\mathbf{x}-\mathbf{x}'|}_{r},\underbrace{t-t'}_{\tau}) &= \underbrace{\frac{1}{\Omega}\sum_{|\mathbf{k}|>k_F}}_{\int_{|\mathbf{k}|>k_F}\frac{d^3\mathbf{k}}{(2\pi)^3}} e^{i\mathbf{k}\cdot(\mathbf{x}-\mathbf{x}')} e^{-i\varepsilon_{\mathbf{k}}\,\tau/\hbar} \\
&= \frac{1}{(2\pi)^3}\int_{k>k_F} k^2\, dk\, e^{-i\varepsilon_{\mathbf{k}}\,\tau/\hbar}\, 2\pi \underbrace{\int_{-1}^{1} d\,\cos\theta\; e^{ik|\mathbf{x}-\mathbf{x}'|\cos\theta}}_{\frac{2\sin kr}{kr}} \\
&= \frac{1}{2\pi^2 r}\int_{k_F}^{\infty} dk\, k \sin kr\; e^{-i\varepsilon_k\,\tau/\hbar}
\end{aligned} \tag{9.87}$$

For $\tau = 0$ the integral can be evaluated analytically yielding the equal-time correlation function

$$G(r,0) = \frac{3n_p}{2}\,\frac{z\cos z - \sin z}{z^3} \qquad z \equiv rk_F \tag{9.88}$$

this describes decaying oscillations with wavevector k_F (Friedel oscillations) produced by adding a particle.

Another interesting information is the behavior of 9.87 for large τ. In this case, it can be seen that the leading contribution to the k integral comes by expanding ε_k around k_F: $\varepsilon_k \approx \varepsilon_{k_F} + \hbar v_F(k - k_F)$, where v_F is the so-called Fermi velocity. Due to the *sinkr*, one has in the exponent terms of the form

$$e^{-i\varepsilon_{k_F}\,\tau/\hbar} e^{-i(v_F\tau \mp r)(k-k_F)} e^{\pm irk_F}\ ,$$

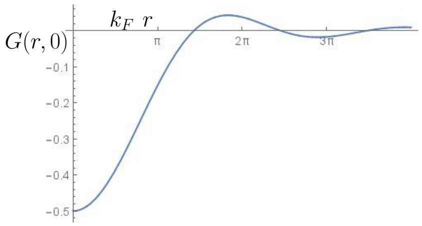


Figure 9.6: Equal time correlation function 9.88

where ± come from the sin. Due to the integral over k, the term in the center oscillates fast, and cancels out unless the argument $v_F\tau \mp r \approx 0$. This describes particles moving with the Fermi velocity v_F. On top of this, there are again spatial oscillations with momentum k_F and time oscillations with frequency $\varepsilon_{k_F}/\hbar$.

9.8.4 Pair distribution function

The evaluation of the pair distribution function illustrates how fermions affect each other even without interaction. We start from the state $\hat{\Psi}_\sigma(\mathbf{x})\,|F\rangle$ in which a particle has been removed from the Fermi sphere at position $\mathbf{x}$. Its normalisation is given by

$$\langle F|\,\hat{\Psi}^\dagger_\sigma(\mathbf{x})\hat{\Psi}_\sigma(\mathbf{x})\,|F\rangle = \langle F|\,\hat{\rho}_\sigma(\mathbf{x})\,|F\rangle = n_p/2\ . \tag{9.89}$$

Here, we used the density operator $\hat{\rho}_\sigma(\mathbf{x})$ (with given spin) cf. 9.35 , and since the filled Fermi sphere is translation invariant, its expectation value, the average density is $\mathbf{x}$-independent. We now determine the probability density $\frac{n_p}{2}g_{\sigma,\sigma'}(\mathbf{r})$ to find a particle with spin σ' at a distance $\mathbf{r}$ from the fist one. This is given by the expectation value of $\hat{\rho}_{\sigma'}(\mathbf{x}+\mathbf{r})$ in this state. We get:

$$\left(\frac{n_p}{2}\right)^2 g_{\sigma,\sigma'}(\mathbf{r}) = \langle F|\,\hat{\Psi}^\dagger_\sigma(\mathbf{x})\hat{\Psi}^\dagger_{\sigma'}(\mathbf{x}+\mathbf{r})\hat{\Psi}_{\sigma'}(\mathbf{x}+\mathbf{r})\hat{\Psi}_\sigma(\mathbf{x})\,|F\rangle \tag{9.90}$$

$$= \frac{1}{\Omega^2}\sum_{\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_3,\mathbf{k}_4} e^{-i(\mathbf{k}_1-\mathbf{k}_4+\mathbf{k}_2-\mathbf{k}_3)\cdot\mathbf{x}}e^{-i(\mathbf{k}_2-\mathbf{k}_3)\cdot\mathbf{r}}\,\langle F|\,c^\dagger_{\mathbf{k}_1,\sigma}c^\dagger_{\mathbf{k}_2,\sigma'}c_{\mathbf{k}_3,\sigma'}c_{\mathbf{k}_4,\sigma}\,|F\rangle$$

We now distinguish between two cases:

- $\sigma = -\sigma'$
  In this case, it is clear that in 9.90 for each spin separately the particles that has been destroyed must be created with the same $\mathbf{k}$, i.e. we get $\mathbf{k}_1 = \mathbf{k}_4$ and $\mathbf{k}_2 = \mathbf{k}_3$. Then, the result is independent of $\mathbf{r}$ and is given by

$$g_{\sigma,-\sigma}(\mathbf{r}) = \left(\frac{2}{n_p\,\Omega}\sum_{|\mathbf{k}|<k_F} 1\right)^2 = 1 \tag{9.91}$$

- $\sigma = \sigma'$
  In this case, we have two terms contributing in the sum 9.90 . The first one with $\mathbf{k}_1 = \mathbf{k}_4$ and $\mathbf{k}_2 = \mathbf{k}_3$, whose contribution is the same as before. The second one has $\mathbf{k}_1 = \mathbf{k}_3$ and $\mathbf{k}_2 = \mathbf{k}_4$. Its contribution (exchange contribution) is

$$\left(\frac{n_p}{2}\right)^2 g^{ex}_{\sigma,\sigma}(\mathbf{r}) = \frac{1}{\Omega^2}\sum_{\mathbf{k}_1,\mathbf{k}_2} e^{-i(\mathbf{k}_2-\mathbf{k}_1)\cdot\mathbf{r}}\,\langle F|\, c^\dagger_{\mathbf{k}_1,\sigma} c^\dagger_{\mathbf{k}_2,\sigma'} \underbrace{c_{\mathbf{k}_1,\sigma} c_{\mathbf{k}_2,\sigma}}_{-c_{\mathbf{k}_2,\sigma} c_{\mathbf{k}_1,\sigma}} |F\rangle$$

In the expectation value $\langle F| \cdots |F\rangle$ (with the minus sign) one first destroys a particle in $\mathbf{k}_1$ then in $\mathbf{k}_2$, then creates the one in $\mathbf{k}_2$ then in $\mathbf{k}_1$. This gives 1 provided $|\mathbf{k}_1|$ and $|\mathbf{k}_2| < k_F$. In this way, the sums over k_1 and k_2 are independent of each other, we thus get

$$g^{ex}_{\sigma,\sigma}(\mathbf{r}) = -\left|\frac{1}{\Omega}\sum_{|\mathbf{k}_1|<k_F} e^{i\,\mathbf{k}_1\cdot\mathbf{r}}\right|^2$$

The sum is like the one in 9.87 for $\tau = 0$ and one integrates from 0 to k_F instead, yielding $-G(r,0)$. In total, thus

$$g_{\sigma,\sigma}(\mathbf{r}) = 1 + g^{ex}_{\sigma,\sigma}(\mathbf{r}) = 1 - \frac{9}{z^6}(\sin z - z\cos z)^2 \qquad z = k_F r \qquad (9.92)$$

This pair distribution function is suppressed at low distances. This is a pure exchange effect depending on the asymmetry of the wave function. It signals the fact that the probability to find two fermions with the same spin at a distance $r \lesssim \frac{1}{k_F}$ is suppressed.

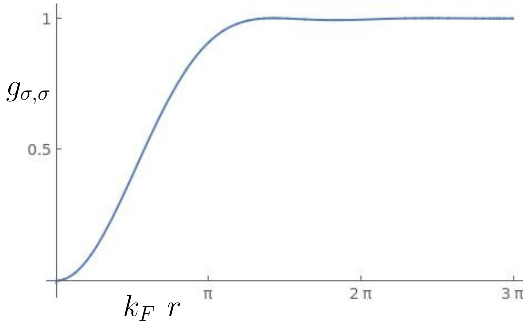


Figure 9.7: Equal spin pair distribution function $g_{\sigma,\sigma}$ 9.92

Chapter 10

Quantisation of the free electromagnetic field

The quantisation of the electromagnetic field is also necessary in order to end up with a description in terms of **photons**. Like in the case of the elastic string of Chap. 8 one starts from a contiuous object and ends up with discrete oscillators describing particles.

The procedure for quantisation of the electromagnetic field is similar to the case of the Schrödinger field in Chap. 9, there are, however, some important differences leading to technical issues.

- The dynamical variable is the vector potential **A**, which, being a vector, has three components.
- In the Coulomb gauge, $\boldsymbol{\nabla}\cdot\mathbf{A} = 0$ so the three components of the vector are not independent from each other
- **A** is a real field, with the consequence that Fourier components with opposite **k** are not independent

10.1 Lagrangian and Hamiltonian

The electric and the magnetic field can be determined from a scalar and a vector potential

$$\begin{aligned}\mathbf{E} &= -\frac{1}{c}\frac{\partial\mathbf{A}}{\partial t} - \boldsymbol{\nabla}\phi \\ \mathbf{B} &= \boldsymbol{\nabla}\times\mathbf{A}\end{aligned} \tag{10.1}$$

We use Gaussian units and c is the speed of light. For simplicity, we use units in which $c = 1$. We use the Coulomb gauge for which

$$\boxed{\phi = 0 \qquad \nabla \cdot \mathbf{A} = 0\,.} \tag{10.2}$$

The homogeneous Maxwell equations can be eliminated by using 10.1 . The inhomogeneous Maxwell equations reduce (by using 10.2) to the wave equation for $\mathbf{A}$:

$$\boxed{\nabla^2 \mathbf{A} - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathbf{A} = 0\,.} \tag{10.3}$$

We now show that the Lagrange function

$$\mathscr{L} = \int d^3\mathbf{r}\, \frac{\mu}{2} \left(\dot{\mathbf{A}}^2 - (\nabla \times \mathbf{A})^2 \right) = \int d^3\mathbf{r}\, \frac{\mu}{2} \left(\mathbf{E}^2 - \mathbf{B}^2 \right) \tag{10.4}$$

which gives the conjugate momentum density Π_n

$$\Pi_n = \frac{\delta \mathscr{L}}{\delta \dot{A}_n} = \mu\, \dot{A}_n = -\mu E_n \tag{10.5}$$

leads to the correct equation of motion 10.3 . This is proven here: Sec. A.31
Here, we introduced the factor μ, from which, of course the equations of motions do not depend, but which in the end has to be fixed to

$$\mu = \frac{1}{4\pi} \tag{10.6}$$

in order to reproduce the correct energy of the electromagnetic field in Gauss' units.
As usual, we obtain the Hamilton function H from the Legendre transformation

$$\begin{aligned} H = \int d^3\mathbf{r}\, \mathbf{\Pi} \cdot \dot{\mathbf{A}} - \mathscr{L} = & \boxed{\int d^3\mathbf{r}\, \frac{\mu}{2} \left(\frac{\mathbf{\Pi}^2}{\mu^2} + (\nabla \times \mathbf{A})^2 \right)} \\ = & \int d^3\mathbf{r}\, \frac{\mu}{2} \left(\mathbf{E}^2 + \mathbf{B}^2 \right) \end{aligned} \tag{10.7}$$

which, gives the total energy of the electromagnetic field (c.g.s units).
Quantisation cannot be yet applied, since not all variables are independent, due to 10.2 . In other words, commutation rules in the form

$$[\hat{A}_n(\mathbf{r}), \hat{\Pi}_m(\mathbf{r}')] = i\hbar\, \delta_{n,m}\, \delta(\mathbf{r} - \mathbf{r}') \qquad \textbf{NO!} \tag{10.8}$$

would contradict 10.2 . (See here: Sec. A.33).

10.2 Normal modes

To make progress, we now carry out a discrete Fourier transformation. (See Sec. 9.6) More specifically, we consider a cubic "box" with volume $\Omega = L^3$ and periodic boundary conditions, and we expand $\mathbf{A}$ in terms of the orthonormal functions $\frac{1}{\sqrt{\Omega}} e^{i\mathbf{k}\cdot\mathbf{r}}$

$$\boxed{\mathbf{A}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}\ \mathbf{A}_{\mathbf{k}}} \tag{10.9}$$

The inversion rules are

$$\mathbf{A}_{\mathbf{k}} = \frac{1}{\sqrt{\Omega}} \int d^3\mathbf{r}\ e^{-i\mathbf{k}\cdot\mathbf{r}}\ \mathbf{A}(\mathbf{r})\ . \tag{10.10}$$

The same transformation applies for $\mathbf{\Pi}(\mathbf{r})$

$$\mathbf{\Pi}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}\ \mathbf{\Pi}_{\mathbf{k}}\ . \tag{10.11}$$

The periodic boundary conditions make the $\mathbf{k}$ discrete:

$$\mathbf{k} = \frac{2\pi}{L}(n_1, n_2, n_3) \qquad n_i \text{ integers.} \tag{10.12}$$

Moreover, since $\mathbf{A}(\mathbf{x})$ and $\mathbf{\Pi}(\mathbf{x})$ are real fields,

$$\mathbf{A}_{\mathbf{k}} = \mathbf{A}^*_{-\mathbf{k}} \qquad \mathbf{\Pi}_{\mathbf{k}} = \mathbf{\Pi}^*_{-\mathbf{k}} \tag{10.13}$$

10.3 Quantisation

In analogy to 8.16 , we would expect second quantisation to be generated by introducing the commutators $[\hat{A}_{n\mathbf{k}}, \hat{\Pi}_{m\mathbf{k}'}] = i\hbar\ \delta_{nm}\ \delta_{\mathbf{k}\mathbf{k}'}$ (here, n, m are components of the vectors). However, there are two issues: First, due to the fact that the Fourier basis is complex, one has to require instead

$$[\hat{A}_{n\mathbf{k}}, \hat{\Pi}_{m-\mathbf{k}'}] = i\hbar\ \delta_{nm}\ \delta_{\mathbf{k}\mathbf{k}'} \qquad \textbf{not yet correct!} \tag{10.14}$$

in order to obtain **local** commutation rules in $\mathbf{r}$ space: details here: Sec. A.32

$$\begin{aligned}
[\hat{A}_n(\mathbf{r}), \hat{\Pi}_m(\mathbf{r}')] &= \frac{1}{\Omega} \sum_{\mathbf{k}\mathbf{k}'} e^{i\mathbf{k}\cdot\mathbf{r}} e^{-i\mathbf{k}'\cdot\mathbf{r}'} [\hat{A}_{n\mathbf{k}}, \hat{\Pi}_{m-\mathbf{k}'}] \\
&= i\hbar\ \delta_{nm} \frac{1}{\Omega} \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} = i\hbar\ \delta_{nm}\ \delta(\mathbf{r}-\mathbf{r}') \qquad \textbf{not yet correct!}
\end{aligned}$$

Notice that a change in sign of $\mathbf{k}'$ in the commutators, would have introduced a change in sign in $\mathbf{r}'$, which is not correct.
This is not yet the whole story: these commutation rules are still incorrect, as discussed in Eq. 10.8. They are in contradiction with the **transversality condition 10.2** (See here: Sec. A.33). To enforce this condition, we express $\mathbf{A}_{\mathbf{k}}$ and $\mathbf{\Pi}_{\mathbf{k}}$ in terms of two real units vectors (polarisations) $\mathbf{u}_{\mathbf{k},s}$ with $s = \pm 1$, which are mutually orthogonal and orthogonal to $\mathbf{k}$:

$$\boxed{\mathbf{k}\cdot\mathbf{u}_{\mathbf{k},s} = 0 \qquad \mathbf{u}_{\mathbf{k},s}\cdot\mathbf{u}_{\mathbf{k},s'} = \delta_{ss'}} \tag{10.15}$$

$$\boxed{\hat{\mathbf{A}}_{\mathbf{k}} = \sum_s \hat{q}_{\mathbf{k},s}\,\mathbf{u}_{\mathbf{k},s} \qquad \hat{\mathbf{\Pi}}_{\mathbf{k}} = \sum_s \hat{p}_{\mathbf{k},s}\,\mathbf{u}_{\mathbf{k},s}} \tag{10.16}$$

and now assume canonical **commutation rules between the coefficients** in the form

$$\boxed{[\hat{q}_{\mathbf{k},s}, \hat{p}_{-\mathbf{k}',-s'}] = i\hbar\,\delta_{s,s'}\,\delta_{k,k'}} \tag{10.17}$$

We use the conventions, motivated by 10.13

$$\mathbf{u}_{\mathbf{k},s} = \mathbf{u}_{-\mathbf{k},-s} = \mathbf{u}^*_{\mathbf{k},s} \qquad \hat{q}_{\mathbf{k},s} = \hat{q}^\dagger_{-\mathbf{k},-s} \qquad \hat{p}_{\mathbf{k},s} = \hat{p}^\dagger_{-\mathbf{k},-s} \tag{10.18}$$

The Hamiltonian 10.7 becomes (again, we omit the " ˆ " from the notation)

$$\begin{aligned} H &= \frac{\mu}{2}\sum_{\mathbf{k}}\left[\frac{\mathbf{\Pi}_{-\mathbf{k}}\cdot\mathbf{\Pi}_{\mathbf{k}}}{\mu^2} + (\mathbf{k}\times\mathbf{A}_{-\mathbf{k}})\cdot(\mathbf{k}\times\mathbf{A}_{\mathbf{k}})\right] \\ &= \frac{1}{2\mu}\sum_{\mathbf{k}}\left[\mathbf{\Pi}_{-\mathbf{k}}\cdot\mathbf{\Pi}_{\mathbf{k}} + \mu^2\,k^2\mathbf{A}_{-\mathbf{k}}\cdot\mathbf{A}_{\mathbf{k}}\right] \;, \end{aligned} \tag{10.19}$$

where in the last line we have exploited the fact that $\mathbf{k}\cdot\mathbf{A}_{\mathbf{k}} = 0$.
Inserting 10.16 in one of the terms in H yields

$$\begin{aligned} \mathbf{\Pi}_{-\mathbf{k}}\cdot\mathbf{\Pi}_{\mathbf{k}} &= \sum_{s_1 s_2}\mathbf{u}_{-\mathbf{k},s_1}p_{-\mathbf{k},s_1}\cdot\mathbf{u}_{\mathbf{k},s_2}p_{\mathbf{k},s_2} = \sum_{s_1 s_2}\mathbf{u}_{\mathbf{k},-s_1}\cdot\mathbf{u}_{\mathbf{k},s_2}\;p_{-\mathbf{k},s_1}\;p_{\mathbf{k},s_2} \\ &= \sum_s p_{-\mathbf{k},-s}\;p_{\mathbf{k},s} \end{aligned}$$

where we have exploited the orthogonality of the $\mathbf{u}$ and 10.18 . Similarly

$$\mathbf{A}_{-\mathbf{k}}\cdot\mathbf{A}_{\mathbf{k}} = \sum_s q_{-\mathbf{k},-s}\;q_{\mathbf{k},s}$$

The Hamiltonian 10.19 , thus becomes

$$H = \frac{1}{2\mu}\sum_{\mathbf{k}}\sum_s\left(p_{-\mathbf{k},-s}\;p_{\mathbf{k},s} + \mu^2k^2\;q_{-\mathbf{k},-s}\;q_{\mathbf{k},s}\right) \tag{10.20}$$

The treatment is similar to the case of the harmonic oscillator, with slight variations. One introduces creation and destruction operators (remember that $k \equiv |\mathbf{k}|$)

$$
\begin{aligned}
a_{\mathbf{k},s} &= \frac{1}{\sqrt{2\hbar\mu k}}\left(\mu k\,\hat{q}_{\mathbf{k},s} + i\,\hat{p}_{\mathbf{k},s}\right) \\
a^{\dagger}_{\mathbf{k},s} &= \frac{1}{\sqrt{2\hbar\mu k}}\left(\mu k\,\hat{q}_{-\mathbf{k},-s} - i\,\hat{p}_{-\mathbf{k},-s}\right) = \left(a_{\mathbf{k},s}\right)^{\dagger}
\end{aligned}
\tag{10.21}
$$

The inverse of this expression is

$$
\begin{aligned}
\hat{q}_{\mathbf{k},s} &= \sqrt{\frac{\hbar}{2\mu k}}\left(a_{\mathbf{k},s} + a^{\dagger}_{-\mathbf{k},-s}\right) \\
\hat{p}_{\mathbf{k},s} &= -i\sqrt{\frac{\hbar\mu k}{2}}\left(a_{\mathbf{k},s} - a^{\dagger}_{-\mathbf{k},-s}\right)
\end{aligned}
\tag{10.22}
$$

These operators obey usual commutation relations (easy to show by using 10.17)

$$
\boxed{[a_{\mathbf{k},s}, a^{\dagger}_{\mathbf{k}',s'}] = \delta_{\mathbf{k}\mathbf{k}'}\,\delta_{ss'}}
\tag{10.23}
$$

with all other commutators being zero. In terms of these, 10.20 acquires the familiar form, where we reintroduce the speed of light c, so that $\omega_k = ck$:

$$
\boxed{H = \sum_{\mathbf{k}}\sum_{s} \hbar\omega_k\, a^{\dagger}_{\mathbf{k},s} a_{\mathbf{k},s} + \text{const.}}
\tag{10.24}
$$

Here, the (infinite) constant comes, as for the usual harmonic oscillator, from commutations of p and q and describes the zero-point energy.
10.23 together with 10.24 describe again a set of **independent harmonic oscillators**. Each one of these oscillator describes a **photon mode with wavevector k and polarisation vector $\mathbf{u}_{\mathbf{k},s}$**. The "creation" operator $a^{\dagger}_{\mathbf{k},s}$ increases by 1 the number of photons in this mode, while $a_{\mathbf{k},s}$ decreases it by 1.
The commutators of the fields are evaluated here: Sec. A.34

Chapter 11

Interaction of radiation field with matter

Starting from the results of the previous chapters, we will treat here the interaction between radiation field and matter, and apply the formalism to two cases of interest:
(i) Absorption and emission of radiation
(ii) Bremsstrahlung

In both cases, the electromagnetic field will be treated in second quantisation according to the results of Sec. 10. The electron Hamiltonian will be treated in first quantisation for case (i), this means that we will consider just one electron at a time. We will use the full second quantisation (for both radiation and electrons) formalism for case (ii).

11.1 Free radiation field

The Hamiltonian of the free electromagnetic (radiation) field follows from the corresponding Hamilton function, that we derived in 10.24 .

HAMILTONIAN OF THE FREE ELECTROMAGNETIC FIELD

$$H_{em} = \sum_{\mathbf{k},s} \hbar\omega_{\mathbf{k}} a^{\dagger}_{\mathbf{k},s} a_{\mathbf{k},s} \tag{11.1a}$$

$$\omega_{\mathbf{k}} = |\mathbf{k}|\, c\,.$$

11.2 Electron and interaction term

The Hamiltonian of a single electron in an electromagnetic field is given in 4.1 .

$$H = \frac{1}{2m}\left(\mathbf{p} - \frac{q}{c}\mathbf{A}(\mathbf{r},t)\right)^2 + V(\mathbf{r}) \tag{11.2}$$

We consider the contribution of a static field $V(\mathbf{r})$, plus an electromagnetic field in the Coulomb gauge described by the vector potential $\mathbf{A}$. For simplicity, we neglect electron spin.

We split 11.2 in a term describing an electron in an external potential (for example in an atomic orbital)

$$H_{el} = \frac{1}{2m}\mathbf{p}^2 + V(\mathbf{r}) \tag{11.3}$$

and the **electron-photon interaction** term

$$H_{el-ph} = \underbrace{-\frac{q}{mc}\mathbf{A}(\mathbf{r},t)\cdot\mathbf{p}}_{H'} + \underbrace{\frac{q^2}{2mc^2}\mathbf{A}(\mathbf{r},t)^2}_{H''}\,. \tag{11.4}$$

The two terms in 11.4 are termed paramagnetic (H') and diamagnetic (H''), respectively. Notice that despite of the fact that $\mathbf{r}$ and $\mathbf{p}$ are noncommuting operators, the order in the product $\mathbf{A}(\mathbf{r},t)\cdot\mathbf{p}$ doesn't matter due to the Coulomb gauge $\boldsymbol{\nabla}\cdot\mathbf{A} = 0$.

We will consider H_{el-ph} 11.4 as a perturbation of the unperturbed Hamiltonian $H_0 \equiv H_{el} + H_{em}$. Since radiation is treated in second quantisation, we have to replace in H_{el-ph} the vector potential $\mathbf{A}$ with its second quantisation expression

10.9 with 10.16 , 10.22 and $\mu = 1/(4\pi)$, leading to

$$\begin{aligned}\mathbf{A}(\mathbf{r}) &= \sum_{\mathbf{k}} \left(\frac{2\pi\hbar c^2}{\Omega\omega_k}\right)^{1/2} \sum_s \mathbf{u}_{\mathbf{k},s}\, e^{i\mathbf{k}\cdot\mathbf{r}} \left(a_{\mathbf{k},s} + a^\dagger_{-\mathbf{k},-s}\right) \\ &= \sum_{\mathbf{k}} \frac{\gamma_k}{\sqrt{\Omega}} \sum_s \mathbf{u}_{\mathbf{k},s} \left(a_{\mathbf{k},s} e^{i\mathbf{k}\cdot\mathbf{r}} + a^\dagger_{\mathbf{k},s} e^{-i\mathbf{k}\cdot\mathbf{r}}\right), \end{aligned} \tag{11.5}$$

$$\gamma_k \equiv \left(\frac{2\pi\hbar c^2}{\omega_k}\right)^{1/2} \tag{11.6}$$

where we have used the symmetry 10.18 , and reintroduced the speed of light c.

The paramagnetic interaction term in 11.4 , thus becomes

$$H' = -\frac{q}{mc} \sum_{\mathbf{k},s} \frac{\gamma_k}{\sqrt{\Omega}} \left(a_{\mathbf{k},s} e^{i\mathbf{k}\cdot\mathbf{r}} + a^\dagger_{\mathbf{k},s} e^{-i\mathbf{k}\cdot\mathbf{r}}\right) \mathbf{u}_{\mathbf{k},s} \cdot \mathbf{p} \tag{11.7}$$

11.3 Transition rate

We evaluate the rate for a transition between an initial state $|i\rangle$ and a final state $|f\rangle$ under the influence of the perturbation H' within Fermi's golden rule 3.27 . We neglect contributions coming from H'': we will discuss why later.

First, the states $|i\rangle$ and $|f\rangle$ are eigenstates of the unperturbed hamiltonian

$$H_0 \equiv H_{el} + H_{em} \tag{11.8}$$

These are product states of the form

$$|m\rangle = |\text{electron state}_m\rangle \otimes |\text{photon state}_m\rangle \qquad m = i, f\,. \tag{11.9}$$

Here, $|\text{electron state}_m\rangle$ is an eigenstate of H_{el}, which we assume discrete, for example an atomic or molecular orbital, with energy ε_m and denote it as $|\varepsilon_m\rangle$.

$|\text{photon state}_m\rangle$ is an eigenstate of the many-body photon Hamiltonian H_{em}, and can be written in the occupation number representation as $\left|\{n^m_{\mathbf{k}s}\}, \forall(\mathbf{k}, s)\right\rangle$, (See Sec. 7.3). Here $n^m_{\mathbf{k}s}$ is the number of photons with momentum $\mathbf{k}$ and polarisation s in the state $|\text{photon state}_m\rangle$.

The total energy E_m of the state $|m\rangle$ is, thus given by (neglecting the zero-point energy)

$$E_m = \varepsilon_m + \sum_{\mathbf{k},s} \hbar\omega_k\, n^m_{\mathbf{k}s}\,. \tag{11.10}$$

Fermi's golden rule 3.27 for the transition rate, thus becomes

$$W_{i\to f} = \frac{2\pi}{\hbar} \left| \langle\varepsilon_f| \otimes \langle\{n^f_{\mathbf{k}s}\}|\, H' \;|\varepsilon_i\rangle \otimes |\{n^i_{\mathbf{k}s}\}\rangle \right|^2 \delta(E_f - E_i)$$

From the expression 11.7 it is clear that H' can create or destroy a single photon. Therefore, $|f\rangle$ can differ from $|i\rangle$ by having one photon more (photon emission) in a given mode, or one less (photon absorbtion). We consider these two processes separately.

11.3.1 Photon emission

The final state will have just one additional photon in a single mode, say $(\mathbf{k}, s)$, i.e.

$$\begin{aligned} n^f_{\mathbf{k}'s'} &= n^i_{\mathbf{k}'s'} \qquad (\mathbf{k}', s') \neq (\mathbf{k}, s) \\ n^f_{\mathbf{k}s} &= n^i_{\mathbf{k}s} + 1 \end{aligned} \tag{11.11}$$

For the energy difference we, thus, have

$$E_f - E_i = \varepsilon_f - \varepsilon_i + \hbar\omega_k$$

The matrix element of 11.7 is given by

$$\langle f|H'|i\rangle = -\frac{q}{mc}\sum_{k',s'}\frac{\gamma_{k'}}{\sqrt{\Omega}}\mathbf{u}_{\mathbf{k}',s'}\cdot\langle\varepsilon_f|\mathbf{p}e^{-i\mathbf{k}'\cdot\mathbf{r}}|\varepsilon_i\rangle\langle\{n^f_{\mathbf{k}s}\}|a^\dagger_{\mathbf{k}',s'}|\{n^i_{\mathbf{k}s}\}\rangle\,. \tag{11.12}$$

Due to 11.11 , the photon matrix element is given by

$$\langle\{n^f_{\mathbf{k}s}\}|a^\dagger_{\mathbf{k}',s'}|\{n^i_{\mathbf{k}s}\}\rangle = \sqrt{n^i_{\mathbf{k}s}+1}\;\delta_{\mathbf{k},\mathbf{k}'}\delta_{s,s'}$$

In total, using 11.6 , we have for the emission rate

$$W^e_{i\to f} = \frac{4\pi^2 q^2}{\Omega m^2\omega_k}\,\delta(\varepsilon_f - \varepsilon_i + \hbar\omega_k)(n^i_{\mathbf{k}s}+1)\left|\mathbf{u}_{\mathbf{k},s}\cdot\langle\varepsilon_f\left|\mathbf{p}e^{-i\mathbf{k}\cdot\mathbf{r}}\right|\varepsilon_i\rangle\right|^2 \tag{11.13}$$

This term describes the transition from a higher ε_i to a lower $\varepsilon_f = \varepsilon_i - \hbar\omega_k$ electronic state upon emitting a photon. This can occur spontaneously, i.e. without the presence of other photons i.e. $n^i_{\mathbf{k}s} = 0$ **“spontaneous emission”**. The presence of an external field $n^i_{\mathbf{k}s} > 0$ with that resonance frequency enhances the emission rate by a factor proportional to its intensity **“stimulated emission”**.

11.3.2 Photon absorption

For a photon absorption process the discussion is similar. In this case, the final state will have one photon less in $\mathbf{k}, s$, i.e.

$$\begin{aligned} n^f_{\mathbf{k}'s'} &= n^i_{\mathbf{k}'s'} \quad (\mathbf{k}', s') \neq (\mathbf{k}, s) \\ n^f_{\mathbf{k}s} &= n^i_{\mathbf{k}s} - 1 \end{aligned} \tag{11.14}$$

The energy difference

$$E_f - E_i = \varepsilon_f - \varepsilon_i - \hbar\omega_k$$

The matrix element is given by

$$\langle f|H'|i\rangle = -\frac{q}{mc}\sum_{k',s'}\frac{\gamma_{k'}}{\sqrt{\Omega}}\mathbf{u}_{\mathbf{k}',s'}\cdot\left\langle\varepsilon_f\middle|\mathbf{p}e^{i\mathbf{k}'\cdot\mathbf{r}}\middle|\varepsilon_i\right\rangle\underbrace{\left\langle\{n^f_{\mathbf{k}s}\}\middle|a_{\mathbf{k}',s'}\middle|\{n^i_{\mathbf{k}s}\}\right\rangle}_{\sqrt{n^i_{\mathbf{k}s}}\delta_{\mathbf{k},\mathbf{k}'}\delta_{s,s'}} \tag{11.15}$$

Finally, the absorption rate becomes

$$W^e_{i\to f} = \frac{4\pi^2 q^2}{\Omega m^2\omega_k}\,\delta(\varepsilon_f - \varepsilon_i - \hbar\omega_k)\,n^i_{\mathbf{k}s}\,\left|\mathbf{u}_{\mathbf{k},s}\cdot\left\langle\varepsilon_f\middle|\mathbf{p}e^{i\mathbf{k}\cdot\mathbf{r}}\middle|\varepsilon_i\right\rangle\right|^2 \tag{11.16}$$

In this case the absorption rate is proprotional to $n^i_{\mathbf{k}s}$, i.e. absorption takes place only if photons with that frequency are present, which is somewhat obvious.

11.3.3 Electric dipole transition

An expansion in multipoles of the charge corresponds to an expansion in powers of a_0/λ. Here, a_0 is the typical spatial extension of the charge (e.g. Bohr's radius) and λ the wavelength of radiation. For $a_0 \ll \lambda$ one can restrict to the lowest order, i.e. the electric dipole term. This corresponds to neglecting the $i\mathbf{k}\cdot\mathbf{r}$ term in the exponent of 11.13 and 11.16 which is of the order of a_0/λ.
The remaining matrix element of the momentum can be then transformed into

$$\begin{aligned}\left\langle\varepsilon_f\middle|\mathbf{p}\middle|\varepsilon_i\right\rangle &= \frac{im}{\hbar}\left\langle\varepsilon_f\middle|[H_{el},\mathbf{r}]\middle|\varepsilon_i\right\rangle = \frac{im}{\hbar}\left\langle\varepsilon_f\middle|H_{el}\mathbf{r} - \mathbf{r}H_{el}\middle|\varepsilon_i\right\rangle \\ &= \frac{im}{\hbar}(\varepsilon_f - \varepsilon_i)\left\langle\varepsilon_f\middle|\mathbf{r}\middle|\varepsilon_i\right\rangle\ . \end{aligned} \tag{11.17}$$

I.e. it is proportional to the dipole matrix element.

Selection rules

The dipole matrix element 11.17 is nonzero only between certain pair of states. This leads to the so called **dipole selection rules**. For example, the two states $|\varepsilon_f\rangle$ $|\varepsilon_i\rangle$ must have different parity under reflection $\mathbf{r} \to -\mathbf{r}$, and, in case of atomic orbitals, must have the quantum number l differing by ± 1, i.e.

$$l_f = l_i \pm 1 \tag{11.18}$$

This can be understood by the fact that a photon has angular momentum $j = 1$. In the case of photon absorption, the initial state consisting of the electron and

one photon has, according to the general rules of addition of angular momenta 6.19, a total angular momentum $j_{tot,i}$ where $l_i - 1 \leq j_{tot,i} \leq l_i + 1$. In the final state the photon has been absorbed, so angular momentum conservation fixes l_f to be equal to $j_{tot,i}$. Considering the fact that $l_f = l_i$ is excluded since it has the same parity, this gives the selection rule 11.18. The same discussion holds upon exchanging final and initial state for the case of photon emission.
This discussion neglects the contribution of the spatial part of the photon wave function to j_{tot}. This is correct within the electric dipole approximation in which $\mathbf{k}$ is neglected, i.e. the photon wave function is a constant. Higher orders in $\mathbf{k}$, i.e. higher orders in the multipole expansion, allow for transitions between more distant angular momenta.

11.3.4 Lifetime of an excited state

In the absence of external radiation there can be only spontaneous photon emission acompanied by a decay from an excited state i into a state with lower energy. Since $\sum_f W^e_{i\to f} = -\frac{dP_i}{dt}$ describes the rate of decrease of the average occupation (population) of the excited state, this is equal to the inverse lifetime $\frac{1}{\tau}$.
From 11.13, and in the electric dipole approximation 11.17, we obtain in the absence of photons in the initial state ($n_{\mathbf{k},s} = 0$)

$$\frac{1}{\tau} = \sum_{\varepsilon_f}\sum_{\mathbf{k}} \frac{4\pi^2 q^2}{\Omega\hbar^2\omega_k}\,\delta(\varepsilon_f - \varepsilon_i + \hbar\omega_k)(\varepsilon_f - \varepsilon_i)^2 \sum_s \left|\mathbf{u}_{\mathbf{k},s}\cdot\langle\varepsilon_f|\mathbf{r}|\varepsilon_i\rangle\right|^2 \qquad (11.19)$$

Where we have explicitly written the sum over the final states f as a sum over the photon momentum $\mathbf{k}$ the polarisation s, and the electron final states ε_f.
In the infinite volume limit, we can replace (cf. A.50)

$$\frac{1}{\Omega}\sum_{\mathbf{k}} \longrightarrow \frac{1}{(2\pi)^3}\int d^3\mathbf{k} = \frac{1}{(2\pi)^3}\int k^2\, dk\, d\cos\theta\, d\varphi\ .$$

The sum over the photon polarisation in 11.19

$$\sum_s \left|\mathbf{u}_{\mathbf{k},s}\cdot\underbrace{\langle\varepsilon_f|\mathbf{r}|\varepsilon_i\rangle}_{\mathbf{d}_{if}}\right|^2 \qquad (11.20)$$

can be carried out in the following way: Without restriction we can take $\mathbf{u}_{\mathbf{k},s=-1}$ perpendicular to $\mathbf{d}_{if}$, so that there is only a contribution from $s = 1$. Let us call α the angle between $\mathbf{u}_{\mathbf{k},1}$ and $\mathbf{d}_{if}$. Then, due to the fact that $\mathbf{u}_{\mathbf{k},1}$ and $\mathbf{k}$ are orthogonal, the angle between $\mathbf{k}$ and $\mathbf{d}_{if}$ is $\theta = \frac{\pi}{2} - \alpha$. One obtains for 11.20

$$|\mathbf{d}_{if}|^2\cos^2\alpha = |\mathbf{d}_{if}|^2\sin^2\theta$$

Here, again,

$$\mathbf{d}_{if} \equiv \left\langle \varepsilon_f \middle| \mathbf{r} \middle| \varepsilon_i \right\rangle \tag{11.21}$$

is the dipole matrix element between initial and final state.
For a fixed final state ε_f in 11.19 , we carry out the integration by taking $\mathbf{d}_{if}$ in the z direction. Therefore, 11.19 becomes

$$\begin{aligned}\frac{1}{\tau} &= \sum_{\varepsilon_f} \int k^2\, dk\, d\cos\theta\, d\varphi \frac{4\pi^2 q^2}{(2\pi)^3\, \hbar^2 ck}\, \delta(\varepsilon_f - \varepsilon_i + \hbar c\, k)(\varepsilon_f - \varepsilon_i)^2\, |\mathbf{d}_{if}|^2 \sin^2\theta \\ &= \sum_{\varepsilon_f} \frac{q^2}{\hbar^4\, c^3} |\mathbf{d}_{if}|^2 (\varepsilon_i - \varepsilon_f)^3 \int \sin^2\theta\, d\cos\theta \\ &= \sum_{\varepsilon_f} \underbrace{\frac{q^2}{\hbar c}}_{\approx 1/137} \frac{4}{3c^2} |\mathbf{d}_{if}|^2 \frac{(\varepsilon_i - \varepsilon_f)^2}{\hbar^2} \frac{(\varepsilon_i - \varepsilon_f)}{\hbar}\end{aligned} \tag{11.22}$$

$\hbar/\tau$ describes the energy uncertainty $\Delta\varepsilon_i$ (lifetime broadening) of the level ε_i. Accordingly: the ratio $\Delta\varepsilon_i/(\varepsilon_i - \varepsilon_f)$ describes how sharp a certain transition is.
Let us estimate this ratio it from 11.22 : $\frac{(\varepsilon_i - \varepsilon_f)}{\hbar}$ is a typical frequency, whose inverse is the typical time for an electron to go around an orbit. d_{if} is the typical radius of an orbit, so that $\beta_e = d_{if}\, \frac{(\varepsilon_i - \varepsilon_f)}{\hbar}/c$ is a typical speed of the electron in units of the speed of light.
In total, $\Delta\varepsilon_i/(\varepsilon_i - \varepsilon_f) \sim \beta_e^2 \alpha$, where α is the fine structure constant $\frac{q^2}{\hbar c} \approx 1/137$.

11.4 Nonrelativistic Bremsstrahlung

As we know from classical electrodynamics, accerated charges emit radiation. If two particles scatter with each other, they will emit radiation. We would like to treat this process quantum-mechanically. Therefore we consider the scattering of an electron with a nucleus described by a static potential $V(\mathbf{r})$, an take into account the interaction with radiation as well. For simplicity, we neglect the electron spin, since it does not change during scattering and has no effect on the result. As we consider scattering of a single electron, the result is independent of particle statistics and is also valid for bosons.
The Hamiltonian initially consists of three parts:

$$H = H_{kin} + H_{em} + H_{int}\ ,$$

the kinetic energy of the electron, the contribution from the free electromagnetic field 11.1a and the interaction between charge and field.

11.5 Kinetic energy of the electron

We now rewrite the kinetic part of the Hamiltonian of the electrons in second quantisation (cf. 9.11a , 9.9 or 9.29). We use as eigenfunctions $\varphi_n(\mathbf{x})$ plane waves with periodic boundary conditions in a cubic box of the length L (cf. Sec. 9.6)

PLANE WAVE BASIS

$$\varphi_{\mathbf{q}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{q}\mathbf{r}} \tag{11.23a}$$

$$q_\alpha = \frac{2\pi n_\alpha}{L}; \qquad n_\alpha \in \mathfrak{N}_0 \tag{11.23b}$$

$$\sum_q \varphi_{\mathbf{q}}(\mathbf{r}) \varphi^*_{\mathbf{q}}(\mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \tag{11.23c}$$

$$\int \varphi^*_{\mathbf{q}}(\mathbf{r}) \varphi_{\mathbf{q}'}(\mathbf{r})\, d^3\mathbf{r} = \delta_{\mathbf{q},\mathbf{q}'} \tag{11.23d}$$

The completeness and orthogonality of plane waves follow from the fact that they are eigenfunctions of the momentum operator. It also follows that the kinetic energy is diagonal in this basis. As in 9.11a we get

KINETIC ENERGY FOR PLANE WAVES

$$H_{kin} = \sum_{\mathbf{q}} E_{\mathbf{q}} c^\dagger_{\mathbf{q}} c_{\mathbf{q}} \tag{11.24a}$$

$$E_{\mathbf{q}} = \frac{\hbar^2 \mathbf{q}^2}{2m}\ . \tag{11.24b}$$

11.6 Interaction between charge and radiation field

We use once again $c = 1$. To derive the interaction between radiation field and electron, we start from the expression of the total electron Hamiltonian 4.1 . As described in chapter 9 we use the energy expectation value and transform the electron wave function into a field operator. The result is the kinetic energy **plus** the interaction

$$
\begin{aligned}
H_{kin}+H_{int} &= \int d^3\mathbf{r}\Psi^\dagger(\mathbf{r})\left[\frac{1}{2m}\big(\frac{\hbar}{i}\boldsymbol{\nabla}-e\mathbf{A}(\mathbf{r})\big)^2+V(\mathbf{r})\right]\Psi(\mathbf{r}) \\
&= \underbrace{\int d^3\mathbf{r}\Psi^\dagger(\mathbf{r})\frac{-\hbar^2\boldsymbol{\nabla}^2}{2m}\Psi(\mathbf{r})}_{H_{kin}}\underbrace{-\frac{e\hbar}{im}\int d^3\mathbf{r}\Psi^\dagger(\mathbf{r})\mathbf{A}(\mathbf{r})\cdot\boldsymbol{\nabla}\Psi(\mathbf{r})}_{H'}+\dots \\
&\dots+\underbrace{\int d^3\mathbf{r}\Psi^\dagger(\mathbf{r})V(\mathbf{r})\Psi(\mathbf{r})}_{H_V}+\underbrace{\frac{e^2}{2m}\int d^3\mathbf{r}\Psi^\dagger(\mathbf{r})\mathbf{A}^2(\mathbf{r})\Psi(\mathbf{r})}_{H''}\ . \qquad (11.25)
\end{aligned}
$$

We evaluate again the interaction term H' 11.25 , now with the electron field in second quantisation. We use again 11.5 for the vector potential. For a more efficient notation, we define the operators

$$
a^\tau_{\mathbf{k},s}=\begin{cases} a^\dagger_{\mathbf{k},s} & \text{für} \quad \tau=+1 \\ a_{\mathbf{k},s} & \text{für} \quad \tau=-1 \end{cases}
$$

and use them to rewrite 11.5 in a more compact form

$$
\mathbf{A}(\mathbf{r})=\sum_{\substack{\mathbf{k}\\ s=\pm1\\ \tau=\pm1}}\left(\frac{2\pi\hbar}{\Omega k}\right)^{1/2}\mathbf{u}_{\mathbf{k},s}a^\tau_{\mathbf{k},s}e^{-i\tau\mathbf{k}\mathbf{r}}\ . \qquad (11.26)
$$

Please remember that $\boldsymbol{\nabla}\cdot\mathbf{A}=0$. Therefore, $\boldsymbol{\nabla}(\cdot\mathbf{A}f(\mathbf{r}))=\mathbf{A}\cdot\boldsymbol{\nabla}f(\mathbf{r})$. Thereby, the Hamiltonian representing the interaction H' in 11.25 becomes (we reintroduce c, so that $\omega_k=ck$)

$$
\begin{aligned}
H' &= -\frac{e\hbar}{imc}\int d^3\mathbf{r}\Psi^\dagger(\mathbf{r})\left[\sum_{\mathbf{k},s,\tau}\left(\frac{2\pi\hbar c^2}{\Omega\omega_k}\right)^{1/2}\mathbf{u}_{\mathbf{k},s}a^\tau_{\mathbf{k},s}e^{-i\tau\mathbf{k}\mathbf{r}}\right]\cdot\boldsymbol{\nabla}\Psi(\mathbf{r}) \\
&= -\frac{e\hbar}{imc}\sum_{\mathbf{k}s,\tau}\left(\frac{2\pi\hbar c^2}{\Omega\omega_k}\right)^{1/2}\mathbf{u}_{\mathbf{k},s}a^\tau_{\mathbf{k},s}\cdot\left[\int d^3\mathbf{r}\Psi^\dagger(\mathbf{r})e^{-i\tau\mathbf{k}\mathbf{r}}\boldsymbol{\nabla}\Psi(\mathbf{r})\right] \qquad (11.27)
\end{aligned}
$$

For the expression in square brackets we introduce the expansion of the field operators in plane waves (cf. 9.9 with 11.23a), as we did for the kinetic energy.

$$
\begin{aligned}
[\ldots] &= \sum_{\mathbf{q},\mathbf{q}'} c^\dagger_{\mathbf{q}} c_{\mathbf{q}'} \int \frac{d^3\mathbf{r}}{\Omega} e^{-i\mathbf{q}\mathbf{r}} e^{-i\tau\mathbf{k}\mathbf{r}} \nabla e^{i\mathbf{q}'\mathbf{r}} \\
&= i \sum_{\mathbf{q},\mathbf{q}'} c^\dagger_{\mathbf{q}} c_{\mathbf{q}'}\, \mathbf{q}' \int \frac{d^3\mathbf{r}}{\Omega} e^{i(\mathbf{q}'-\mathbf{q}-\tau\mathbf{k})\mathbf{r}} \\
&= i \sum_{\mathbf{q},\mathbf{q}'} c^\dagger_{\mathbf{q}} c_{\mathbf{q}'}\, \mathbf{q}'\, \delta_{\mathbf{q}-(\mathbf{q}'-\tau\mathbf{k})} \\
&= i \sum_{\mathbf{q}'} \mathbf{q}' c^\dagger_{\mathbf{q}'-\tau\mathbf{k}} c_{\mathbf{q}'} \, . \qquad (11.28)
\end{aligned}
$$

This result is plugged in the square brackets in the Hamiltonian 11.27 and leads to

$$
\begin{aligned}
H' &= -\frac{e\hbar}{mc} \sum_{\substack{\mathbf{k}\mathbf{q}\\ s,\tau}} \left(\frac{2\pi\hbar c^2}{\Omega\omega_k}\right)^{1/2} \mathbf{q}\cdot\mathbf{u}_{\mathbf{k},s}\, c^\dagger_{\mathbf{q}-\tau\mathbf{k}} c_{\mathbf{q}} a^\tau_{\mathbf{k},s} \\
&= -\frac{e\hbar}{mc} \sum_{\mathbf{k}\mathbf{q}s} \left(\frac{2\pi\hbar c^2}{\Omega\omega_k}\right)^{1/2} \mathbf{q}\cdot\mathbf{u}_{\mathbf{k},s} \left(c^\dagger_{\mathbf{q}+\mathbf{k}} c_{\mathbf{q}} a_{\mathbf{k},s} + c^\dagger_{\mathbf{q}} c_{\mathbf{q}+\mathbf{k}} a^\dagger_{\mathbf{k},s} \right) . \qquad (11.29)
\end{aligned}
$$

For the last transformation, we used $\mathbf{k}\cdot\mathbf{u}_{\mathbf{k},s} = 0$.
The interaction term consists of two parts, shown in Fig. 375 with Feynman diagramms. The picture on the left represents the first part of the Hamiltonian, in which an electron with momentum $\mathbf{q}_i$ and a photon with momentum $\mathbf{k}$ and polarisation s are annihilated and a new electron with mometum $\mathbf{q}_f = \mathbf{q}_i + \mathbf{k}$ is created. The second term describes the inverse process - first, an electron is annihilated and then, a photon and an electron are created.

11.7 Diamagnetic contribution*(Addendum)*

Now we will evaluate the so-called diamagnetic part H'' in 11.25 . As we will see, this part does not contribute to the Bremmstrahlung. Once again we use 11.26 for $\mathbf{A}$,

$$
\begin{aligned}
H'' &= \frac{e^2}{2mc^2} \int d^3\mathbf{r} \Psi^\dagger(\mathbf{r}) \mathbf{A}^2(\mathbf{r}) \Psi(\mathbf{r}) \\
\mathbf{A}^2 &= \frac{2\pi\hbar c^2}{\Omega} \sum_{\substack{\mathbf{k},\mathbf{k}'\\ s,s'\\ \tau,\tau'}} \frac{1}{\sqrt{\omega_{\mathbf{k}}\omega_{\mathbf{k}'}}} \mathbf{u}_{\mathbf{k},s}\cdot\mathbf{u}_{\mathbf{k}',s'}\; a^\tau_{\mathbf{k},s} a^{\tau'}_{\mathbf{k}',s'} e^{-i(\tau\mathbf{k}+\tau'\mathbf{k}')\cdot\mathbf{r}}
\end{aligned}
$$

Figure 11.1: Feynman diagramms for the two Scattering events of the interaction term of the Hamiltonian 11.29 .

$$H'' = \frac{\pi\hbar e^2}{m\Omega} \sum_{\substack{\mathbf{k},\mathbf{k}' \\ s,s' \\ \tau,\tau'}} \frac{1}{\sqrt{\omega_{\mathbf{k}}\omega_{\mathbf{k}'}}} \mathbf{u}_{\mathbf{k},s} \cdot \mathbf{u}_{\mathbf{k}',s'} \; a^{\tau}_{\mathbf{k},s} a^{\tau'}_{\mathbf{k}',s'} \dots$$

$$\dots \left[\int d^3\mathbf{r} \Psi^{\dagger}(\mathbf{r}) e^{-i(\tau\mathbf{k}+\tau'\mathbf{k}')\mathbf{r}} \Psi(\mathbf{r}) \right]$$

The term $[\dots]$ is the same as in 11.27 , with the only difference that $\tau\mathbf{k} \to (\tau\mathbf{k} + \tau'\mathbf{k}')$. Accordingly, we use the result in 11.28

$$[\dots] = \sum_{\mathbf{q}} c^{\dagger}_{\mathbf{q}} c_{\mathbf{q}+\tau\mathbf{k}+\tau'\mathbf{k}'}$$

$$H'' = \frac{\pi\hbar e^2}{m\Omega} \sum_{\substack{\mathbf{q},\mathbf{k},\mathbf{k}' \\ s,s' \\ \tau,\tau'}} \frac{1}{\sqrt{\omega_{\mathbf{k}}\omega_{\mathbf{k}'}}} \mathbf{u}_{\mathbf{k},s} \cdot \mathbf{u}_{\mathbf{k}',s'} \; a^{\tau}_{\mathbf{k},s} a^{\tau'}_{\mathbf{k}',s'} c^{\dagger}_{\mathbf{q}} c_{\mathbf{q}+\tau\mathbf{k}+\tau'\mathbf{k}'} \; .$$

DIAMAGNETIC TERM

$$\begin{aligned}H'' = \frac{\pi\hbar e^2}{m\Omega} \sum_{\substack{\mathbf{q},\mathbf{k},\mathbf{k}' \\ s,s'}} \frac{1}{\sqrt{\omega_{\mathbf{k}}\omega_{\mathbf{k}'}}} \mathbf{u}_{\mathbf{k},s} \cdot \mathbf{u}_{\mathbf{k}',s'} \Big\{ & a^{\dagger}_{\mathbf{k},s} a^{\dagger}_{\mathbf{k}',s'} c^{\dagger}_{\mathbf{q}} c_{\mathbf{q}+\mathbf{k}+\mathbf{k}'} \\ & + a_{\mathbf{k},s} a_{\mathbf{k}',s'} c^{\dagger}_{\mathbf{q}} c_{\mathbf{q}-\mathbf{k}-\mathbf{k}'} + a^{\dagger}_{\mathbf{k},s} a_{\mathbf{k}',s'} c^{\dagger}_{\mathbf{q}} c_{\mathbf{q}+\mathbf{k}-\mathbf{k}'} \\ & + a_{\mathbf{k},s} a^{\dagger}_{\mathbf{k}',s'} c^{\dagger}_{\mathbf{q}} c_{\mathbf{q}-\mathbf{k}+\mathbf{k}'} \Big\} \end{aligned} \tag{11.30}$$

The two lower processes describe scattering of an electron with a photon. For those, the total momentum is conserved. This is **Compton scattering**, where one photon is scattered off a (free) electron.

11.8 Potential term

Finally, we are left with the term representing the potential in 11.25 . In second quantisation the expression is derived using 9.29 (we neglect spin for simplicity):

POTENTIAL TERM

$$\begin{aligned} H_V &= \sum_{q,q'} V(\mathbf{q},\mathbf{q}') c^{\dagger}_{\mathbf{q}} c_{\mathbf{q}'} \\ V(\mathbf{q},\mathbf{q}') &= \int \varphi^{*}_{\mathbf{q}}(\mathbf{r}) V(\mathbf{r})\, \varphi_{\mathbf{q}'}(\mathbf{r})\, d^3\mathbf{r} \\ &= \frac{1}{\Omega} \int e^{i\mathbf{r}(\mathbf{q}-\mathbf{q}')} V(\mathbf{r})\, d^3\mathbf{r} \quad = V(\mathbf{q}-\mathbf{q}') \end{aligned} \tag{11.31}$$

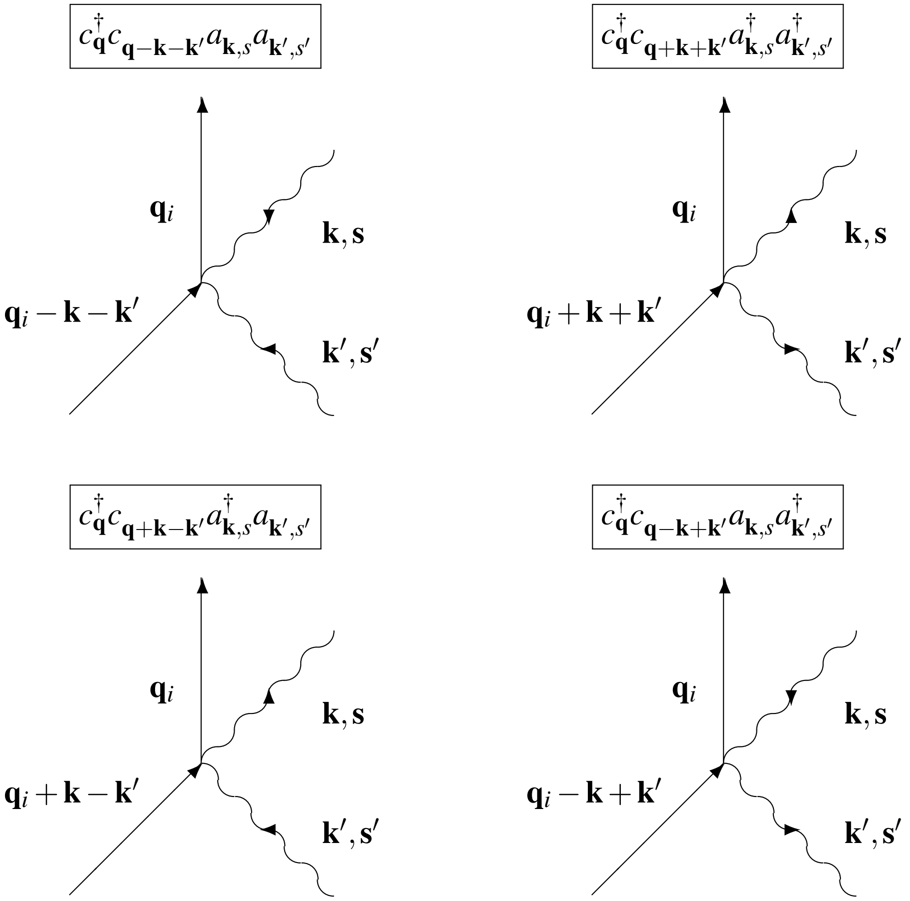


Figure 11.2: The contributions to H'' (11.30). The lower two terms contribute to Compton scattering. The upper terms describe emission and absorption of two photons.

For the Coulomb potential for atomic number Z we have

$$\begin{aligned} V(\mathbf{r}) &= -\frac{Ze^2}{r} \\ V(\mathbf{q}-\mathbf{q}') &= -\frac{4\pi Ze^2}{\Omega\,|\mathbf{q}-\mathbf{q}'|^2}\;. \end{aligned} \tag{11.32}$$

Derivation of the Fourier transformation here: Sec. A.35 .

11.9 Transistion amplitude

11.9.1 First order

We now split the Hamiltonian, which at this point consists of the following terms,

$$H = \underbrace{H_{kin} + H_{em}}_{H_0} + \underbrace{H_V + H' + H''}_{H_{int}}\,,$$

into an unperturbed term H_0 and a perturbation term H_{int}. Eigenvectors of H_0 have the form (Electron spin is neglected)

$$|\Psi\rangle = c^\dagger_{\mathbf{q}_1} c^\dagger_{\mathbf{q}_2} \cdots a^\dagger_{\mathbf{k}_1,s_1} a^\dagger_{\mathbf{k}_2,s_2} \cdots |0\rangle\;.$$

We are interested in processes where an electron is scattered and a photon is emitted. That means

$$\text{Initial state:} \qquad |i\rangle = c^\dagger_{\mathbf{q}_i}|0\rangle \tag{11.33a}$$

$$\text{Final state:} \qquad |f\rangle = c^\dagger_{\mathbf{q}_f} a^\dagger_{\mathbf{k},s}|0\rangle\;.$$

We use Fermis Golden Rule (3.27 with 3.33), to determine the transition rate

$$\begin{aligned} W_{i\to f} &= \frac{2\pi}{\hbar}\left|M_{fi}\right|^2\,\delta(E_f - E_i) \\ M_{fi} &= H_{fi} + \sum_n \frac{H_{fn}H_{ni}}{E_i - E_n + iO^+} \end{aligned} \tag{11.33b}$$

In principle, H' 11.29 in first order already could describe the process we are interested in. The matrix element would then be

$$\begin{aligned} M_{fi} = \langle f|H'|i\rangle &= -\frac{e\hbar}{mc}\sum_{\mathbf{k}'\mathbf{q}s'}\left(\frac{2\pi\hbar c^2}{\Omega\omega_{\mathbf{k}'}}\right)^{1/2}\mathbf{q}\cdot\mathbf{u}_{\mathbf{k}',s'} \\ &\times \langle 0|c_{\mathbf{q}_f} a_{\mathbf{k},s}\left(c^\dagger_{\mathbf{q}+\mathbf{k}'} c_{\mathbf{q}} a_{\mathbf{k}',s'} + c^\dagger_{\mathbf{q}-\mathbf{k}'} c_{\mathbf{q}} a^\dagger_{\mathbf{k}',s'}\right) c^\dagger_{\mathbf{q}_i}|0\rangle \end{aligned} \tag{11.34}$$

Obviously, only the second summand contributes and we require

$$\mathbf{k}' = \mathbf{k}, \qquad s' = s, \qquad \mathbf{q} = \mathbf{q}_i, \qquad \mathbf{q}_f = \mathbf{q}_i - \mathbf{k}$$

Therefore, we have

$$M_{fi} = -\frac{e\hbar}{mc}\left(\frac{2\pi\hbar c^2}{\Omega\omega_{\mathbf{k}}}\right)^{1/2} \mathbf{q}_i \cdot \mathbf{u}_{\mathbf{k},s}\ \delta_{\mathbf{q}_f - \mathbf{q}_i + \mathbf{k}}\ .$$

Nevertheless, one can show, that in this process energy and momentum cannot be simultaneously conserved. Proof here: Sec. A.36 .

11.9.2 Second order

Therefore, first order perturbation theory does not contribute to the bremsstrahlung process and we proceed to second order, i.e. the second term in 11.33b . (The Compton term 11.30 needs a photon in the initial state or two photons in the initial/final state and does not contribute either.

We consider the matrix elements (of H' 11.29 and H_V 11.31)

$$\begin{aligned} H_{fn}H_{ni} &= \left(H_{V\,fn} + H'_{fn}\right)\left(H_{V\,ni} + H'_{ni}\right) \\ &= H_{V\,fn}H_{V\,ni} + H'_{fn}H'_{ni} + H'_{fn}H_{V\,ni} + H_{V\,fn}H'_{ni}\ . \end{aligned}$$

The first two matrix elements vanish. In the first term, no photons are created by H_V, thus the final state cannot be reached. In the second term, a photon exists in an intermediate state, but applying H' once more, it either annihilates this photon or creates a second one. Both possible results do not correspond to the final state. Therefore, we are left with

$$H_{fn}H_{ni} = H'_{f,n_1}H_{V\,n_1,i} + H_{V\,f,n_2}H'_{n_2,i}\ .$$

The corresponding processes are shown in 11.3 . Here, we have two possible intermediate states

$$\begin{aligned} |n_1\rangle &= c^\dagger_{\mathbf{q}}|0\rangle \\ |n_2\rangle &= c^\dagger_{\mathbf{q}} a^\dagger_{\mathbf{k},s}|0\rangle\ , \end{aligned} \tag{11.35}$$

were we still have to sum over $\mathbf{q}, \mathbf{k}, s$.

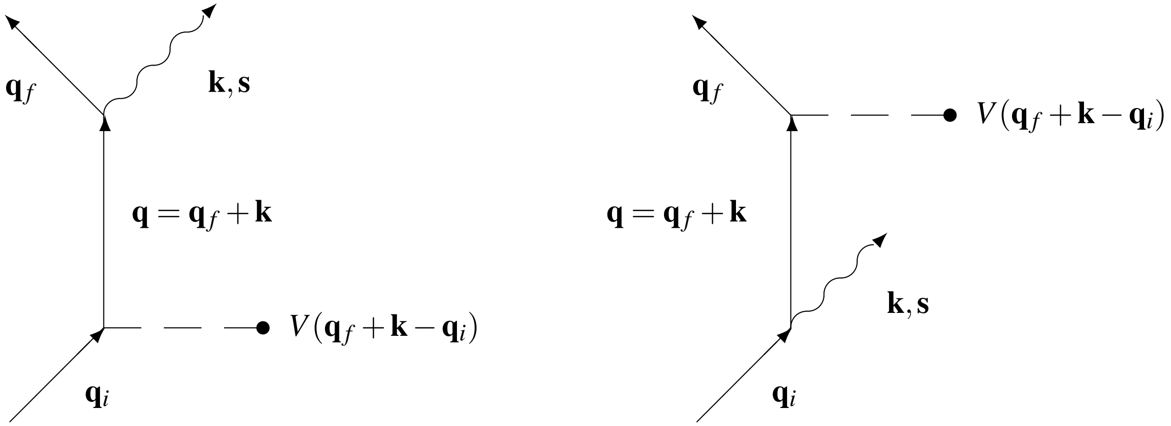


Figure 11.3: Second order processes for bremsstrahlung (cf. 11.29 , 11.31). On the left, with intermediate state n_1 and on the right with intermediate state n_2.

The contributing matrix elements (cf. 11.29 , 11.31 , 11.33a , 11.35) are

$$\begin{aligned}
\langle f|H'|n_1\rangle = &-\frac{e\hbar}{mc}\left(\frac{2\pi\hbar c^2}{\Omega}\right)^{\frac{1}{2}}\sum_{k'\mathbf{q}'s'}\frac{1}{\sqrt{\omega_{k'}}}\mathbf{q}'\cdot\mathbf{u}_{\mathbf{k}',s'}\\
&\times\langle 0|a_{\mathbf{k}_f,s_f}c_{\mathbf{q}_f}\left(c^\dagger_{\mathbf{q}'+\mathbf{k}'}c_{\mathbf{q}'}a_{\mathbf{k}',s'}+c^\dagger_{\mathbf{q}'}c_{\mathbf{q}'+\mathbf{k}'}a^\dagger_{\mathbf{k}',s'}\right)c^\dagger_{\mathbf{q}}|0\rangle\\
=&-\frac{e\hbar}{mc}\left(\frac{2\pi\hbar c^2}{\Omega}\right)^{\frac{1}{2}}\sum_{k'\mathbf{q}'s'}\frac{1}{\sqrt{\omega_{k'}}}\mathbf{q}'\cdot\mathbf{u}_{\mathbf{k}',s'}\langle 0|a_{\mathbf{k}_f,s_f}c_{\mathbf{q}_f}c^\dagger_{\mathbf{q}'}c_{\mathbf{q}'+\mathbf{k}'}a^\dagger_{\mathbf{k}',s'}c^\dagger_{\mathbf{q}}|0\rangle
\end{aligned}$$

$$\begin{aligned}
&=-\frac{e\hbar}{mc}\left(\frac{2\pi\hbar c^2}{\Omega}\right)^{\frac{1}{2}}\sum_{k'\mathbf{q}'s'}\frac{1}{\sqrt{\omega_{k'}}}\mathbf{q}'\cdot\mathbf{u}_{\mathbf{k}',s'}\langle 0|c_{\mathbf{q}_f}c^\dagger_{\mathbf{q}'}c_{\mathbf{q}'+\mathbf{k}'}c^\dagger_{\mathbf{q}}|0\rangle\\
&\qquad\times\langle 0|a_{\mathbf{k}_f,s_f}a^\dagger_{\mathbf{k}',s'}|0\rangle\\
&=-\frac{e\hbar}{mc}\left(\frac{2\pi\hbar c^2}{\Omega}\right)^{\frac{1}{2}}\sum_{k'\mathbf{q}'s'}\frac{1}{\sqrt{\omega_{k'}}}\mathbf{q}'\cdot\mathbf{u}_{\mathbf{k}',s'}\delta_{\mathbf{q}',\mathbf{q}_f}\delta_{\mathbf{q}'+\mathbf{k}',\mathbf{q}}\delta_{\mathbf{k}',\mathbf{k}_f}\delta_{s',s_f}\\
&=-\frac{e\hbar}{mc}\left(\frac{2\pi\hbar c^2}{\Omega}\right)^{\frac{1}{2}}\frac{1}{\sqrt{\omega_{\mathbf{k}_f}}}\mathbf{q}_f\cdot\mathbf{u}_{\mathbf{k}_f,s_f}\;\delta_{\mathbf{q},\mathbf{q}_f+\mathbf{k}_f}=\langle f|H'|n_1\rangle \qquad (11.36)
\end{aligned}$$

$$\begin{aligned}
\langle n_2|H'|i\rangle &= -\frac{e\hbar}{mc}\left(\frac{2\pi\hbar c^2}{\Omega}\right)^{\frac{1}{2}}\sum_{k'\mathbf{q}'s'}\frac{1}{\sqrt{\omega_{k'}}}\mathbf{q}'\cdot\mathbf{u}_{\mathbf{k}',s'} \\
&\quad\times\langle 0|a_{\mathbf{k},s}c_{\mathbf{q}}\left(c^{\dagger}_{\mathbf{q}'+\mathbf{k}'}c_{\mathbf{q}'}a_{\mathbf{k}',s'}+c^{\dagger}_{\mathbf{q}'}c_{\mathbf{q}'+\mathbf{k}'}a^{\dagger}_{\mathbf{k}',s'}\right)c^{\dagger}_{\mathbf{q}_i}|0\rangle \\
&= -\frac{e\hbar}{mc}\left(\frac{2\pi\hbar c^2}{\Omega}\right)^{\frac{1}{2}}\sum_{k'\mathbf{q}'s'}\frac{1}{\sqrt{\omega_{k'}}}\mathbf{q}'\cdot\mathbf{u}_{\mathbf{k}',s'}\langle 0|a_{\mathbf{k},s}c_{\mathbf{q}}c^{\dagger}_{\mathbf{q}'}c_{\mathbf{q}'+\mathbf{k}'}a^{\dagger}_{\mathbf{k}',s'}c^{\dagger}_{\mathbf{q}_i}|0\rangle
\end{aligned}$$

$$\begin{aligned}
&= -\frac{e\hbar}{mc}\left(\frac{2\pi\hbar c^2}{\Omega}\right)^{\frac{1}{2}}\sum_{k'\mathbf{q}'s'}\frac{1}{\sqrt{\omega_{k'}}}\mathbf{q}'\cdot\mathbf{u}_{\mathbf{k}',s'}\langle 0|c_{\mathbf{q}}c^{\dagger}_{\mathbf{q}'}c_{\mathbf{q}'+\mathbf{k}'}c^{\dagger}_{\mathbf{q}_i}|0\rangle \\
&\quad\times\langle 0|a_{\mathbf{k},s}a^{\dagger}_{\mathbf{k}',s'}|0\rangle \\
&= -\frac{e\hbar}{mc}\left(\frac{2\pi\hbar c^2}{\Omega}\right)^{\frac{1}{2}}\sum_{k'\mathbf{q}'s'}\frac{1}{\sqrt{\omega_{k'}}}\mathbf{q}'\cdot\mathbf{u}_{\mathbf{k}',s'}\delta_{\mathbf{q}',\mathbf{q}}\delta_{\mathbf{q}'+\mathbf{k}',\mathbf{q}_i}\delta_{\mathbf{k}',\mathbf{k}}\delta_{s',s} \\
&= -\frac{e\hbar}{mc}\left(\frac{2\pi\hbar c^2}{\Omega}\right)^{\frac{1}{2}}\frac{1}{\sqrt{\omega_k}}\mathbf{q}\cdot\mathbf{u}_{\mathbf{k},s}\ \delta_{\mathbf{q},\mathbf{q}_i-\mathbf{k}} \\
&= -\frac{e\hbar}{mc}\left(\frac{2\pi\hbar c^2}{\Omega}\right)^{\frac{1}{2}}\frac{1}{\sqrt{\omega_k}}\mathbf{q}_i\cdot\mathbf{u}_{\mathbf{k},s}\ \delta_{\mathbf{q},\mathbf{q}_i-\mathbf{k}} = \langle n_2|H'|i\rangle\ . \qquad (11.37)
\end{aligned}$$

For the last step we used that $\mathbf{k}\cdot\mathbf{u}_{\mathbf{k},s}=0$. We need the matrix elements of H_V 11.31

$$\begin{aligned}
\langle n_1|H_V|i\rangle &= \langle 0|c_{\mathbf{q}}H_V c^{\dagger}_{\mathbf{q}_i}|0\rangle \\
&= \sum_{\mathbf{q}',\mathbf{q}''}V(\mathbf{q}'-\mathbf{q}'')\langle 0|c_{\mathbf{q}}c^{\dagger}_{\mathbf{q}'}c_{\mathbf{q}''}c^{\dagger}_{\mathbf{q}_i}|0\rangle \\
&= \sum_{\mathbf{q}',\mathbf{q}''}V(\mathbf{q}'-\mathbf{q}'')\delta_{\mathbf{q}',\mathbf{q}}\delta_{\mathbf{q}'',\mathbf{q}_i} \\
&= V(\mathbf{q}-\mathbf{q}_i)\ .
\end{aligned}$$

This matrix element has to be multiplied with ${H'}_{f,n_1}$ 11.36 and we get

$$H'_{f,n_1}H_{V\,n_1,i} = -\frac{e\hbar}{mc}\left(\frac{2\pi\hbar c^2}{\Omega}\right)^{\frac{1}{2}}\frac{1}{\sqrt{\omega_{\mathbf{k}_f}}}\mathbf{q}_f\cdot\mathbf{u}_{\mathbf{k},s}V(\mathbf{q}_f+\mathbf{k}-\mathbf{q}_i)\ \delta_{\mathbf{q},\mathbf{q}_f+\mathbf{k}}\ .$$

The contributions to $M_{f,i}$ are therefore (cf. 11.35)

$$\begin{aligned} M^{(1)}_{fi} &= \sum_{\mathbf{q}} \frac{H'{}_{f,n_1} H_{V\,n_1,i}}{E_i - E_{n_1}(\mathbf{q}) + iO^+} \qquad (11.38) \\ &= -\frac{e\hbar}{mc}\left(\frac{2\pi\hbar c^2}{\Omega}\right)^{\frac{1}{2}} \frac{1}{\sqrt{\omega_{\mathbf{k}_f}}}\mathbf{q}_f \cdot \mathbf{u}_{\mathbf{k},s} \, \frac{V(\mathbf{q}_f + \mathbf{k} - \mathbf{q}_i)}{E_i - E_{n_1}(\mathbf{q}_f + \mathbf{k}) + iO^+} \end{aligned}$$

$$E_{n_1}(\mathbf{q}) := \frac{\hbar^2 \mathbf{q}^2}{2m}$$

Due to energy conservation, we require

$$E_i = E_f = \frac{\hbar^2 {\mathbf{q}_f}^2}{2m} + \hbar\omega_{\mathbf{k}_f}$$

The energy denominator in 11.38 is therefore

$$\begin{aligned} \mathscr{E}_1 &:= E_f - E_{n_1}(\mathbf{q}_f + \mathbf{k}_f) + iO^+ \\ &= \frac{\hbar^2({\mathbf{q}_f}^2 - (\mathbf{q}_f + \mathbf{k}_f)^2)}{2m} + \hbar\omega_{\mathbf{k}_f} + iO^+ \\ &= \hbar\omega_{\mathbf{k}_f} - \frac{\hbar^2(2\mathbf{q}_f \cdot \mathbf{k}_f + \mathbf{k}_f^2)}{2m} + iO^+ \\ &= \hbar\omega_{\mathbf{k}_f} - \hbar\mathbf{v}_f \cdot \mathbf{k}_f - \frac{\hbar^2 \mathbf{k}_f^2}{2m} + iO^+ \\ &= \hbar\omega_{\mathbf{k}_f}\left(1 - \frac{\mathbf{k}_f \cdot \mathbf{v}_f}{|\mathbf{k}_f|\, c} - \frac{\hbar\,|\mathbf{k}_f|}{2mc}\right) + iO^+ \approx \hbar\omega_{\mathbf{k}_f} \end{aligned}$$

where the last approximation is valid in the nonrelativistic limit $\mathbf{v}_f \ll c$. Moreover, we have

$$\begin{aligned} \langle f|H_V|n_2\rangle &= \langle 0|c_{\mathbf{q}_f} a_{\mathbf{k}_f,s_f} H_V c^\dagger_{\mathbf{q}} a^\dagger_{\mathbf{k},s}|0\rangle \\ &= \sum_{\mathbf{q}',\mathbf{q}''} V(\mathbf{q}' - \mathbf{q}'')\langle 0|c_{\mathbf{q}_f} a_{\mathbf{k}_f,s_f} c^\dagger_{\mathbf{q}'} c_{\mathbf{q}''} c^\dagger_{\mathbf{q}} a^\dagger_{\mathbf{k},s}|0\rangle \\ &= \sum_{\mathbf{q}',\mathbf{q}''} V(\mathbf{q}' - \mathbf{q}'')\delta_{\mathbf{q}',\mathbf{q}_f}\delta_{\mathbf{q}'',\mathbf{q}}\delta_{\mathbf{k},\mathbf{k}_f}\delta_{s,s_f} \\ &= V(\mathbf{q} - \mathbf{q}_f)\delta_{\mathbf{k},\mathbf{k}_f}\delta_{s,s_f} \,. \end{aligned}$$

This matrix element has to be multiplied with $H'{}_{n_2,i}$ 11.37 and we get

$$\begin{aligned} & H_{V\,f,n_2} H'{}_{n_2,i} \\ &= -\frac{e\hbar}{mc}\left(\frac{2\pi\hbar c^2}{\Omega}\right)^{\frac{1}{2}} \frac{1}{\sqrt{\omega_{\mathbf{k}_f}}}\mathbf{q}_i \cdot \mathbf{u}_{\mathbf{k}_f,s_f} V(\mathbf{k}_f + \mathbf{q}_f - \mathbf{q}_i)\; \delta_{\mathbf{q},\mathbf{q}_i - \mathbf{k}_f}\delta_{\mathbf{k},\mathbf{k}_f}\delta_{s,s_f} \,. \end{aligned}$$

The contribution to M_{fi} is

$$
\begin{aligned}
M_{fi}^{(2)} &= \sum_{\mathbf{q},\mathbf{k},s} \frac{H_{V\,f,n_2} H'_{n_2,i}}{E_i - E_{n_2}(\mathbf{q},\mathbf{k}) + iO^+} \\
&= -\frac{e\hbar}{mc}\left(\frac{2\pi\hbar c^2}{\Omega}\right)^{\frac{1}{2}} \frac{1}{\sqrt{\omega_{\mathbf{k}_f}}}\mathbf{q}_i \cdot \mathbf{u}_{\mathbf{k}_f,s_f} \frac{V(\mathbf{k}_f + \mathbf{q}_f - \mathbf{q}_i)}{E_i - E_{n_2}(\mathbf{q}_i - \mathbf{k}_f, \mathbf{k}_f) + iO^+} \qquad (11.39)
\end{aligned}
$$

The energy denominator is therefore

$$
\begin{aligned}
\mathscr{E}_2 &:= E_i - E_{n_2}(\mathbf{q}_i - \mathbf{k}_f, \mathbf{k}_f) + iO^+ \\
&= \frac{\hbar^2\left(\mathbf{q}_i{}^2 - (\mathbf{q}_i - \mathbf{k}_f)^2\right)}{2m} - \hbar\omega_{\mathbf{k}_f} \\
&= -\hbar\omega_{\mathbf{k}_f} + \frac{\hbar^2 \mathbf{q}_i \cdot \mathbf{k}_f}{m} - \frac{\hbar^2 \mathbf{k}_f^2}{2m} \\
&= -\hbar\omega_{\mathbf{k}_f}\left(1 - \frac{\mathbf{k}_f \cdot \mathbf{v}_i}{\left|\mathbf{k}_f\right| c} + \frac{\hbar\left|\mathbf{k}_f\right|}{2mc}\right) + iO^+ \approx -\hbar\omega_{\mathbf{k}_f}
\end{aligned}
$$

The matrix element we were looking for is (cf. 11.38 , 11.39)

$$
\begin{aligned}
M_{fi} &= M_{fi}^{(1)} + M_{fi}^{(2)} \\
&= -\frac{e\hbar}{mc}\left(\frac{2\pi c^2}{\hbar\Omega\omega_{\mathbf{k}_f}^3}\right)^{\frac{1}{2}} \frac{-4\pi Z e^2}{\Omega(\mathbf{k}_f + \mathbf{q}_f - \mathbf{q}_i)^2}\, \mathbf{u}_{\mathbf{k}_f,s_f} \cdot \left(\mathbf{q}_f - \mathbf{q}_i\right) \\
&= -\left(\frac{2\pi e^2}{\hbar\Omega\omega_{\mathbf{k}_f}^3}\right)^{\frac{1}{2}} \frac{4\pi Z e^2}{\Omega(\mathbf{k}_f + \mathbf{q}_f - \mathbf{q}_i)^2}\, \mathbf{u}_{\mathbf{k}_f,s_f} \cdot \underbrace{\left(\mathbf{v}_f - \mathbf{v}_i\right)}_{=:\Delta\mathbf{v}}
\end{aligned}
$$

The photon momentum is much smaller than the one of the electron ($k = \omega_k / c$), so that we can omit $\mathbf{k}_f$ in the central term and replace there $\mathbf{q}_f - \mathbf{q}_i \to m\Delta\mathbf{v}$. Finally, we get

$$
M_{fi} = \left(\frac{4\pi Z e^2 \hbar^2}{\Omega m^2 (\Delta\mathbf{v})^2}\right)\left(\frac{2\pi e^2}{\hbar\Omega\omega_{\mathbf{k}_f}^3}\right)^{\frac{1}{2}} \mathbf{u}_{\mathbf{k}_f,s_f} \cdot \Delta\mathbf{v} \qquad (11.40)
$$

11.10 Cross-section

The total **cross-section σ_{total}** defines an effective scattering surface: Particles going through that surface are scattered by the bremsstrahlung process:

$$
\sigma_{\text{total}} = \frac{\text{number of scattered particles/time}}{\text{flux (or current density) of incident particles}} \equiv \frac{I_{scatt}}{J_{incid}}
$$

If N_p is the total number of incident particles in volume Ω, then

$$J_{incid} = \frac{N_p}{\Omega}\, v_i \qquad v_i = \text{particle velocity}$$

The probability per unit time that one particle is scattered, is given by the transition rate summed over all final states, $\sum_f W_{i\to f}$. The total current of scattered particles is thus given by

$$I_{scatt} = N_p \sum_f W_{i\to f}$$

In total, we thus have

$$\sigma_{\text{total}} = \frac{I_{scatt}}{J_{incid}} = \frac{N_p \sum_f W_{i\to f}}{\frac{N_p}{\Omega}\, v_i} \tag{11.41}$$

using 11.41 , 11.40 and 3.27 we get

$$\begin{aligned}
\sigma_{\text{total}} &= \frac{\Omega}{v_i} \sum_{\mathbf{k}_f s_f \mathbf{q}_f} \frac{2\pi}{\hbar} \left|M_{fi}\right|^2 \delta\big(\frac{\hbar^2 \mathbf{q}_f{}^2}{2m} + \hbar\omega_{\mathbf{k}_f} - E_i\big) \\
&= \frac{2\pi}{\hbar} \sum_{\mathbf{k}s\mathbf{q}} \frac{\Omega}{v_i} \left(\frac{16\pi^2 Z^2 e^4 \hbar^4}{\Omega^2 m^4 (\Delta\mathbf{v})^4}\right) \left(\frac{2\pi e^2}{\hbar\Omega\omega_{\mathbf{k}}^3}\right) \\
&\qquad \times |\mathbf{u}_{\mathbf{k},s}\cdot\Delta\mathbf{v}|^2\, \delta\big(\frac{\hbar^2\mathbf{q}^2}{2m} + \hbar\omega_{\mathbf{k}} - E_i\big) \\
&= \frac{4(2\pi)^4 \Omega Z^2 e^6 \hbar^4}{\hbar^2 v_i \Omega^3 m^4} \sum_{\mathbf{k}s\mathbf{q}} \frac{|\mathbf{u}_{\mathbf{k},s}\cdot\Delta\mathbf{v}|^2}{|\Delta\mathbf{v}|^4\, \omega_{\mathbf{k}}^3}\, \delta\big(\frac{\hbar^2\mathbf{q}^2}{2m} + \hbar\omega_{\mathbf{k}} - E_i\big) \\
&= \frac{4(2\pi)^4 Z^2 e^6 \hbar^2}{v_i \Omega^2 m^4} \sum_{\mathbf{k}s\mathbf{q}} \frac{|\mathbf{u}_{\mathbf{k},s}\cdot\Delta\mathbf{v}|^2}{|\Delta\mathbf{v}|^4\, \omega_{\mathbf{k}}^3}\, \delta\big(\frac{\hbar^2\mathbf{q}^2}{2m} + \hbar\omega_{\mathbf{k}} - E_i\big)
\end{aligned}$$

Trasforming the sum into an integral, we get (cf. A.50)

$$\frac{1}{\Omega}\sum_{\mathbf{q}} \longrightarrow \frac{1}{(2\pi)^3}\int d^3\mathbf{q} = \frac{1}{(2\pi)^3}\int q^2\, dq\, d\Omega_q\,,$$

where $d\Omega_q$ is the differential spherical angle.
For the cross-section the sum over wavevectors of the photon as well as of the electron is transformed into an integral and we get an expression independent of the volume.

$$\begin{aligned}
\sigma_{\text{total}} &= \frac{4Z^2 e^6 \hbar^2}{v_i m^4 (2\pi)^2} \sum_s \int q^2 dq\, d\Omega_q \int k^2 dk d\Omega_k \frac{|\mathbf{u}_{\mathbf{k},s}\cdot\Delta\mathbf{v}|^2}{|\Delta v|^4\, \omega_{\mathbf{k}}^3} \\
&\quad \times \delta\big(\frac{\hbar^2\mathbf{q}^2}{2m} + \hbar\omega_{\mathbf{k}} - E_i\big)\,.
\end{aligned}$$

We use the relation $k = \omega_{\mathbf{k}}/c$ and get

$$\sigma_{\text{total}} = \frac{4Z^2e^6\hbar^2}{c^3 v_i m^4 (2\pi)^2}\sum_s \int q^2 dq d\Omega_q d\Omega_k \frac{d\omega}{\omega}\frac{|\mathbf{u}_{\mathbf{k},s}\cdot\Delta\mathbf{v}|^2}{|\Delta v|^4}\delta\big(\frac{\hbar^2\mathbf{q}^2}{2m}+\hbar\omega-E_i\big)\ . \tag{11.42}$$

Note that the polarisation vector $\mathbf{u}_{\mathbf{k},s}$ in only dependent on the direction of $\mathbf{k}$, but not on its absolute value.

We consider now low energy photons, that means that the energy of the photons is much smaller than the energy of the electrons. Due to the δ function ($q_f^2 = q_i^2$), we have elastic scattering. This results in

$$\begin{aligned}
&\left|\mathbf{v}_f\right| = |\mathbf{v}_i| \\
\Rightarrow \quad &|\Delta\mathbf{v}|^2 = \big(v_i^2 - 2v_i v_f\cos(\theta) + v_f^2\big) \\
&\qquad = v_i^2 2\big(1-\cos(\theta)\big) \\
&\qquad = 4v_i^2\sin^2(\frac{\theta}{2})\ ,
\end{aligned}$$

where θ is the scattering angle. 11.42 gives

$$\begin{aligned}
\sigma_{\text{total}} &= \frac{4Z^2e^6\hbar^2}{16c^3 v_i m^4 (2\pi)^2}\sum_s \int q^2 dq d\Omega_q d\Omega_k \frac{d\omega}{\omega}\frac{|\mathbf{u}_{\mathbf{k},s}\cdot\Delta\mathbf{v}|^2}{v_i^4\sin^4\frac{\theta}{2}}\frac{2m}{\hbar^2}\delta\big(q^2-q_i^2\big) \\
&= \frac{Z^2e^6\hbar^2}{16c^3 v_i m^4 \pi^2}\sum_s \int q^2 dq d\Omega_q d\Omega_k \frac{d\omega}{\omega}\frac{|\mathbf{u}_{\mathbf{k},s}\cdot\Delta\mathbf{v}|^2}{v_i^4\sin^4\frac{\theta}{2}}\frac{m\ \delta\big(q-q_i\big)}{\hbar^2 q_i} \\
&= \frac{Z^2e^6\hbar^2}{16c^3 m^4 \pi^2}\underbrace{\frac{mq_i^2}{v_i\hbar^2 q_i}}_{\frac{m^2}{\hbar^3}}\sum_s \int d\Omega_q d\Omega_k \frac{d\omega}{\omega}\frac{|\mathbf{u}_{\mathbf{k},s}\cdot\Delta\mathbf{v}|^2}{v_i^4\sin^4\frac{\theta}{2}} \\
&= \frac{Z^2e^6}{16c^3 m^2 \pi^2\hbar}\sum_s \int d\Omega_q d\Omega_k \frac{d\omega}{\omega}\frac{|\mathbf{u}_{\mathbf{k},s}\cdot\Delta\mathbf{v}|^2}{v_i^4\sin^4\frac{\theta}{2}}
\end{aligned}$$

We can directly read the differential cross-section out of this expression.

DIFFERENTIAL CROSS-SECTION OF THE BREMSSTRAHLUNG

$$\begin{aligned}\frac{d^3\sigma}{d\Omega_k d\Omega_{q_f} d\omega_k} &= \frac{Z^2e^6}{16c^3m^2\pi^2\hbar\omega}\frac{\sum_s|\mathbf{u}_{\mathbf{k},s}\cdot\Delta\mathbf{v}|^2}{v_i^4\sin^4(\frac{\theta}{2})} \\ &= \frac{Z^2e^4}{m^2v_i^4\sin^4(\frac{\theta}{2})}\frac{e^2|\Delta\mathbf{v}_\perp|^2}{16\pi^2c^3\hbar\omega}\end{aligned} \tag{11.43}$$

Here, $\Delta\mathbf{v}_\perp$ is the part of $\Delta\mathbf{v}$ which is perpendicular to $\mathbf{k}$.

The first factor in 11.43 is the formula for Rutherford scattering and the second one gives the probability density for a photon with energy $\hbar\omega$ to be found in the spatial angle unit $d\Omega_k$.
We conclude with some comments

- Z^2 dependence $\Rightarrow$ To generate X-Rays, we need elements with high atomic numbers.
  At the same time, the melting point has to be high, because a large amount of energy is left behind in the substrate in the form of heat. Therefore, tungsten is often used as X-Ray source.

- We have a continous spectrum. However, there is a maximum photon energy.

$$\begin{aligned}E_{ph} &\leq E_i \\ \hbar\omega^{\max} &= E_i = O(\text{eV}) \\ \hbar ck^{\max} &= E_i = O(\text{eV}) \\ \frac{2\pi\hbar c}{\lambda^{\min}} &= (\text{eV}) \\ \lambda^{\min} &= \frac{2\pi\hbar c}{O(\text{eV})} \\ &= \frac{hc}{\text{eV}} \sim 10^{-6}m\end{aligned}$$

Duane and Hunt' Law

Chapter 12

Scattering theory

This chapter essentially follows the treatment by the book by J.J. Sakurai (see Sec. 14), Chap 7.
Scattering describes collision between particles and/or waves. This can be, for example, used experimentally to provide information on the properties of particles (mass, interactions, charge, etc.), radiation, and matter. Scattering takes place if the involved particle interact with each other. However, in such an event one is not interested in what happens in detail during the interaction but rather on the final state at large times, when particle don't interact any more. Specifically, one would like to determine the relation between the initial conditions, before particles or waves start to interact, and the final conditions in which they do not interact anymore. Since in quantum mechanics there are no physical trajectories one is interested in probabilities. The experimentally measured quantity is typically the (differential) cross section (see below).
Scattering processes can be roughly classified as

1. Elastic: The total kinetic energy is conserved.
2. Inelastic: Part of the kinetic energy is transferred to or from internal degrees of freedom of the particles involved (for example: internal excited states are created by using some of the kinetic energy).
3. Non particle conserving: Particles are created or annihilated in the process.

Here, we will mainly consider Elastic processes between two particles.

12.0.1 Laboratory vs. Center-of-Mass frames

Often one considers the case of a particle hitting a fixed target (scattering center). This is justified when the target is bound, e.g, to a solid or when its mass is much larger than the one of the scattered particle. If this is not the case, one has to consider the motion of the target as well. If total momentum is conserved this is easily done by going over into the center-of-mass frame. As in classical physics, this is described by the coordinate

$$\mathbf{R} = \frac{m_1 \mathbf{r_1} + m_2 \mathbf{r_2}}{m_1 + m_2} \tag{12.1}$$

which moves freely. In other words, the **R**-dependence of the wave function is the one of a free particle

$$\psi(\mathbf{R}, \mathbf{r} \equiv \mathbf{r}_1 - \mathbf{r}_2) = e^{i\mathbf{P}\cdot\mathbf{R}} \varphi(\mathbf{r})$$

The relative motion, described by the coordinate $\mathbf{r}$, is controlled by the Hamiltonian

$$H_{rel} = \frac{\hat{\mathbf{p}}^2}{2\mu} + V(\hat{\mathbf{r}}) \; ,$$

where, as in classical physics, $\mu = \frac{m_1 m_2}{m_1 + m_2}$ is the reduced mass, $\mathbf{p}$ is the momentum associated to $\mathbf{r}$, and V is the potential. So the problem becomes equivalent to the one of a target fixed at the origin, however with the replacement of the mass with the reduced mass.

However, experimentally one is interested in the cross section (distribution of scattering angles) in the laboratory frame. This is different from the one in the center-of-mass frame. Thus, after solving the problem in the “simpler” center-of-mass frame one has to carry out the transformation into the laboratory frame. The procedure is identical to the one used in classical mechanics.

In the following, we will consider only the first part of the problem, namely the treatment of the scattering event in the center-of-mass frame. We will also now use m for the reduced mass, and restrict to the nonrelativistic case.

12.1 Formal theory of scattering

Lippmann-Schwinger equation

The system is described by the Hamiltonian

$$\hat{H} = \hat{H}_0 + \hat{V} \qquad\qquad \hat{H}_0 = \frac{\hat{p}^2}{2m} \tag{12.2}$$

i.e. an unperturbed Hamiltonian describing free motion and a perturbation potential. Accordingly, one has unperturbed states $|\varphi_0\rangle$ (typically, momentum eigenstates $\sim e^{i\mathbf{k}\cdot\mathbf{r}}$) satisfying

$$\hat{H}_0 \, |\varphi_0\rangle = E \, |\varphi_0\rangle$$

$|\varphi_0\rangle$ will be the state in the distant past $t \to -\infty$ providing the initial conditions before $\hat{V}$ acts. Since the process is elastic, we look for an eigenstate of the total Hamiltonian $\hat{V}$ with the same energy:

$$\hat{H}\,|\psi\rangle = E\,|\psi\rangle \tag{12.3}$$

Formally, we can consider $\hat{V}$ as being "switched on" adiabatically in the past. This can be done by using

$$\hat{V}(t) = e^{\varepsilon t}\hat{V} \qquad \varepsilon \to 0^+ \qquad (t \leq 0)$$

Formally, the solution of 12.3 satisfies the **Lippmann-Schwinger equation** [1]

$$|\psi\rangle = (E - \hat{H}_0 \pm i\varepsilon)^{-1}\hat{V}\,|\psi\rangle + |\varphi_0\rangle \tag{12.4}$$

The infinitesimal $\varepsilon \to 0^+$ is necessary in order to deal with the singularity at $E = \hat{H}_0$. We will discuss the signs ± later.

Proof:

$$(E - \hat{H}_0)\,|\psi\rangle = \cdots\cdots$$

Which is 12.3 .
The Lippmann-Schwinger equation 12.4 is still basis independent. It is useful to work in the position basis $|\mathbf{x}\rangle$. Here, 12.4 becomes:

$$\langle \mathbf{x}|\psi\rangle = \langle \mathbf{x}|\varphi_0\rangle + \frac{2m}{\hbar^2}\int d^3x'\; G_\pm(\mathbf{x},\mathbf{x}')\,\langle \mathbf{x}'|\,\hat{V}\,|\psi\rangle \tag{12.5}$$

with the **Green's function**

$$G_\pm(\mathbf{x},\mathbf{x}') \equiv \frac{\hbar^2}{2m}\,\langle \mathbf{x}|\cdot(E - \hat{H}_0 \pm i\varepsilon)^{-1}\cdot|\mathbf{x}'\rangle \tag{12.6}$$

For $\hat{H}_0 = \frac{\hat{\mathbf{p}}^2}{2m}$, the wave function associated to $|\varphi_0\rangle$ is the one of a free particle with momentup $\hbar\mathbf{k}$ [2]

$$\langle \mathbf{x}|\varphi_0\rangle = \frac{1}{(2\pi)^{3/2}}\,e^{i\mathbf{k}\cdot\mathbf{x}}$$

---

[1] This is the solution with the correct boundary conditions, namely that $|\psi\rangle \to |\varphi_0\rangle$ for $\hat{V} \to 0$.

[2] We use $\hbar = 1$, so that momentum and wavevector have the same units.

To evaluate 12.6 one inserts the identity $\int d^3\mathbf{p}' \, |\mathbf{p}'\rangle \langle \mathbf{p}'|$ twice at the two "$\cdot$", yielding:

$$G_\pm(\mathbf{x},\mathbf{x}') = \frac{1}{2m}\int d^3p' \, d^3p'' \, \langle \mathbf{x}|\mathbf{p}'\rangle \langle \mathbf{p}'| \, (E - \frac{\hat{\mathbf{p}}^2}{2m} \pm i\varepsilon)^{-1} \, |\mathbf{p}''\rangle \langle \mathbf{p}''|\mathbf{x}'\rangle \; . \quad (12.7)$$

The operator in the expectation value is diagonal in that basis:

$$\langle \mathbf{p}'| \, (E - \frac{\hat{\mathbf{p}}^2}{2m} \pm i\varepsilon)^{-1} \, |\mathbf{p}''\rangle = \delta^3(\mathbf{p}' - \mathbf{p}'')(E - \frac{\mathbf{p}'^2}{2m} \pm i\varepsilon)^{-1} \; .$$

Using $\langle x|p\rangle = \frac{1}{(2\pi)^{3/2}} e^{i\mathbf{p}\cdot\mathbf{x}}$, 12.7 becomes

$$G_\pm(\mathbf{x},\mathbf{x}') = \int \frac{d^3\mathbf{p}'}{(2\pi)^3} \frac{e^{i\,\mathbf{p}'\cdot(\mathbf{x}-\mathbf{x}')}}{\underbrace{2mE}_{\equiv \mathbf{k}^2} - \mathbf{p}'^2 \pm i\varepsilon} \quad (12.8)$$

In order to evaluate $G_\pm$, notice that it satisfies the equation

$$(\mathbf{k}^2 + \nabla^2) G_\pm(\mathbf{x},\mathbf{x}') = \int \frac{d^3\mathbf{p}'}{(2\pi)^3} \frac{\mathbf{k}^2 - \mathbf{p}'^2}{\mathbf{k}^2 - \mathbf{p}'^2 \pm i\varepsilon} e^{i\,\mathbf{p}'\cdot(\mathbf{x}-\mathbf{x}')} = \delta^3(\mathbf{x}-\mathbf{x}') \quad (12.9)$$

From electrodynamics we recognize 12.9 as the equation for the Green's function of the inhomogeneous wave equation. From electrodynamics we also know its solution (we give a proof here: Sec. A.37):

$$G_\pm(\mathbf{x}-\mathbf{x}') = -\frac{1}{4\pi} \frac{e^{\pm ik|\mathbf{x}-\mathbf{x}'|}}{|\mathbf{x}-\mathbf{x}'|} \; , \quad (12.10)$$

where the signs in the exponent depend on the sign in front of $i\varepsilon$. $G_\pm$ clearly depends only on the modulus of the distance between the two points $|\mathbf{x}-\mathbf{x}'|$ 12.10 , thus, describes outgoing $(+)$ or incoming $(-)$ spherical waves. In a scattering process we are obviously interested in outgoing waves only.
Putting everything together, 12.5 becomes

$$\langle \mathbf{x}|\psi\rangle = \psi(\mathbf{x}) = \varphi_0(\mathbf{x}) - \frac{2m}{\hbar^2} \int d^3x' \, \frac{e^{\pm ik|\mathbf{x}-\mathbf{x}'|}}{4\pi|\mathbf{x}-\mathbf{x}'|} V(\mathbf{x}')\psi(\mathbf{x}') \; , \quad (12.11)$$

where we have used the fact that for a local potential

$$\langle \mathbf{x}'| \, \hat{V} \, |\psi\rangle = V(\mathbf{x}')\psi(\mathbf{x}') \; .$$

Notice that 12.11 is an integral equation for $\psi(\mathbf{x})$, which is still prohibitive to solve.

12.1.1 One dimension:

In some cases we may be interested in a one-dimensional (1D) system instead. This is relevant, e.g., for quantum transport, quantum dots, molecular junctions, etc. In 1D 12.5 becomes

$$\psi(\mathbf{x}) = \varphi_0(\mathbf{x}) + \frac{2m}{\hbar^2}\int dx'\; G_{1D}(x-x')\; V(\mathbf{x}')\psi(\mathbf{x}')\;. \tag{12.12}$$

In one dimension, G_{1D} satisfies the 1-D version of 12.9 :

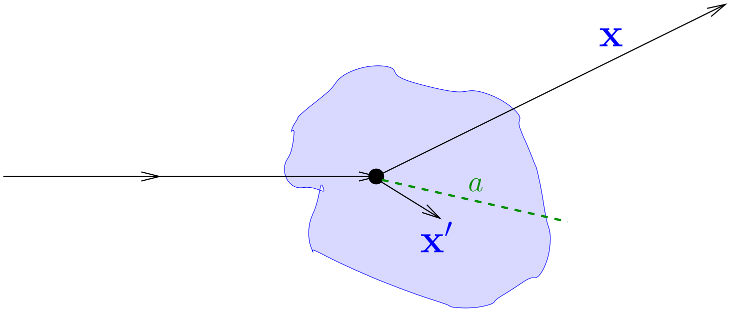
$$(k^2 + \frac{\partial^2}{\partial x^2})G_{1D}(x-x') = \delta(x-x') \qquad k = \sqrt{2mE} > 0$$

with solution (proof: here: Sec. A.38)

$$G_{1D}(x-x') = -\frac{i}{2k}e^{ik|x-x'|} \tag{12.13}$$

12.1.2 Scattering amplitude in 3D:

We are interested in the wave function far away from the scattering center, i.e. $r \equiv |\mathbf{x}| \gg a$, where a is the range of the interaction. (see Fig.) Clearly, this implies that $r \gg |\mathbf{x}'|$ as well.



In this case, we can approximate

$$|\mathbf{x}-\mathbf{x}'| \approx r - \frac{\mathbf{x}}{r}\cdot\mathbf{x}' + o(x'^2) \qquad (\text{ for } r \equiv |\mathbf{x}| \gg a)\;. \tag{12.14}$$

Introducing the directed $\mathbf{k}_{out}$ vector, i.e. the vector with length k in the scattering direction:

$$\mathbf{k}_{out} \equiv k\,\frac{\mathbf{x}}{r}$$

we get from 12.11 with 12.14 (valid for $r \gg x'$)

$$\psi(\mathbf{x}) \approx \underbrace{\varphi_0(\mathbf{x})}_{\text{Plane wave}} - \underbrace{\frac{e^{ikr}}{r}}_{\text{Spherical wave}} \underbrace{\frac{(2\pi)^{3/2}m}{2\pi\hbar^2}\int d^3x'\;\frac{e^{-i\mathbf{k}_{out}\cdot\mathbf{x}'}}{(2\pi)^{3/2}}V(\mathbf{x}')\psi(\mathbf{x}')}_{\text{Amplitude}} \tag{12.15}$$

With

$$\varphi_0(\mathbf{x}) = \frac{e^{i\mathbf{k}\cdot\mathbf{x}}}{(2\pi)^{3/2}} \tag{12.16}$$

12.15 becomes

$$\psi(\mathbf{x}) = \frac{1}{(2\pi)^{3/2}}\left(e^{i\mathbf{k}\cdot\mathbf{x}} + \frac{e^{i\,k\,r}}{r} f(\mathbf{k},\mathbf{k}_{out})\right) \tag{12.17}$$

with the **scattering amplitude**

$$\mathbf{f}(\mathbf{k},\mathbf{k_{out}}) = -\frac{(2\pi)^2 m}{\hbar^2}\int d^3x' \, \frac{e^{-i\mathbf{k}_{out}\cdot\mathbf{x}'}}{(2\pi)^{3/2}} V(\mathbf{x}')\ \psi_{\mathbf{k}}(\mathbf{x}') = -\frac{(2\pi)^2 m}{\hbar^2}\langle \mathbf{k}_{out}|\hat{V}|\psi_{\mathbf{k}}\rangle\ , \tag{12.18}$$

where we have indicated explicitly that ψ depends on $\mathbf{k}$, i.e. on the properties of the incoming wave.

Differential cross section

The scattering amplitude $f(\mathbf{k},\mathbf{k}_{out})$ is directly related to the **differential cross section** $d\sigma/d\Omega$. For a given infinitesimal region $d\Omega$ around a given solid angle this is given by

$$\frac{d\sigma}{d\Omega}d\Omega = \frac{I_{scatt}(d\Omega)}{J_{incid}}\ , \tag{12.19}$$

where $I_{scatt}(d\Omega)$ is the number of particles per unit time (i.e. the current) scattered into $d\Omega$.

J_{incid} is the current density (i.e. the current per area (or flux)) of incident particles. On the other hand, $I_{scatt}(d\Omega)$ is the scattered current density times the area:

$$I_{scatt}(d\Omega) = J_{scatt}\ r^2\ d\Omega\ .$$

Furthermore, for an homogeneous flux of particles one has for both incident and scattered particles

$$J = \text{particle density} \times \text{velocity} = N_p|\psi|^2\frac{\hbar k}{m}\ .$$

From 12.17 we have

$$|\psi_{incid}|^2 = \frac{1}{(2\pi)^3} \qquad |\psi_{scatt}|^2 = \frac{|f(\mathbf{k},\mathbf{k}_{out})|^2}{(2\pi)^3 r^2}$$

which gives for 12.19

$$\frac{d\sigma}{d\Omega} = \frac{J_{scatt}\ r^2}{J_{incid}} = |f(\mathbf{k},\mathbf{k}_{out})|^2 \tag{12.20}$$

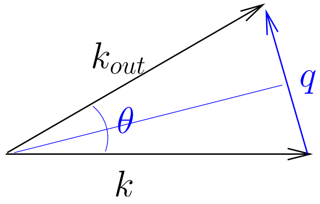
12.1.3 First order Born approximation

Of course, $f(\mathbf{k},\mathbf{k}_{out})$ needs the knowledge of the exact ψ, so this does not solve the problem yet. However, for a weak potential $\hat{V}$, one can replace in 12.18 $\psi(\mathbf{x}) \to \varphi_0(\mathbf{x})$. This is the **First order Born approximation.** This yields

$$f^{(1)}(\mathbf{k},\mathbf{k}_{out}) = -\frac{m}{2\pi\hbar^2} \underbrace{\int d^3x'\, e^{i(\mathbf{k}-\mathbf{k}_{out})\cdot\mathbf{x}'}\, V(\mathbf{x}')}_{\tilde{V}(\mathbf{k}-\mathbf{k}_{out})} \qquad \tilde{V} = \text{Fourier transform.} \tag{12.21}$$

For a spherically symmetric potential $V(r)$, the Fourier transform $\tilde{V}(\mathbf{k}-\mathbf{k}_{out})$ only depends on (see figure)

$$q \equiv |\mathbf{k}-\mathbf{k}_{out}| = 2k\sin\frac{\theta}{2} \tag{12.22}$$



The integral over $\mathbf{x}'$ in 12.21 can be readily carried out in spherical coordinates, by taking the vector $\mathbf{q} \equiv (\mathbf{k}-\mathbf{k}_{out})$ in the z direction. Then one has [3]

$$(\mathbf{k}-\mathbf{k}_{out})\cdot\mathbf{x}' = r'\, q\cos\theta' \qquad \int d^3x' \to \int d\varphi'\, d\cos\theta'\, r'^2 dr'$$

So 12.21 becomes ($c = \cos\theta'$)

$$f^{(1)}(\mathbf{k},\mathbf{k}_{out}) \;=\; \cdots\cdots$$

$$= -\frac{m}{iq\hbar^2}\int_0^\infty r'\, V(r')\, 2i\sin(qr')dr' \tag{12.23}$$

$$= -\frac{2m}{\hbar^2 q}\int_0^\infty r' V(r')\sin(qr')dr' \tag{12.24}$$

Limiting cases

1. For small energies $a\,k, a\,q \ll 1$
   $f^{(1)} = -\frac{2m}{\hbar^2}\int_0^\infty V(r')\, r'^2\, dr'$ is isotropic, i.e. θ-independent
2. For large energies
   $f^{(1)} \to 0$ except for small angles $\theta \sim 1/(k\,a)$

---

[3] Don't confuse θ', which is the angle between $\mathbf{q}$ and $\mathbf{x}'$ with θ (see Fig.).

Example: Yukawa potential

$$V(r) = V_0 \frac{e^{-\mu r}}{\mu r} \tag{12.25}$$

12.23 gives

$$f^{(1)}(q) = -\frac{2mV_0}{\mu\hbar^2}\frac{1}{q^2+\mu^2}$$

$$\Rightarrow \frac{d\sigma}{d\Omega} = |f^{(1)}(2k\sin\frac{\theta}{2})|^2 = \left(\frac{2mV_0}{\mu\hbar^2}\right)^2 \left(\mu^2 + 4k^2\sin^2\frac{\theta}{2}\right)^{-2}$$

The Coulomb potential is obtained by taking

$$\mu \to 0 \qquad \text{with fixed } \frac{V_0}{\mu} = Ze^2$$

This gives Rutherford' formula for Coulomb scattering

$$\frac{d\sigma}{d\Omega} = \frac{m^2 z^2 e^4}{4p^4 \sin^4\frac{\theta}{2}} \qquad p = \hbar k$$

which is the same as in the classical case, and indeed there is no $\hbar$ dependence.

12.1.4 Higher order terms

To go beyond the first order in the Born approximation one introduces the so-called $\hat{T}$-matrix which has the property

$$\hat{V}|\psi\rangle = \hat{T}|\varphi_0\rangle \tag{12.26}$$

Using 12.4 one gets

$$\hat{T}|\varphi_0\rangle = \hat{V}|\varphi_0\rangle + \hat{V}(E-\hat{H}_0+i\varepsilon)^{-1}\hat{T}|\varphi_0\rangle$$

Since this holds for arbitrary initial states $|\varphi_0\rangle$, we have

$$\hat{T} = \hat{V} + \hat{V}(E-\hat{H}_0+i\varepsilon)^{-1}\hat{T} \tag{12.27}$$

This allows to write a formal expansion for $\hat{T}$ in powers of $\hat{V}$. Indeed if $T^{(n)}$ is the scattering matrix evaluated to order $O(V^n)$, then from 12.27 we can get the next order term:

$$\hat{T}^{(n+1)} = \hat{V} + \hat{V}(E-\hat{H}_0+i\varepsilon)^{-1}\hat{T}^{(n)}$$

Since clearly $\hat{T}^{(1)} = \hat{V}$, we get

$$\hat{T} = \hat{V} + \hat{V}\hat{G}_0\hat{V} + \hat{V}\hat{G}_0\hat{V}\hat{G}_0\hat{V} + \cdots \qquad \hat{G}_0 \equiv (E-\hat{H}_0+i\varepsilon)^{-1} \tag{12.28}$$

Once we have $\hat{T}$, the scattering amplitude is given by (we use $|\varphi_0\rangle = |\mathbf{k}\rangle$) cf. 12.18 with 12.26 :

$$f(\mathbf{k},\mathbf{k}_{out}) = \gamma \langle \mathbf{k}_{out}|\, \hat{T}\, |\mathbf{k}\rangle \qquad \gamma = -\frac{(2\pi)^2 m}{\hbar^2} \qquad (12.29)$$

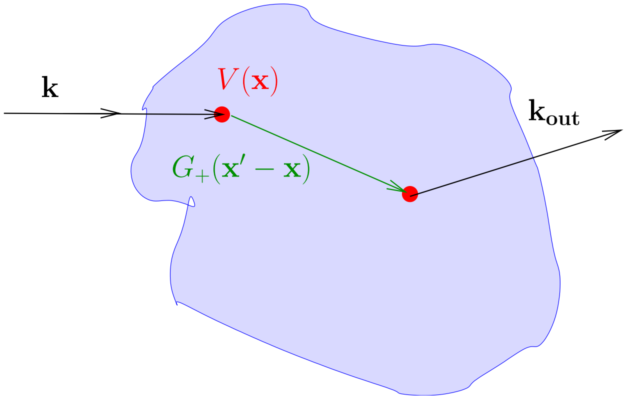
Using 12.28 , one can write a corresponding expansion for $f = f^{(1)} + f^{(2)} + f^{(3)} + \cdots$, where the first order term is obviously the first Born approximation 12.21

$$f^{(1)} = \gamma \langle \mathbf{k}_{out}|\, \hat{V}\, |\mathbf{k}\rangle \ .$$

The second-order term is then

$$\begin{aligned}
f^{(2)} &= \gamma \langle \mathbf{k}_{out}|\, \hat{V} \hat{G}_0 \hat{V}\, |\mathbf{k}\rangle \\
&= \gamma \int \langle \mathbf{k}_{out}|\, \hat{V}\, |\mathbf{x}'\rangle \frac{2m}{\hbar^2} G_+(\mathbf{x}' - \mathbf{x}) \langle \mathbf{x}|\, \hat{V}\, |\mathbf{k}\rangle\, d^3x\, d^3x' \\
& \frac{\gamma}{(2\pi)^3} e^{-i\mathbf{k}_{out}\cdot\mathbf{x}'}\, V(\mathbf{x}') \frac{2m}{\hbar^2} G_+(\mathbf{x}' - \mathbf{x}) V(\mathbf{x}) e^{i\mathbf{k}\cdot\mathbf{x}} d^3x\, d^3x' \qquad (12.30)
\end{aligned}$$

Here G_+ is the Green's function defined in 12.8 and 12.10 . 12.30 can be easily interpreted by going through the equation from right to left. One starts with a particle with momentum $\mathbf{k}$ propagating until the scattering point $\mathbf{x}$, from this point it propagates according to G_+ until the next point $\mathbf{x}'$ and then int exit with momentum $\mathbf{k}_{out}$ (see figure). Higher-order terms (see also 12.28) can be similarly considered as multi-scattering processes in the interaction region with apropagator terg G_+ (outgoing wave) between one point and the next.



Work in progress. For the rest use these handwritten notes, for the time being

Chapter 13

A short introduction to Feynman path integrals

We start from the transition amplitude $\langle \mathbf{x}', t' | \mathbf{x}, t \rangle$ to find a particle in the state $\mathbf{x}'$ at time t', when this was prepared at time t in $\mathbf{x}$. Using the time evolution operator for a <u>not explicitly time-dependent</u> Hamiltonian, we obtain

$$\langle \mathbf{x}', t' | \mathbf{x}, t \rangle = \left\langle \mathbf{x}' \right| e^{-iH\frac{t-t'}{\hbar}} \left| \mathbf{x} \right\rangle \qquad . \tag{13.1}$$

If we know the propagator $\langle \mathbf{x}', t' | \mathbf{x}, t \rangle$ we can determine the time evolution of an arbitrary state vector

$$\begin{aligned}
\psi(\mathbf{x}', t') &= \left\langle \mathbf{x}' \right| e^{-iH\frac{t-t'}{\hbar}} \left| \psi(t) \right\rangle \\
&= \int \left\langle \mathbf{x}' \right| e^{-iH\frac{t-t'}{\hbar}} \left| \mathbf{x} \right\rangle \; \psi(\mathbf{x}, t)\, d^3x \\
&= \int \langle \mathbf{x}', t' | \mathbf{x}, t \rangle \; \psi(\mathbf{x}, t)\, d^3x \qquad .
\end{aligned}$$

We start from the single-particle Hamiltonian

$$H = H_0 + H_1 = \frac{\mathbf{p}^2}{2m} + V(\mathbf{x}) \tag{13.2}$$

Since the two terms do not commute, we have

$$e^{-i\frac{\Delta t}{\hbar}H} = e^{-i\frac{\Delta t}{\hbar}H_0} e^{-i\frac{\Delta t}{\hbar}H_1} + O((\Delta t)^2) \qquad ,$$

with $\Delta t = (t' - t)$. In order to carry out the factorisation we have to make sure that the coefficient of H (here Δt) becomes small. This is obtained by $\Delta t \to \delta \equiv \Delta/N$

$$\langle \mathbf{x}', t' | \mathbf{x}, t \rangle = \left\langle \mathbf{x}' \right| \underbrace{e^{-iH\frac{\Delta t}{N\hbar}} e^{-iH\frac{\Delta t}{N\hbar}} \dots e^{-iH\frac{\Delta t}{N\hbar}}}_{\text{N factors}} \left| \mathbf{x} \right\rangle \qquad .$$

In front of each exponential function we insert the unity operator $1\!\!1 = \int |\mathbf{x}_i\rangle\langle\mathbf{x}_i|\, d^3x_i$ with appropriate index "i" and obtain

$$\langle \mathbf{x}',t'|\mathbf{x},t\rangle = \int\dots\int d^3x_1\dots d^3x_{N-1}\prod_{i=1}^{N}\langle\mathbf{x}_{i-1}|e^{-iH\frac{\delta}{\hbar}}|\mathbf{x}_i\rangle \qquad ,$$

with the definitions $\mathbf{x}_0 = \mathbf{x}'$ and $\mathbf{x}_N = \mathbf{x}$ and $\delta = \frac{\Delta t}{N}$ By exploting 13.2 one obtains

$$\begin{aligned}\langle \mathbf{x}',t'|\mathbf{x},t\rangle &= \int\dots\int d^3x_1\dots d^3x_{N-1}\prod_{i=1}^{N}\left(\langle\mathbf{x}_{i-1}|e^{-i\frac{\mathbf{p}^2}{2m}\frac{\delta}{\hbar}}|\mathbf{x}_i\rangle\, e^{-iV(\mathbf{x}_i)\frac{\delta}{\hbar}}\right) + O\big(\delta^2\big)\\ &= \int\prod_i d^3x_i\left(\prod_{i=1}^{N}\langle\mathbf{x}_{i-1}|e^{-i\frac{\mathbf{p}^2}{2m}\frac{\delta}{\hbar}}|\mathbf{x}_i\rangle\right)e^{-i\sum_i V(\mathbf{x}_i)\frac{\delta}{\hbar}} + O\big(\delta^2\big)\ . \qquad (13.3)\end{aligned}$$

We now transform the matrix elements $\langle\mathbf{x}_{i-1}|e^{-i\frac{\mathbf{p}^2}{2m}\frac{\delta}{\hbar}}|\mathbf{x}_i\rangle$ by inserting the unit operator in terms of momentum eigenstates

$$\begin{aligned}\langle\mathbf{x}_{i-1}|e^{-i\frac{\mathbf{p}^2}{2m}\frac{\delta}{\hbar}}|\mathbf{x}_i\rangle &= \int d^3q\ \langle\mathbf{x}_{i-1}|e^{-i\frac{\mathbf{p}^2}{2m}\frac{\delta}{\hbar}}\ |\mathbf{q}\rangle\,\langle\mathbf{q}|\mathbf{x}_i\rangle\\ &= \int d^3q\ e^{-i\frac{\mathbf{q}^2}{2m}\frac{\delta}{\hbar}}\ \langle\mathbf{x}_{i-1}|\mathbf{q}\rangle\langle\mathbf{q}|\mathbf{x}_i\rangle \qquad .\end{aligned}$$

With

$$\langle\mathbf{x}|\mathbf{q}\rangle = (2\pi\hbar)^{-3/2}e^{\frac{i}{\hbar}\mathbf{q}\cdot\mathbf{x}}$$

it follows

$$\begin{aligned}\langle\mathbf{x}_{i-1}|e^{-i\frac{\mathbf{p}^2}{2m}\frac{\delta}{\hbar}}|\mathbf{x}_i\rangle &= (2\pi\hbar)^{-3}\ \int d^3q\ e^{-i\frac{\mathbf{q}^2}{2m}\frac{\delta}{\hbar}}\ e^{-\frac{i}{\hbar}\mathbf{q}\cdot(\mathbf{x}_i-\mathbf{x}_{i-1})}\\ &= (2\pi\hbar)^{-3}\ \int d^3q\ e^{-i\frac{1}{2m}\frac{\delta}{\hbar}(\mathbf{q}^2+\frac{2m}{\delta}\mathbf{q}\cdot(\mathbf{x}_i-\mathbf{x}_{i-1}))}\\ &= (2\pi\hbar)^{-3}\ \int d^3q\ e^{-i\frac{1}{2m}\frac{\delta}{\hbar}(\mathbf{q}+\frac{m}{\delta}(\mathbf{x}_i-\mathbf{x}_{i-1}))^2}e^{i\frac{1}{2m}\frac{\delta}{\hbar}(\frac{m}{\delta}(\mathbf{x}_i-\mathbf{x}_{i-1}))^2}\\ &= (2\pi\hbar)^{-3}\ \underbrace{\left(\int d^3q'\ e^{-i\frac{1}{2m}\frac{\delta}{\hbar}\mathbf{q}'^2}\right)}_{(\frac{\pi 2m\hbar}{i\delta})^{3/2}}\ e^{i\frac{m}{2}\frac{\delta}{\hbar}\left(\frac{\mathbf{x}_i-\mathbf{x}_{i-1}}{\delta}\right)^2}\\ &= \left(\frac{m}{i\delta 2\pi\hbar}\right)^{-3/2}\ e^{i\frac{m}{2}\frac{\delta}{\hbar}\left(\frac{\mathbf{x}_i-\mathbf{x}_{i-1}}{\delta}\right)^2} \qquad .\end{aligned}$$

In this way 13.3 simplifies to

$$\begin{aligned}&\langle \mathbf{x}',t'|\mathbf{x},t\rangle \qquad (13.4)\\ &= \int\dots\int\prod_i\left(\left(\tfrac{m}{i\delta 2\pi\hbar}\right)^{-3/2}\ d^3x_i\right)\ e^{i\sum_i\left(\frac{m}{2}(\frac{\mathbf{x}_i-\mathbf{x}_{i-1}}{\delta})^2-V(\mathbf{x}_i)\right)\frac{\delta}{\hbar}} + O\big(\delta^2\big)\ .\end{aligned}$$

In the limit $N \to \infty$ the argument of the exponential function becomes

$$\sum_i \left(\frac{m}{2}\left(\frac{\mathbf{x}_i - \mathbf{x}_{i-1}}{\delta}\right)^2 - V(\mathbf{x}_i)\right)\delta \underset{N\to\infty}{\longrightarrow} \int_t^{t'} \left\{\frac{m}{2}\dot{\mathbf{x}}(t)^2 - V(\mathbf{x}(t))\right\} dt$$

$$= \int_t^{t'} L[x(t)]\, dt \;= S[x(t)] \qquad .$$

In this way, we get the alternative approach to quantum mechanics in terms of path integrals suggested by Feynman

FEYNMAN PATH INTEGRAL

$$\langle \mathbf{x}', t' | \mathbf{x}, t\rangle = \int_{\mathbf{x}}^{\mathbf{x}'} \mathscr{D}[x(t)]\, e^{iS[x(t)]/\hbar} \tag{13.5}$$

$$\int_{\mathbf{x}}^{\mathbf{x}'} \mathscr{D}[x(t)] = \lim_{N\to\infty} \int d^3x_1 \ldots \int d^3x_{N-1} \left(\frac{m}{i\delta 2\pi\hbar}\right)^{-3N/2} \qquad .$$

The transition amplitude from $\mathbf{x}$ at time t to $\mathbf{x}'$ at time t' is the sum (integral) over all paths. One averages the phase factor whose argument is given by the action associated with the particular path. **The crucial difference with respect to classical physics is the fact that not only the path with minimal actions contributes.** The action is the time integral of the Lagrange function.

Notice the large similarity with the basic principles of QM which are derived in connection with the double-slit experiment.

Geht man von der allgemeinen Gültigkeit des Pfadintegral-Formalismus 13.5 aus, ist es einfach, den Einfluß eines Vektorpotentials (Magnetfeld) auf die Wahrscheinlichkeitsamplitude eines bestimmten Pfades anzugeben. Man erhält lediglich aufgrund von (siehe Mechanik)

$$L = \frac{1}{2}m\mathbf{v}^2 - q\Phi(\mathbf{x}) + \frac{q}{c}\mathbf{A}\cdot\mathbf{v} \tag{13.6}$$

einen zusätzlichen Phasenfaktor, die sogenannte

PEIERLS-PHASE

$$\varphi_{\text{Peierls}} = e^{i\frac{q}{c\hbar}\int_t^{t'} \mathbf{A}\cdot\frac{d\mathbf{x}}{dt}\, dt} = e^{i\frac{q}{c\hbar}\int_{\mathbf{x}}^{\mathbf{x}'} \mathbf{A}\cdot d\mathbf{x}} \tag{13.7}$$

13.1 Aharonov-Bohm-Effekt

Ein Experiment, in dem die Peierls-Phase beobachtet werden kann, ist der Aharonov-Bohm-Effekt. Hierbei werden Teilchen durch einen Doppelspalt geschickt, hinter dem sich in einem räumlich beschränkten Gebiet, wie in Abbildung 13.1 dargestellt, eine magnetische Spule befindet. Innerhalb der Spule liegt ein konstantes B-Feld der Stärke B_0 vor und außerhalb ist das B-Feld Null. Wir betrachten die beiden in der Abbildung skizzierten Pfade, die zum Pfadintegral beitragen werden. Auf diesen Pfaden liegt kein B-Feld vor. Das Vektorpotential hingegen ist im Bereich außerhalb der Spule im Abstand r vom Spulenzentrum gegeben durch

$$\mathbf{A} = \frac{B_0 R^2}{2r} \mathbf{e}_\varphi \qquad .$$

Wir werden allerdings für die folgenden Überlegungen den tatsächlichen Wert

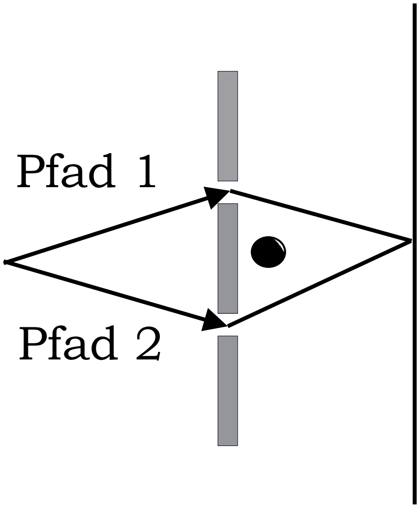


Figure 13.1: Meßanordnung zum Aharonov-Bohm-Effekt. Durch den Kreis verläuft der magnetische Fluß senkrecht zur Bildebene. Außerhalb des Kreises verschwindet das Magnetfeld.

von $\mathbf{A}$ nicht benötigen. Es sei Ψ_α^0 für $\alpha = 1,2$ die Wahrscheinlichkeitsamplitude für den Pfad α bei Abwesenheit der Spule. Der zusätzlich B-Feld-abhängige Phasenfaktor Faktor ist gemäß 13.7

$$e^{-i\left(\frac{e}{\hbar c}\right)\int_{\mathrm{Pfad}_\alpha} \mathbf{A} d\mathbf{x}}$$

Die Summe der Amplituden der beiden Pfade ergibt

$$\begin{aligned}
\Psi_1 + \Psi_2 &= \Psi_1^0 e^{-i\left(\frac{e}{\hbar c}\right)\int_{\mathrm{Pfad}_1} \mathbf{A} d\mathbf{x}} + \Psi_2^0 e^{-i\left(\frac{e}{\hbar c}\right)\int_{\mathrm{Pfad}_2} \mathbf{A} d\mathbf{x}} \\
&= e^{-i\left(\frac{e}{\hbar c}\right)\int_{\mathrm{Pfad}_2} \mathbf{A} d\mathbf{x}} \left(\Psi_1^0 e^{-i\left(\frac{e}{\hbar c}\right)\left(\int_{\mathrm{Pfad}_1} - \int_{\mathrm{Pfad}_2}\right)\mathbf{A} d\mathbf{x}} + \Psi_2^0\right) \\
&= e^{-i\left(\frac{e}{\hbar c}\right)\int_{\mathrm{Pfad}_2} \mathbf{A} d\mathbf{x}} \left(\Psi_1^0 e^{-i\left(\frac{e}{\hbar c}\right)\oint_C \mathbf{A} d\mathbf{x}} + \Psi_2^0\right) \qquad .
\end{aligned}$$

Der Vorfaktor fällt bei der Berechnung von Erwartungswerten heraus. Nicht so das Linienintegral auf einem geschlossenen Weg um das eingeschlossene B-Feld. Die Elektrodynamik (Satz von Stokes) liefert

$$\oint_C \mathbf{A} d\mathbf{x} = \int \mathbf{B} d\mathbf{S} \qquad .$$

Das hintere Integral ist ein Oberflächenintegral, das den magnetischen Fluß Φ durch die von C umschlossene Fläche angibt. Offensichtlich können wir nun die Kurve C deformieren, solange wir nicht den Bereich $B = 0$ verlassen. Mit der Konstanten für das elementare Flußquantum

$$\Phi_0 := 2\pi \frac{c\hbar}{e}$$

erhalten wir schließlich

$$\Psi_1 + \Psi_2 = e^{-i\left(\frac{e}{\hbar c}\right)\int_{\mathrm{Pfad}_2} \mathbf{A} d\mathbf{x}} \left(\Psi_1^0 e^{-i2\pi\frac{\Phi}{\Phi_0}} + \Psi_2^0\right) \qquad .$$

Wenn also $\Phi/\Phi_0 = n$ eine ganze Zahl ist, addieren sich Ψ_1^0 und Ψ_2^0 konstruktiv und bei $\Phi/\Phi_0 = n + 1/2$ destruktiv. Daß heißt, daß bei Variation des B-Feldes eine oszillierendes Signal am Schirm beobachtet wird. Wir haben somit ein Ergebnis abgeleitet, in das in Zwischenschritten das nicht eindeutig festgelegte (eichabhängige) Vektorpotential eingeht. Das Endergebnis hingegen hängt nur von B ab und ist eichinvariant. Das obige Resultat hat weitere interessante Konsequenzen. Wenn geladene Teilchen auf geschlossenen Bahnen umlaufen, z.B. in geeignet geformten Spulen, so muß der eingeschlossene magnetische Fluß in Einheiten von Φ_0 quantisiert sein, damit die Wellenfunktion eindeutig ist. Diese Quantisierung wurde erstmals 1961 mit supraleitenden Spulen in einem homogenen Magnetfeld nachgewiesen. Da in den supraleitenden Spulen Cooper-Paare die elementaren Objekte bilden und diese die Ladung $2e$ haben, wurde als Flußquant der Wert $\Phi_0/2$ gefunden.

13.2 Quanten-Interferenz aufgrund von Gravitation

Wir werden hier untersuchen, wie man den Pfadintegral-Formalismus nutzen kann, um ein überraschendes Interferenz-Experiment zu beschreiben, daß sensitiv genug ist, Interferenz aufgrund des Einflußes der Erdgravitation auf Neutronen zu beobachten. Man beachte, daß der Unterschied zwischen der elektromagnetischen und der Gravitationskraft zwischen Elektronen und Neutronen 10^{40} beträgt. Man verwendet einen annähernd monochromatischen Neutronenstrahl, der ähnlich wie im obigen Doppelspalt-Experiment in zwei Pfade zerlegt wird, die anschließend wieder zusammenlaufen. Einer der Teilstrahlen verläuft auf einem Weg, der eine höhere potentielle Energie im Schwerefeld der Erde hat. Die Apparatur ist auf einer ebenen Platte angebracht, die um eine Achse um einen beliebigen Winkel φ verkippt werden kann, so daß der Beitrag der potentiellen Energie zur Wirkung durch

$$\Delta S = T \cdot m_g g l_1 \sin(\varphi)$$

beschrieben werden kann. l_1 ist hierbei die Breite der Platte und T die Zeit, die das Neutron benötigt, die Länge l_2 der Anordnung zu durchlaufen. Wir können T über $T = m_t\, l_2/p$ durch den Impuls ausdrücken. Der Impuls wiederrum hängt mit der de Broglie Wellenlänge über $p = h/\lambda$ zusammen. Der Unterschied der Wirkung auf den beiden Pfaden ist damit

$$\Delta S = \frac{m_g m_t g l_1 l_2 \lambda \sin(\varphi)}{2\pi\hbar} \qquad .$$

Für Neutronen mit $\lambda = 1.4\overset{\circ}{A}$ wurde die Interferenz als Funktion von φ experimentell ermittelt. Man findet eine Periode von $O(5^\circ)$. Da $\hbar$ im Nenner vorkommt geht die Periodenlänge im klassischen Grenzfall $\hbar \to 0$ gegen Null und die Interferenz-Oszillationen sind nicht mehr beobachtbar. Ein weiterer interessanter Punkt ist die Tatsache, daß hier beide Typen von Massen, träge m_t und schwere m_g eingehen. Dieses Experiment ermöglicht einen Test der Gleichheit dieser Massen auf mikroskopischem Gebiet. Man findet die Gleichheit auch hier bestätigt.

Chapter 14

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Appendix A

Details

A.1 Proof of eq. 1.7

back to pag. 11 Let us call the left and right side of 1.7 $l(\varphi)$ and $r(\varphi)$, respectively. In addition, Differentiating both sides w.r.t. φ yields

$$l'(\varphi) = \begin{pmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} e^{-i\varphi A_{\mathbf{z}}} \quad r'(\varphi) = \begin{pmatrix} -\sin\varphi & -\cos\varphi & 0 \\ \cos\varphi & -\sin\varphi & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{A.1}$$

Multiplying the left expression from the right by $l(\varphi)^{-1}r(\varphi)$ yields the right term, i.e.

$$l'(\varphi)l(\varphi)^{-1}r(\varphi) = r'(\varphi) \Rightarrow \log(l(\varphi))' = \log(r(\varphi))' \, .$$

This equation, with the initial conditions

$$l(0) = r(0)$$

gives

$$l(\varphi) = r(\varphi)$$

A.2 Evaluation of 1.9

back to pag. 11 The calculation is simplified by the fact that novanishing terms only come from mixed products $A_{\mathbf{x}}A_{\mathbf{y}}$. We thus get

$$\begin{aligned} &(1+iA_{\mathbf{y}}\varphi)(1+iA_{\mathbf{x}}\varphi)(1-iA_{\mathbf{y}}\varphi)(1-iA_{\mathbf{x}}\varphi)+\cdots = \\ &= 1+\varphi^2(-A_{\mathbf{y}}A_{\mathbf{x}}+A_{\mathbf{y}}A_{\mathbf{x}}+A_{\mathbf{x}}A_{\mathbf{y}}-A_{\mathbf{y}}A_{\mathbf{x}})+\cdots = 1+\varphi^2[A_{\mathbf{x}},A_{\mathbf{y}}]+\cdots \end{aligned}$$

A.3 Discussion about the phase ω_z in 1.14

back to pag. 12 In the expansion of the r.h.s. of 1.14 we also expand the phase $\omega_{\mathbf{z}}$, since this is also "small" like φ (it vanishes when $\varphi \to 0$). We obtain instead of 1.16

$$1 - \frac{\omega_{\mathbf{z}}^2}{2} + i\left(\frac{\varphi^2}{\hbar} J_{\mathbf{z}} + \omega_{\mathbf{z}} \mathbb{1}\right) . \tag{A.2}$$

If this has to be equal to 1.15 up to $O(\varphi^2)$, it follows that $\omega_{\mathbf{z}} = O(\varphi^2)$. Therefore we have

$$[J_{\mathbf{x}}, J_{\mathbf{y}}] = i\hbar(J_{\mathbf{z}} + d_{\mathbf{z}} \mathbb{1}) \tag{A.3}$$

with $d_{\mathbf{z}} = \frac{\hbar}{\varphi^2}\omega_{\mathbf{z}} = const.$. This constant can be absorbed in the definition: $\widetilde{J}_\alpha = J_\alpha + d_\alpha$ so that 1.17 holds for the $\widetilde{J}_\alpha$ operators.
This means that the rotation operators J_α are not uniquely defined: there is an arbitrary constant, which by convention is set to zero. The choice of the constant does not affect physical results.

A.4 Transformation of the components of a vector

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The projection of a vector **A** on the direction defined by the unit vector **n** is given by $\mathbf{A_n} := \mathbf{n} \cdot \mathbf{A}$. A rotation transforms **n** into $\mathbf{n}' = R\,\mathbf{n}$. Accordingly the projection of the operator is transformed after the same rotation into $\mathbf{A}'_{\mathbf{n}} = \mathbf{n}' \cdot \mathbf{A}$. This gives

$$\mathbf{A}'_{\mathbf{n}} = (R_{\beta\alpha} n_\alpha) A_\beta \ . \tag{A.4}$$

In order to determine the α-component $\mathbf{A}'_\alpha$ we set $\mathbf{n} = \mathbf{e}_\alpha$, i.e.

$$\mathbf{A}'_\alpha = R_{\beta\alpha} A_\beta = \left(R^T A\right)_\alpha \tag{A.5}$$

This shows that the components of a vactor transform according to $R^T = R^{-1}$.

A.5 Commutation rules of the orbital angular momentum

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We start by proving 1.20 with $\mathbf{A} = \mathbf{r}$:

$$\begin{aligned}[L_\alpha, r_\beta] &= \varepsilon_{\alpha\gamma\rho}[r_\gamma p_\rho, r_\beta] \\ &= \varepsilon_{\alpha\gamma\rho} r_\gamma \underbrace{[p_\rho, r_\beta]}_{-i\hbar\delta_{\rho\beta}} \\ &= -i\hbar\varepsilon_{\alpha\gamma\beta} r_\gamma \\ &= i\hbar\varepsilon_{\alpha\beta\gamma} r_\gamma \qquad . \end{aligned} \tag{A.6}$$

The proof for $\mathbf{A} = \mathbf{p}$ is analogous.
We now evaluate the commutator $[L_x, L_y]$.

$$[L_x, L_y] = [L_x, r_z p_x - r_x p_z] = i\hbar(-r_y p_x + r_x p_y) = i\hbar L_z \tag{A.7}$$

together with its cyclic permutations, this proves that L satisfies 1.17 .

A.6 Further Commutation rules of J

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$$\begin{aligned}[J^2, J_\beta] &= [J_\alpha J_\alpha, J_\beta] \\ &= J_\alpha[J_\alpha, J_\beta] + [J_\alpha, J_\beta]J_\alpha \\ &= i\hbar\big(\varepsilon_{\alpha\beta\gamma} J_\alpha J_\gamma + \varepsilon_{\alpha\beta\gamma} J_\gamma J_\alpha\big) \qquad . \end{aligned}$$

After renaming $\alpha \leftrightarrow \gamma$ in the last term it follows

$$\begin{aligned}[J^2, J_\beta] &= i\hbar\big(\varepsilon_{\alpha\beta\gamma} J_\alpha J_\gamma + \varepsilon_{\gamma\beta\alpha} J_\alpha J_\gamma\big) \\ &= i\hbar\big(\varepsilon_{\alpha\beta\gamma} J_\alpha J_\gamma - \varepsilon_{\alpha\beta\gamma} J_\alpha J_\gamma\big) = 0 \qquad . \end{aligned}$$

$$\begin{aligned}[J_+, J_-] &= [J_x + iJ_y, J_x - iJ_y] \\ &= \underbrace{[J_x, J_x]}_{=0} + \underbrace{[J_y, J_y]}_{=0} + i[J_y, J_x] - i[J_x, J_y] \\ &= -2i[J_x, J_y] = -2i \cdot i\hbar J_z = 2\hbar J_z \end{aligned}$$

$$\begin{aligned}[J_z, J_\pm] &= [J_z, J_x] \pm i[J_z, J_y] \\ &= i\hbar\varepsilon_{zxy} J_y \pm i(i\hbar)\varepsilon_{zyx} J_x \\ &= i\hbar J_y \pm \hbar J_x = \pm\hbar(J_x \pm iJ_y) \end{aligned}$$

$$[J^2, J_\pm] = 0$$

This follows immediately from 1.21 .

A.7 Uncertainty relation for $j = 0$

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The uncertainty relation implies in general

$$|\,(\Delta J_x)^2\,| \cdot |\,(\Delta J_y)^2\,| \geq \frac{\hbar}{2} \cdot j \qquad .$$

For $j = 0$ one has

$$|\langle [J_x, J_y] \rangle| = \hbar |\langle J_z \rangle| = \hbar^2 \cdot |m| = 0 \tag{A.8}$$

$$\tag{A.9}$$

$$\Rightarrow \qquad (\Delta J_x)^2 \cdot (\Delta J_y)^2 \text{can become zero.} \tag{A.10}$$

A.8 $\mathbf{J} \times \mathbf{J}$

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$$\begin{aligned}
(\mathbf{J} \times \mathbf{J})_\alpha &= \varepsilon_{\alpha\beta\gamma} J_\beta J_\gamma \\
&= \frac{1}{2}(\varepsilon_{\alpha\beta\gamma} J_\beta J_\gamma + \varepsilon_{\alpha\gamma\beta} J_\gamma J_\beta) \\
&= \frac{1}{2}\varepsilon_{\alpha\beta\gamma}[J_\beta, J_\gamma] \\
&= \frac{1}{2}\varepsilon_{\alpha\beta\gamma} i\hbar \varepsilon_{\beta\gamma\delta} J_\delta \\
&= \frac{i\hbar}{2} 2 \cdot \delta_{\alpha\delta} J_\delta \\
&= i\hbar J_\alpha
\end{aligned}$$

A.9 Explicit derivation of angular momentum operators and their eigenfunctions

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Using 1.50 the components of the angular momentum operator can be expressed as

$$\left.\begin{array}{rcl} L_x &=& \frac{\hbar}{i}(y\frac{\partial}{\partial z}-z\frac{\partial}{\partial y}) \\ L_y &=& \frac{\hbar}{i}(z\frac{\partial}{\partial x}-x\frac{\partial}{\partial z}) \\ L_z &=& \frac{\hbar}{i}(x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}) \end{array}\right\} \quad \Rightarrow \quad L_\pm = \frac{\hbar}{i}\left((y\mp ix)\frac{\partial}{\partial z}-z(\frac{\partial}{\partial y}\mp i\frac{\partial}{\partial x})\right)$$

With the spherical coordinates

$$x = r\cdot\sin\theta\cos\varphi$$
$$y = r\cdot\sin\theta\sin\varphi$$
$$z = r\cdot\cos\theta$$

$$\begin{aligned}\frac{\partial}{\partial\theta} &= \frac{\partial x}{\partial\theta}\frac{\partial}{\partial x}+\frac{\partial y}{\partial\theta}\frac{\partial}{\partial y}+\frac{\partial z}{\partial\theta}\frac{\partial}{\partial z} \\ &= \underbrace{r\cos\theta\cos\varphi}_{\cot\theta\cdot x}\frac{\partial}{\partial x}+\underbrace{r\cos\theta\sin\varphi}_{\cot\theta\cdot y}\frac{\partial}{\partial y}-r\sin\theta\frac{\partial}{\partial z}\end{aligned}$$

$$\begin{aligned}\frac{\partial}{\partial\varphi} &= \frac{\partial x}{\partial\varphi}\frac{\partial}{\partial x}+\frac{\partial y}{\partial\varphi}\frac{\partial}{\partial y}+\frac{\partial z}{\partial\varphi}\frac{\partial}{\partial z} \\ &= -\underbrace{r\sin\theta\sin\varphi}_{y}\frac{\partial}{\partial x}+\underbrace{r\sin\theta\cos\varphi}_{x}\frac{\partial}{\partial y} \\ &= x\frac{\partial}{\partial y}-y\frac{\partial}{\partial x}\end{aligned}$$

Thus

$$L_z = \frac{\hbar}{i}\frac{\partial}{\partial\varphi} \tag{A.11}$$

We now show that

$$L_\pm = \hbar e^{\pm i\varphi}(\pm\frac{\partial}{\partial\theta}+i\cot\theta\frac{\partial}{\partial\varphi}) \tag{A.12}$$

Proof:

$$\begin{aligned}L_\pm = \quad & \hbar e^{\pm i\varphi}(\pm r\cos\theta\cos\varphi\frac{\partial}{\partial x}\pm r\cos\theta\sin\varphi\frac{\partial}{\partial y}\mp r\sin\theta\frac{\partial}{\partial z} \\ & +i\cdot r\cdot\underbrace{\cot\theta\cdot\sin\theta}_{\cos\theta}\cos\varphi\frac{\partial}{\partial y}-i\cdot r\cdot\underbrace{\cot\theta\cdot\sin\theta}_{\cos\theta}\sin\varphi\frac{\partial}{\partial x})\end{aligned}$$

$$
\begin{aligned}
= \quad & \hbar e^{\pm i\varphi}\left[\mp r\cdot\sin\theta\frac{\partial}{\partial z}+(ir\cdot\cos\theta\cos\varphi\pm r\cdot\cos\theta\sin\varphi)\frac{\partial}{\partial y}\right. \\
& \qquad \left.-(ir\cdot\cos\theta\sin\varphi\mp r\cos\theta\cos\varphi)\frac{\partial}{\partial x}\right] \\
= \quad & \hbar e^{\pm i\varphi}\left[\mp r\cdot\sin\theta\frac{\partial}{\partial z}+ir\cdot\cos\theta\,\underbrace{(\cos\varphi\mp i\sin\varphi)}_{e^{\mp i\varphi}}\frac{\partial}{\partial y}\right. \\
& \qquad \left.\pm r\cdot\cos\theta\,\underbrace{(\cos\varphi\mp i\sin\varphi)}_{e^{\mp i\varphi}}\frac{\partial}{\partial x}\right] \\
= \quad & \hbar\left[\mp e^{\mp i\varphi}r\cdot\sin\theta\frac{\partial}{\partial z}+iz\frac{\partial}{\partial y}\pm z\frac{\partial}{\partial x}\right] \\
= \quad & \hbar\left[(\mp\underbrace{r\cdot\sin\theta\cos\varphi}_{x}-i\underbrace{r\sin\theta\sin\varphi}_{y})\frac{\partial}{\partial z}+iz(\frac{\partial}{\partial y}\mp i\frac{\partial}{\partial x})\right] \\
= \quad & \hbar(-i)\left[(y\mp ix)\frac{\partial}{\partial z}-z(\frac{\partial}{\partial y}\mp i\frac{\partial}{\partial x})\right]
\end{aligned}
$$

q.e.d

Firs we determine the φ-part of the eigenfunctions $Y_l^m(\theta,\varphi)$. From Eqs. 1.40b and 1.51 it follows

$$
\begin{aligned}
\frac{\partial}{\partial\varphi}Y_l^m(\theta,\varphi) &= im\,Y_l^m(\theta,\varphi) \\
\Rightarrow Y_l^m(\theta,\varphi) &= \frac{1}{\sqrt{2\pi}}e^{im\varphi}\Theta_l^m(\theta) \qquad \text{(A.13)}
\end{aligned}
$$

Θ_l^m is still an arbitrary function which depends on θ only. Instead of 1.48 we now use 1.31 , i.e. $L_+|l,m=l\rangle=0$ and obtain the equation

$$
\begin{aligned}
\frac{\partial}{\partial\theta}Y_l^{m=l}(\theta,\varphi) \quad + \quad & i\frac{\cos\theta}{\sin\theta}\underbrace{\frac{\partial}{\partial\varphi}Y_l^{m=l}(\theta,\varphi)}_{ilY_l^l(\theta,\varphi)} = \\
& \overset{(A.13)}{=} \frac{e^{im\varphi}}{\sqrt{2\pi}}\left(\frac{\partial}{\partial\theta}\Theta_l^{m=l}(\theta)-l\frac{\cos\theta}{\sin\theta}\Theta_l^{m=l}(\theta)\right)\overset{!}{=}0
\end{aligned}
$$

$$\begin{aligned} \Rightarrow \frac{\partial}{\partial\theta}\Theta_l^l(\theta) &= l\cdot\frac{\cos\theta}{\sin\theta}\Theta_l^l(\theta) \\ \Rightarrow \qquad \Theta_l^l(\theta) &= C_l\cdot\sin^l\theta \end{aligned}$$

Proof: $$\frac{\partial}{\partial\theta}\sin^l\theta = l\cdot\cos\theta\sin^{l-1}\theta = l\cdot\frac{\cos\theta}{\sin\theta}\Theta_l^l(\theta)$$

The normalisation gives

$$\begin{aligned} \int d\Omega\left|Y_l^{m=l}(\theta,\varphi)\right|^2 &= |C_l|^2\int_0^\pi \sin^{2l}\theta\sin\theta\,d\theta \\ &= |C_l|^2\cdot\int_0^\pi \sin^{2l+1}\theta\,d\theta \\ &= |C_l|^2\sqrt{\pi}\frac{\Gamma(l+1)}{\Gamma(l+1+\frac{1}{2})} \\ &= |C_l|^2\frac{(l!2^l)^2\cdot 2}{(2l+1)!}\overset{!}{=}1 \end{aligned}$$

Convention

$$\boxed{C_l = \frac{(-1)^l}{2^l l!}\sqrt{\frac{(2l+1)!}{2}}}$$

From this it follows

$$Y_l^{m=l}(\theta,\varphi) = \frac{(-1)^l}{2^l l!}\sqrt{\frac{(2l+1)!}{4\pi}}e^{il\varphi}\sin^l\theta$$

The eigenfunction associated to smaller values of the magnetic quantum number m are obtained by repeated application of equation 1.43

$$\begin{aligned} |l,m-1\rangle &= [l(l+1)-m(m-1)]^{-\frac{1}{2}}\ \frac{L_-}{\hbar}|l,m\rangle \\ &= [(l+m)(l-m+1)]^{-\frac{1}{2}}\ \frac{L_-}{\hbar}|l,m\rangle \end{aligned}$$

$$\Rightarrow$$

$$\underline{m = l:}$$

$$|l, l-1\rangle = [(2l)\cdot 1]^{-\frac{1}{2}} \frac{L_-}{\hbar}|l,l\rangle$$

$$\underline{m = l-1:}$$

$$|l, l-2\rangle = (2l)^{-\frac{1}{2}}[(2l-1)\cdot 2]^{-\frac{1}{2}}\left(\frac{L_-}{\hbar}\right)^2|l,l\rangle$$

$$\vdots$$

$$\begin{aligned} [l, l-n\rangle &= [(2l)(2l-1)\ldots(2l-n+1)n!]^{-\frac{1}{2}}\left(\frac{L_-}{\hbar}\right)^n|l,l\rangle \\ &= \left[\frac{(2l-n)!}{(2l)!n!}\right]^{\frac{1}{2}}\left(\frac{L_-}{\hbar}\right)^n|l,l\rangle \end{aligned}$$

or with $(n = l-m)$

$$|l,m\rangle = \left[\frac{(l+m)!}{(2l)!(l-m)!}\right]^{\frac{1}{2}}\left(\frac{L_-}{\hbar}\right)^{l-m}|l,l\rangle$$

$$Y_l^m(\theta,\varphi) = \left[\frac{(l+m)!}{(2l)!(l-m)!}\right]^{\frac{1}{2}}\left(-e^{-i\varphi}(\frac{\partial}{\partial\theta} - i\cot\theta\frac{\partial}{\partial\varphi})\right)^{l-m} Y_l^l(\theta,\varphi)$$

$Y_l^l(\theta,\varphi)$ is of the form $C_l e^{i\varphi l}\cdot\sin^l\theta =: C_l e^{i\varphi l} f(\theta)$.
A single application of $\frac{L_-}{\hbar}$ to Y_l^l yields

$$\begin{aligned} &-C_l e^{-i\varphi}e^{i\varphi l}\left(\frac{\partial}{\partial\theta} - i\cdot\cot\theta\cdot(+il)\right)f(\theta) \\ &= -C_l e^{i(l-1)\varphi}\underbrace{\left(\frac{\partial}{\partial\theta} + \cot\theta\cdot l\right)f(\theta)}_{\xi} \end{aligned}$$

Conjecture:

$$\xi = \frac{1}{\sin^l\theta}\frac{d}{d\theta}(\sin^l\theta\cdot f(\theta))$$

Proof

$$\begin{aligned}
\xi &= \frac{1}{\sin^l \theta}\left[(\frac{d}{d\theta}\sin^l\theta)\, f(\theta) + \sin^l(\theta)\frac{d}{d\theta}f(\theta)\right] \\
&= \frac{1}{\sin^l \theta}\left[l\cdot\cot\theta\sin^l\theta\, f(\theta)\ +\ \sin^l\theta\frac{d}{d\theta}f(\theta)\right] \\
&= \left[\frac{d}{d\theta} + l\cdot\cot\theta\right] f(\theta)
\end{aligned}$$

q.e.d.

Thus, ξ can also be expressed as

$$\begin{aligned}
\xi &= -\frac{1}{\sin^{l-1}\theta}\cdot\frac{d}{d(\cos\theta)}(\sin^l\theta\cdot f(\theta)) \\
\Rightarrow \qquad (\frac{L_-}{\hbar})Y_l^l(\theta,\varphi) &= C_l e^{i(l-1)\varphi}\frac{1}{\sin^{l-1}\theta}\cdot\frac{d}{d(\cos\theta)}(\sin^l\theta\cdot f(\theta))
\end{aligned}$$

We have started from the general form

$$Y_l^l(\theta,\varphi) = C_l e^{il\varphi} f(\theta)$$

The application of $\frac{L_-}{\hbar}$ ist therefore

$$\begin{aligned}
& e^{il\varphi} \rightarrow e^{i(l-1)\varphi} \\
\text{and:} \qquad & f(\theta) \rightarrow \tilde{f} = \frac{1}{\sin^{l-1}\theta}\frac{d}{d\cos\theta}(\sin^l\theta\cdot f(\theta))
\end{aligned}$$

A second application leads to

$$\begin{aligned}
(\frac{L_-}{\hbar})^2 Y_l^l &= C_l e^{i(l-2)\varphi}\frac{1}{\sin^{l-2}\theta}\frac{d}{d\cos\theta}(\sin^{l-1}\tilde{f}) \\
&= C_l e^{i(l-2)\varphi}\frac{1}{\sin^{l-2}\theta}\frac{d^2}{d(\cos\theta)^2}\sin^l\theta\cdot f(\theta)
\end{aligned}$$

We recognize the regularity

$$(\frac{L_-}{\hbar})^n Y_l^l = C_l e^{i(l-n)\varphi}\frac{1}{\sin^{l-n}\theta}\frac{d^n}{d(\cos\theta)^n}\sin^l\theta\cdot f(\theta) \qquad .$$

We now insert the special form $f(\theta) = \sin^l\theta$ and obtain

SPHERICAL HARMONICS

$$Y_l^m(\theta,\varphi) = \frac{(-1)^l}{2^l l!}\sqrt{\frac{(2l+1)(l+m)!}{2(l-m)!}}\,\frac{e^{im\varphi}}{\sqrt{2\pi}}\cdot\frac{1}{\sin^m\theta}\cdot\frac{d^{l-m}}{d(\cos\theta)^{l-m}}\,\sin^{2l}\theta \quad \text{(A.14)}$$

Y_l^m are termed SPHERICAL HARMONICS.

A.10 Relation betwen $\mathbf{L}^2$ and $\mathbf{p}^2$

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$$\begin{aligned}
\mathbf{L}^2 &= \Big(\mathbf{r}\times\mathbf{p}\Big)_\alpha\cdot\Big(\mathbf{r}\times\mathbf{p}\Big)_\alpha \\
&= \varepsilon_{\alpha\beta\gamma}\,\varepsilon_{\alpha\beta'\gamma'}\; r_\beta p_\gamma\, r_{\beta'} p_{\gamma'} \\
&= (\delta_{\beta\beta'}\,\delta_{\gamma\gamma'} - \delta_{\beta\gamma'}\,\delta_{\gamma\beta'}) r_\beta p_\gamma\, r_{\beta'} p_{\gamma'} \\
&= r_\beta \underbrace{p_\gamma\, r_\beta}_{r_\beta p_\gamma - i\hbar\delta_{\beta\gamma}} p_\gamma - r_\beta p_\gamma \underbrace{r_\gamma p_\beta}_{p_\beta r_\gamma + i\hbar\delta_{\beta\gamma}} \\
&= \mathbf{r}^2\mathbf{p}^2 - i\hbar\,\mathbf{r}\cdot\mathbf{p} - \hat{r}_\beta\hat{p}_\gamma\hat{p}_\beta\hat{r}_\gamma - i\hbar\,\mathbf{rp} \\
&= \mathbf{r}^2\mathbf{p}^2 - 2i\hbar\,\mathbf{r}\cdot\mathbf{p} - r_\beta p_\beta \cdot \underbrace{p_\gamma r_\gamma}_{r_\gamma p_\gamma - 3i\hbar} && \text{(A.15)} \\
\mathbf{L}^2 &= \mathbf{r}^2\mathbf{p}^2 + i\hbar\,\mathbf{r}\cdot\mathbf{p} - (\mathbf{r}\cdot\mathbf{p})^2
\end{aligned}$$

A.11 Proof that $\sigma \leq 0$ solutions in 2.17 must be discarded

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The second solution of 2.17 , $\sigma = -l$, must be discarded because it is too singular around $r = 0$, as we show below.

The wave function is

$$\psi(\mathbf{r}) = \frac{\chi(r)}{r} Y(\theta,\varphi) \tag{A.16}$$

Its norm is

$$\begin{aligned}\int |\psi(\mathbf{r})|^2 d^3\mathbf{r} &= \underbrace{\int |Y(\theta,\varphi)|^2 d\Omega}_{=1} \cdot \int_0^\infty \frac{\chi(r)^2}{r^2} r^2 \, dr \\ &= \int_0^\infty \chi(r)^2 \, dr \quad .\end{aligned}$$

Its contribution around $r = 0$ gives (for $c_0 \neq 0$)

$$\int |c_0|^2 r^{2\sigma} \, dr$$

which diverges for $\sigma \leq -1$.
For $\sigma = l = 0$ the norm does not diverge, however the kinetic energy does.

$$E_{\text{kin}} = \frac{\hbar^2}{2m} \int_{\mathbb{R}^3} |\nabla\psi(\mathbf{r})|^2 d^3\mathbf{r} \quad . \tag{A.17}$$

The angular part of the wave function $Y_0^0 = \frac{1}{\sqrt{4\pi}}$ is a constant. We consider again the behavior for $r \to 0$

$$\nabla\psi(\mathbf{r}) \sim \nabla(\frac{c_0}{r}) \sim -\frac{\mathbf{e}_r}{r^2}$$
$$\Rightarrow ||\nabla\psi(\mathbf{r})||^2 \sim \frac{|c_0|^2}{r^4}$$

Therefore the integral A.17 diverges.

A.12 Details of the evaluation of the radial wave function for hydrogen

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Aus dem Verhältnis der Entwicklungskoeffizienten 2.19 und 2.27 wird somit

$$\begin{aligned}\frac{c_{\mu+1}}{c_\mu} &= \frac{2\gamma(\mu+l+1) - 2\frac{Z}{a_0}}{(\mu+l+2)(\mu+l+1) - l(l+1)} \\ &= 2\gamma \frac{\mu+1+l-n}{(\mu+l+2)(\mu+l+1) - l(l+1)}\end{aligned} \quad . \tag{A.18}$$

Es ist sinnvoll, dimensionslose Entwicklungskoeffizienten

$$d_\mu := (2\gamma)^{-\mu}\, c_\mu$$

einzuführen, mit

$$\begin{aligned}
\frac{d_{\mu+1}}{d_\mu} &= \frac{\mu+l+1-n}{(\mu+l+2)(\mu+l+1)-l(l+1)} \\
&= \frac{\mu+l+1-n}{l^2+l(3+2\mu)+(1+\mu)(2+\mu)-l^2-l} \\
&= \frac{\mu+l+1-n}{2l(1+\mu)+(1+\mu)(2+\mu)} \\
&= \frac{l-n+\mu+1}{(2l+2+\mu)(1+\mu)} \qquad .
\end{aligned}$$

Die Koeffizienten sind mit den Abkürzungen $\nu = n-l-1$ und $\alpha = 2l+2$

$$\begin{aligned}
d_1 &= \frac{-\nu}{\alpha\cdot 1}\, d_0 \\
d_2 &= \frac{-\nu+1}{(\alpha+1)\cdot 2}\, d_1 = \frac{-\nu(-\nu+1)}{\alpha(\alpha+1)\cdot 1\cdot 2}\, d_0 \\
d_3 &= \frac{-\nu+2}{(\alpha+2)\cdot 3}\, d_2 = \frac{-\nu(-\nu+1)(-\nu+2)}{\alpha(\alpha+1)(\alpha+2)\cdot 1\cdot 2\cdot 3}\, d_0 \\
&\vdots \\
d_\mu &= \frac{-\nu(-\nu+1)\ldots(-\nu+\mu-1)}{\alpha(\alpha+1)\ldots(\alpha+\mu-1)}\, \frac{1}{\mu!}\, d_0 \qquad .
\end{aligned} \tag{A.19}$$

Diese Koeffizienten in die Reihe

$$R_{nl}(r) = \sum_{\mu=0}^{n-l-1} c_\mu\, r^\mu = \sum_{\mu=0}^{n-l-1} d_\mu\, (2\gamma r)^\mu$$

eingesetzt führen mit $d_0 = 1$ auf die entartete Hypergeometrische Funktion

$$R_{nl}(r) = {}_1\mathrm{F}_1(-\nu,\alpha;2\gamma r) := \sum_{\mu=0}^{\nu} \frac{-\nu(-\nu+1)\ldots(-\nu+\mu-1)}{\alpha(\alpha+1)\ldots(\alpha+\mu-1)}\, \frac{(2\gamma r)^\mu}{\mu!} \qquad .$$

Es handelt sich um orthogonale Polynome vom Grade ν mit den Eigenschaft

$${}_1\mathrm{F}_1(-\nu,\alpha;0) = 1 \tag{A.20}$$

$${}_1\mathrm{F}_1(0,\alpha;r) = 1 \qquad . \tag{A.21}$$

Die entartete Hypergeometrische Funktion hängt mit dem orthogonalen Laguerre-Polynom[1] $L_\nu^{\alpha-1}$ vom Grad ν zusammen

$$L_\nu^{\alpha-1}(r) = \binom{\nu+\alpha-1}{\nu}\ {}_1\mathrm{F}_1(-\nu,\alpha;2\gamma r) \qquad .$$

Das führt uns zum Endergebnis 2.28

A.13 Potential of an electron in the ground state of a H-like atom

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The potential $V(R)$ produced in a point $\mathbf{R}$ by an electron with wave function $\psi(\mathbf{r}) = \left(\frac{Z^3}{\pi}\right)^{\frac{1}{2}} e^{-Z\,r}$ (see 5.3) centered in the origin of the coordinates is given by

$$-V(R) = \int d^3r\, |\psi(\mathbf{r})|^2 \frac{1}{|\mathbf{R}-\mathbf{r}|}\ .$$

The radial component of the electric field in $\mathbf{R}$ is given by Gauss' law:

$$E(R) = \frac{Q_R}{R^2}$$

with the total charge contained between 0 and R:

$$-Q_R = 4\pi \int_0^R r^2 |\psi(\mathbf{r})|^2 = 1-(1+2RZ(1+RZ))e^{-2RZ}$$

The potential $V(R)$ is given by

$$-V(R) = \int_\infty^R E(R')d\,R' = \frac{1}{R}\left(1-(1+ZR)e^{-2ZR}\right) \qquad \text{(A.22)}$$

A.14 Heisenberg representation a bit more precise

back to pag. 60 Reminder: given an operator $O^H(t)$ in the Heisenberg representation, its time derivative is given by

$$\frac{d}{dt}O^H(t) = i[H^H(t),O^H(t)] + \frac{d}{dt}O^S(t) \qquad \text{(A.23)}$$

---

[1] Es gibt in der Literatur zwei unterschiedliche Definitionen der Laguerre-Polynome. Zwischen der hier verwendeten Definition L_n^α und der anderen Definition $\tilde{L}$ besteht die Beziehung $L_n^\alpha = \frac{(-1)^\alpha}{(n+\alpha)!}\tilde{L}_{n+\alpha}^\alpha$

where $O^S(t)$ is the operator in the Schrödinger picture. We will consider mainly operators which are time independent in the Schrödinger picture, i. e. the second term vanishes.

We now use the fact that for any operator (taking the initial time $t_0 = 0$ for simplicity)

$$O^H(t) = U(t)^\dagger O^S U(t)$$

Inserting in A.23 we obtain (for simplicity of notation we omit to indicate the time dependence (t) everywhere)

$$\frac{d}{dt} O^H = i\, U^\dagger [H^S, O^S] U = i[H^S, O^S]^H \tag{A.24}$$

This means that the time derivative of an operator in the Heisenberg picture is obtained by computing the usual commutator for the operators in the Schrödinger picture and interpreting the resulting operator as been in the Heisenberg picture. That's way in the literature one can simply omit the index ^{H} still understanding the operators as being in the Heisenberg picture.

A.15 More about Löwdin orthonormalisation

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As shown below, the Löwdin-Orthogonalization corresponds to the orthonormalization of a arbitrary non-orthonormal basis.We exploited this fact in 5.5 . We could have just as well orthonormalized the basis beforehand, in which case $S = \mathbb{1}$.

Let us start from a non-orthonormal, yet linear independent basis

$$\langle \psi_i | \psi_j \rangle = S_{ij}$$

S_{ij} is invertible and hermitian: $S^*_{ji} = S_{ij}$.

An orthonormal basis is given by the vectors $|\varphi_\alpha\rangle$ obtained as (Einstein sum convention)

$$|\varphi_\alpha\rangle = |\psi_j\rangle\, S^{-\frac{1}{2}}_{j\alpha} \tag{A.25}$$

Proof:

$$\langle \varphi_\beta | \varphi_\alpha \rangle = S^{-\frac{1}{2}*}_{i\beta} \langle \psi_i | \psi_j \rangle S^{-\frac{1}{2}}_{j\alpha} = S^{-\frac{1}{2}}_{\beta i} S_{ij} S^{-\frac{1}{2}}_{j\alpha} = (S^{-\frac{1}{2}} S S^{-\frac{1}{2}})_{\alpha\beta} = \delta_{\alpha\beta}$$

That $S^{-\frac{1}{2}} S S^{-\frac{1}{2}} = \mathbb{1}$ can be shown by introducing the unitary matrix U that diagonalizes S:

$$U^\dagger S U = S_{diag}$$

Then

$$S^{-\frac{1}{2}}SS^{-\frac{1}{2}} = UU^\dagger S^{-\frac{1}{2}}UU^\dagger SUU^\dagger S^{-\frac{1}{2}}UU^\dagger = US_{diag}^{-\frac{1}{2}}S_{diag}S_{diag}^{-\frac{1}{2}}U^\dagger =$$

$$= U\mathbb{1}U^\dagger = \mathbb{1}\ .$$

$S_{diag}^{-\frac{1}{2}}S_{diag}S_{diag}^{-\frac{1}{2}}$ is a diagonal matrix with diagonal elements of the form $s_n^{-\frac{1}{2}}s_n\, s_n^{-\frac{1}{2}} = 1$, and thus equal to $\mathbb{1}$.

A.16 Some details for the total S

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Generators of rotations

Let us consider a product state of two single spin states

$$|\Phi_1\rangle_1 \otimes |\Phi_2\rangle_2\ .$$

Let us carry out a rotation by an angle α around, say, the z-axis, then

$$\left|\Phi_1'\right\rangle = e^{-i\alpha\frac{S_1^z}{\hbar}}\,|\Phi_1\rangle$$

$$\left|\Phi_2'\right\rangle = e^{-i\alpha\frac{S_2^z}{\hbar}}\,|\Phi_2\rangle$$

are the rotated spin states, and

$$\left|\Phi_1'\right\rangle_1 \otimes \left|\Phi_2'\right\rangle_2$$

the rotated product state. Now, it is easy to show that the latter equals

$$e^{-i\alpha\frac{S^z}{\hbar}}\,|\Phi_1\rangle_1 \otimes |\Phi_2\rangle_2\ .$$

I.e., $\frac{S^z}{\hbar}$ is the generator of rotation in the product space.

Commutators

Although the above result should be sufficient, we now explicitly prove the commutation relations of the total spin operator **S**:

$$\begin{aligned}
[S^\alpha, S^\beta] &= [(S_1^\alpha + S_2^\alpha), (S_1^\beta + S_2^\beta)] \\
&= [S_1^\alpha, S_1^\beta] + [S_2^\alpha, S_2^\beta] \\
&= i\hbar\varepsilon_{\alpha\beta\gamma}\big(S_1^\gamma + S_2^\gamma\big) \\
[S^\alpha, S^\beta] &= \varepsilon_{\alpha\beta\gamma}\, S^\gamma \qquad .
\end{aligned} \tag{A.26}$$

A.17 Proof of Wigner Eckart's theorem for vectors

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The idea consists in showing the proportionality

$$\langle a,j,m|\,\hat{\mathbf{V}}_{\mathbf{M}}\,|\mathbf{b},\mathbf{j_2},\mathbf{m_2}\rangle \propto \langle j,m||\mathbf{j_1}=\mathbf{1},\mathbf{m_1}=\mathbf{M}\rangle\,|\mathbf{j_2},\mathbf{m_2}\rangle \tag{A.27}$$

To do this, we go back to the definition of the Clebsch-Gordan coefficients 6.16 , which describe the coefficients of the expansion of the $|j,m\rangle$ in the product basis (here the complex conjugate):

$$C(j_1,m_1;j_2,m_2|j,m)^* = \langle j,m|\,|j_1,m_1\rangle\,|j_2,m_2\rangle \tag{A.28}$$

We rephrase in another language the procedure we carried out in Sec. 6.6.4: We insert the operator $\hat{J}^+ = \hat{J}_1^+ + \hat{J}_2^+$ in A.28 and apply it once to the right and once to the left (in this case it acts as a $\hat{J}^-$) and set the results equal

$$\begin{aligned}&\alpha^+(j_1,m_1)\langle j,m|\,|j_1,m_1+1\rangle\,|j_2,m_2\rangle\\&+\alpha^+(j_2,m_2)\langle j,m|\,|j_1,m_1\rangle\,|j_2,m_2+1\rangle\\&=\alpha^-(j,m)\langle j,m-1|\,|j_1,m_1\rangle\,|j_2,m_2\rangle\end{aligned} \tag{A.29}$$

where

$$\alpha^\pm(j,m) = \sqrt{j(j+1)-m(m\pm 1)} \tag{A.30}$$

this gives a recursion equation for the coefficients containing $\langle j,m-1|$ in terms of the ones containing $\langle j,m|$. In this way, starting from the one with the largest m, i.e. $\langle j,j|$, we get all the others down to $\langle j,-j|$. Finally, since in A.29 with $m=-j$ the r.h.s. vanishes, the l.h.s. gives a further proportionality relation between the two terms. This means that for fixed j, j_1, j_2 once one of the coefficients A.28 is fixed, all the others are proportional and uniquely determined by A.29 .
The commutation rules for vector operators 1.20 lead for 6.29 to commutation rules similar to 1.24 , i.e

$$[\hat{J}^+,\hat{V}_{-1}] = \sqrt{2}\hbar\,\hat{V}_0 \qquad [\hat{J}^+,\hat{V}_{+1}] = 0 \qquad [\hat{J}^+,\hat{V}_0] = \sqrt{2}\hbar\,\hat{V}_{+1}$$

which can be summarized to

$$[\hat{J}^+,\hat{V}_M] = \alpha^+(1,M)\,\hbar\,\hat{V}_{M+1} \tag{A.31}$$

where the $\alpha^+(1,M)$ are the A.30 with $j=1$ and a $^+$. For simplicity, we now use $\hbar = 1$.
We now put both sides of A.31 between two states (l.h.s. of A.27):

$$\langle a,j,m|\,[\hat{J}^+,\hat{V}_M]\,|b,j_2,m_2\rangle = \alpha^+(1,M)\,\langle a,j,m|\,\hat{V}_{M+1}\,|b,j_2,m_2\rangle$$

expanding the commutator yields

$$\alpha^-(j,m)\,\langle a,j,m-1|\,\hat{V}_M\,|b,j_2,m_2\rangle - \alpha^+(j_2,m_2)\,\langle a,j,m|\,\hat{V}_M\,|b,j_2,m_2+1\rangle$$
$$= \alpha^+(1,M)\,\langle a,j,m|\,\hat{V}_{M+1}\,|b,j_2,m_2\rangle$$

i.e.

$$\begin{aligned}&\alpha^+(1,M)\,\langle a,j,m|\,\hat{V}_{M+1}\,|b,j_2,m_2\rangle\\&+\alpha^+(j_2,m_2)\,\langle a,j,m|\,\hat{V}_M\,|b,j_2,m_2+1\rangle\\&=\alpha^-(j,m)\,\langle a,j,m-1|\,\hat{V}_M\,|b,j_2,m_2\rangle\end{aligned} \qquad (A.32)$$

This has the same form as A.29 with $j_1 = 1, m_1 = M$. Remember, there we said that A.29 is sufficient to get all coefficients for a given fixed set j, j_1, j_2 starting from just one of them. Since the recursion relation A.32 is formally the same, it means that within a given set of $(a, j; b, j_2)$ the matrix elements of all three components of $\hat{\mathbf{V}}$ between all pairs of m, m_2 are proportional to the $\langle j,m|\,|j_1 = 1, m_1 = M\rangle\,|j_2,m_2\rangle = C(j_1 = 1, m_1 = M; j_2, m_2|j,m)^*$. This gives 6.30, where $\langle a, j|\,|\hat{\mathbf{V}}|\,|b, j_2\rangle$ is the proportionality constant and can be determined by evaluating just one of the matrix elements on the left, i.e. for one set of m, M, m_2. Then one automatically has all of them. Eq. 6.30, compared with 6.16 suggests that $\hat{V}_M$ behaves similarly to a state with angular momentum quantum numbers $j_1 = 1, m_1 = M$. This also implies that the only nonzero matrix elements are such that $|j - j_2| \leq 1$ and $m = m_2 + M$.

A.18 Proof of Wigner Eckart's theorem for scalars

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A scalar operator $\hat{S}$ is per definition invariant under rotation, therefore

$$[\hat{S}, \mathbf{J}] = 0\,.$$

and consequently

$$[\hat{S}, \mathbf{J}^2] = 0\,.$$

Therefore $\hat{J}_z, \mathbf{J}^2$, and $\hat{S}$ have a common eigenbasis, or in other words, the quantum numbers j,m are not changed by $\hat{S}$. Let us see an example with $\mathbf{J}^2$:

$$0 = \langle a,j,m|\,[\mathbf{J}^2,\hat{S}]\,|b,j_2,m_2\rangle = \langle a,j,m|\,\mathbf{J}^2\,\hat{S}\,|b,j_2,m_2\rangle - \langle a,j,m|\,\hat{S}\,\mathbf{J}^2\,|b,j_2,m_2\rangle =$$

$$= (j(j+1) - j_2(j_2+1))\,\langle a,j,m|\,\hat{S}\,|b,j_2,m_2\rangle$$

Which means that $j = j_2$ or else $\langle a, j, m | \hat{S} | b, j_2, m_2 \rangle$ has to vanish. Here we have used the eigenvalue conditions, e.g. from the left $\langle a, j, m | \ \mathbf{J}^2 = j(j+1) \ \langle a, j, m|$. Similarly one shows that $m = m_2$ for the matrix element to be nonzero.
We only need to show that that this matrix element does not depend on m. For this we exploit the commutation with the ladder operators

$$[\hat{S}, \hat{J}_\pm] = 0 \, .$$

So taking $m_2 = m - 1$

$$\langle a, j, m | \mathbf{J}_+ \, \hat{S} | b, j, m-1 \rangle = \langle a, j, m | \hat{S} \, \mathbf{J}_+ | b, j, m-1 \rangle$$

Taking into accoun the fact that $\mathbf{J}_+$ acts as a $\mathbf{J}_-$ to the left, we have

$$\alpha^-(j,m) \langle a, j, m-1 | \hat{S} | b, j, m-1 \rangle = \alpha^+(j, m-1) \langle a, j, m | \hat{S} | b, j, m \rangle$$

where the α are the usual square root factors, see A.30 . Since $\alpha^-(j,m) = \alpha^+(j,m-1)$, this means that

$$\langle a, j, m-1 | \hat{S} | b, j, m-1 \rangle = \langle a, j, m | \hat{S} | b, j, m \rangle$$

Iterating this over the m, this means that the matrix element of the scalar is independent of m, i.e. 6.31 .

A.19 Some consideration about compex conjugation in Wigner-Eckart coefficients

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Notice that while

$$\langle a, j, m | \hat{V}_M | b, j_2, m_2 \rangle = \langle b, j_2, m_2 | \hat{V}_M^\dagger | a, j, m \rangle^*$$

and using the fact that $\hat{V}_M^\dagger = (-1)^M \hat{V}_{-M}$,

$$= (-1)^M \langle b, j_2, m_2 | \hat{V}_{-M} | a, j, m \rangle \ ,$$

there is no such simple relation between $\langle a, j | | \hat{\mathbf{V}} | | b, j_2 \rangle$ and $\langle b, j_2 | | \hat{\mathbf{V}} | | a, j \rangle$.
The reason is that (using again 6.30), and, say, $M = 0$ for simplicity

$$\langle b, j_2, m_2 | \hat{V}_0 | a, j, m \rangle = \langle j_2, m_2 | | j_1 = 1, m_1 = 0 \rangle | j, m \rangle \langle b, j_2 | | \hat{\mathbf{V}} | | a, j \rangle \ .$$

But, on the other hand, the two Clebsch-Gordan coefficients $\langle j, m | | j_1 = 1, m_1 = 0 \rangle | j_2, m_2 \rangle$ and $\langle j_2, m_2 | | j_1 = 1, m_1 = 0 \rangle | j, m \rangle$ are not necessarily related to each other by any kind of complex conjugation.
For example, take $j_2 = 0, m_2 = 0$ and $j = 1, m = 0$, then the first term is the coefficient of the expansion of $| j, m \rangle$ in $| 1, 0 \rangle | 0, 0 \rangle$, which is obviously 1. The second coefficient is (see table) $-1/\sqrt{3}$.

A.20 Proof of the projection theorem

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Consider that with the representation 6.29 the scalar product of two vectors reads

$$\hat{\mathbf{A}} \cdot \hat{\mathbf{B}} = \sum_M (-1)^M \hat{A}_M \hat{B}_{-M} \tag{A.33}$$

We evaluate

$$\begin{aligned}\langle n,j,m_1 | \hat{\mathbf{V}} \cdot \hat{\mathbf{J}} | n,j,m_2 \rangle &= \sum_M (-1)^M \langle n,j,m_1 | \hat{V}_M \hat{J}_{-M} | n,j,m_2 \rangle \\ = \sum_M (-1)^M \sum_{m'} \langle n,j,m_1 | \hat{V}_M | n,j,m' \rangle \langle n,j,m' | \hat{J}_{-M} | n,j,m_2 \rangle\end{aligned}$$

since $\hat{\mathbf{J}}$ does not change n, j. From 6.40 this becomes

$$\begin{aligned}&= \gamma(n,j) \sum_M (-1)^M \sum_{m'} \langle n,j,m_1 | \hat{J}_M | n,j,m' \rangle \langle n,j,m' | \hat{J}_{-M} | n,j,m_2 \rangle \\ &= \gamma(n,j) \langle n,j,m_1 | \hat{\mathbf{J}}^2 | n,j,m_2 \rangle\end{aligned}$$

i.e.

$$\gamma(n,j) = \frac{\langle n,j,m_1 | \hat{\mathbf{V}} \cdot \hat{\mathbf{J}} | n,j,m_2 \rangle}{\langle n,j,m_1 | \hat{\mathbf{J}}^2 | n,j,m_2 \rangle} \tag{A.34}$$

which gives 6.41 .

A.21 A representation of the delta distribution

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Die Funktion ist auf Eins normiert:

$$\int \Delta_t(\omega)\, d\omega = 1.$$

Das Verhalten von $\Delta_t(\omega)$ ist in Abbildung A.1 als Funktion von ω zu festem t wiedergegeben. Man erkennt, daß $\Delta_t(\omega)$ bei $\omega = 0$ konzentriert ist, eine Breite proportional zu $\frac{1}{t}$ und eine Höhe proportional zu t hat. Diese Funktion verhält sich im Limes $t \to \infty$ also wie die Delta-Funktion.

$$\lim_{t\to\infty} \int f(\omega)\, \Delta_t(\omega)\, d\omega = f(0) \qquad ,$$

vorausgesetzt, die Test-Funktion $f(\omega)$ hat die Eigenschaft $\lim_{\omega\to\infty} \frac{f(\omega)}{\omega} = 0$. Für diese Klasse von Funktionen gilt 3.26

$$\lim_{t\to\infty} \Delta_t(\omega) = \delta(\omega) \qquad .$$

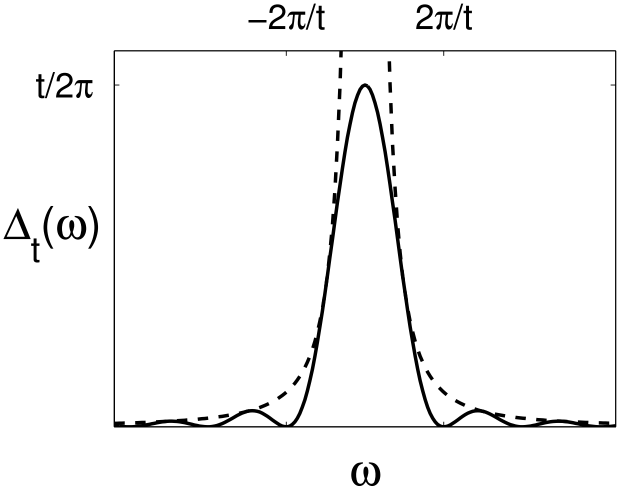

Figure A.1: *Plot der Funktion* $\Delta_t(\omega)$ *(durchgezogen) und der Einhüllenden* $\frac{2}{\omega_{fi}^2 t\pi}$ *(gestrichelt).*

A.22 Expectation values of interaction term

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To evaluate $\langle\Psi^{orb}|H_1^{orb}|\Psi^{orb}\rangle$, we insert the identity

$$\begin{aligned} \hat{I} = \quad & \hat{I}_1 \otimes \hat{I}_2 = \left(\int d\mathbf{r}_1 \left|\mathbf{r}_1\right\rangle \left\langle\mathbf{r}_1\right|\right) \otimes \left(\int d\mathbf{r}_2 \left|\mathbf{r}_2\right\rangle \left\langle\mathbf{r}_2\right|\right) \\ & = \int d\mathbf{r}_1 d\mathbf{r}_2 \;\; \left|\mathbf{r}_1\right\rangle \left|\mathbf{r}_2\right\rangle \left\langle\mathbf{r}_1\right| \left\langle\mathbf{r}_2\right| \end{aligned} \tag{A.35}$$

left and right of the interaction term: $\hat{H}_1^{orb} \Rightarrow \hat{I}\hat{H}_1^{orb}\hat{I}$, and use the fact that

$$\left\langle\mathbf{r}_1\right| \left\langle\mathbf{r}_2\right| \frac{1}{|\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|} \left|\mathbf{r}_1'\right\rangle \left|\mathbf{r}_2'\right\rangle = \delta(\mathbf{r}_1 - \mathbf{r}_1')\delta(\mathbf{r}_2 - \mathbf{r}_2') \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \; . \tag{A.36}$$

In this way,

$$\hat{H}_1^{orb} = \frac{1}{|\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|} = \int d\mathbf{r}_1 \; d\mathbf{r}_2 \;\; \left|\mathbf{r}_1\right\rangle \left|\mathbf{r}_2\right\rangle \;\; \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \;\; \left\langle\mathbf{r}_1\right| \left\langle\mathbf{r}_2\right| \tag{A.37}$$

Now, taking the expression for

$$\left|\Psi^{orb}\right\rangle = |n = 1, l = 0, m_l = 0\rangle_1 \otimes |n = 1, l = 0, m_l = 0\rangle_2 \equiv |\varphi_0\rangle_1 \otimes |\varphi_0\rangle_2$$

we get

$$\begin{aligned}\left\langle \Psi^{orb} \middle| \hat{H}_1^{orb} \middle| \Psi^{orb} \right\rangle = & \int d\mathbf{r}_1\, d\mathbf{r}_2\, \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}\, {}_1\langle \varphi_0 | \mathbf{r}_1 \rangle \langle \mathbf{r}_1 | \varphi_0 \rangle_1 \cdot \\ & \cdot {}_2\langle \varphi_0 | \mathbf{r}_2 \rangle \langle \mathbf{r}_2 | \varphi_0 \rangle_2 = \\ & = \int d\mathbf{r}_1\, d\mathbf{r}_2\, \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} | \langle \mathbf{r}_1 | \varphi_0 \rangle |^2 | \langle \mathbf{r}_2 | \varphi_0 \rangle |^2 = \\ & = \int d\mathbf{r}_1\, d\mathbf{r}_2\, \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} |\varphi_0(\mathbf{r}_1)|^2 |\varphi_0(\mathbf{r}_2)|^2 \qquad \text{(A.38)}\end{aligned}$$

A.23 Integral evaluation of 7.12

back to pag. 113 Wir wollen die Berechnung des Zwei-Zentren-Integrals 7.12 explizit vorführen. Da die Dichten rotationssymmetrisch sind, ist es sinnvoll, Kugelkoordinaten zu verwenden

$$\Delta E^{(1)} = \frac{Z}{32\pi^2} \int_0^\infty dx_1\, x_1^2\, e^{-x_1} \int_0^\infty dx_2\, x_2^2\, e^{-x_2} \int d\Omega_1 \int d\Omega_2\, \frac{1}{|\vec{x}_1 - \vec{x}_2|} \qquad .$$

Zur Auswertung des inneren Winkelintegrals legen wir die z-Achse in Richtung von $\vec{x}_1$. Man erhält dann ein vollständiges Differential

$$\begin{aligned}\int d\Omega_2\, \frac{1}{|\vec{x}_1 - \vec{x}_2|} &= 2\pi \int_0^\pi d\cos(\theta) \frac{1}{\sqrt{x_1^2 + x_2^2 - 2x_1x_2\cos(\theta)}} \\ &= 2\pi \int_{-1}^1 d\xi \frac{1}{\sqrt{x_1^2 + x_2^2 - 2x_1x_2\xi}} \\ &= -\frac{2\pi}{x_1x_2} \sqrt{x_1^2 + x_2^2 - 2x_1x_2\xi}\, \Bigg|_{\xi=-1}^{\xi=+1} \\ &= \frac{2\pi}{x_1x_2} \left(x_1 + x_2 - |x_1 - x_2| \right)\end{aligned}$$

Da es nun keine Winkelabhängigkeit mehr gibt, liefert das zweite Winkelintegral $\int d\Omega_2 = 4\pi$. Wenn wir schließlich die verbleibenden Radialanteile berechnen, erhalten wir

$$\begin{aligned}
\Delta E^{(1)} &= \frac{Z8\pi^2}{32\pi^2}\int_0^\infty dx_1\, x_1\, e^{-x_1}\int_0^\infty dx_2\, r_2\, e^{-x_2}\left(x_1+x_2-\left|x_1-x_2\right|\right)\\
&= \frac{Z}{4}\int_0^\infty dx_1\, x_1\, e^{-x_1}\left(2\int_0^{x_1} dx_2\, x_2^2\, e^{-x_2}+2x_1\int_{x_1}^\infty dx_2\, x_2\, e^{-2Zx_2}\right)\\
&= \frac{Z}{2}\int_0^\infty dx_1\, x_1\, e^{-x_1}\left(\underbrace{\int_0^{x_1} dx_2\, x_2^2\, e^{-x_2}}_{2-e^{-x_1}(2+2x_1+x_1^2)}+x_1\underbrace{\int_{x_1}^\infty dx_2\, x_2\, e^{-2Zx_2}}_{e^{-x_1}(1+x_1)}\right)
\end{aligned}$$

$$\begin{aligned}
&= \frac{Z}{2}\int_0^\infty dx_1\, x_1\, e^{-x_1}\left(2-e^{-x_1}(2+2x_1+x_1^2-x_1-x_1^2\right)\\
&= Z\left(\int_0^\infty dt\, t\, e^{-t}-\int_0^\infty dt\, t\, e^{-2t}-\frac{1}{2}\int_0^\infty dt\, t^2\, e^{-2t}\right)\\
&= Z\left(\int_0^\infty dt\, t\, e^{-t}-\frac{1}{4}\int_0^\infty dx\, x\, e^{-x}-\frac{1}{16}\int_0^\infty dx\, x^2\, e^{-x}\right)\\
&= Z\left(\Gamma(2)-\frac{1}{4}\Gamma(2)-\frac{1}{16}\Gamma(3)\right)=Z\left(1--\frac{1}{4}-\frac{1}{8}\right)=\frac{5}{8}Z \quad .
\end{aligned}$$

Wir haben somit 7.13 .

A.24 Example of evaluation of matrix elements in product states

back to pag. 116 As an example, we determine the last matrix element in 7.16 .

$$\left(\langle 2lm|_1\otimes\langle 100|_2\right)\frac{1}{|\hat{\mathbf{r}}_1-\hat{\mathbf{r}}_2|}\left(|100\rangle_1\otimes|2lm\rangle_2\right)$$

To do this, we insert the identity

$$I=\int d\mathbf{r}_1 d\mathbf{r}_2\; |\mathbf{r}_1\rangle_1\,|\mathbf{r}_2\rangle_2\,\langle\mathbf{r}_1|_1\,\langle\mathbf{r}_2|_2$$

$$\int d\mathbf{r}_1 d\mathbf{r}_2\left(\langle 2lm|_1\otimes\langle 100|_2\right)\frac{1}{|\hat{\mathbf{r}}_1-\hat{\mathbf{r}}_2|}|\mathbf{r}_1\rangle_1\,|\mathbf{r}_2\rangle_2\,\langle\mathbf{r}_1|_1\,\langle\mathbf{r}_2|_2\left(|100\rangle_1\otimes|2lm\rangle_2\right)$$

Since $|\mathbf{r}_1\rangle_1\,|\mathbf{r}_2\rangle_2$ is an eigenstate of $\frac{1}{|\hat{\mathbf{r}}_1-\hat{\mathbf{r}}_2|}$ this becomes

$$\int d\mathbf{r}_1 d\mathbf{r}_2\left(\langle 2lm|_1\otimes\langle 100|_2\right)|\mathbf{r}_1\rangle_1\,|\mathbf{r}_2\rangle_2\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}\langle\mathbf{r}_1|_1\,\langle\mathbf{r}_2|_2\left(|100\rangle_1\otimes|2lm\rangle_2\right)$$

$$= \int d\mathbf{r}_1 d\mathbf{r}_2 \langle 2lm|_1 \, |\mathbf{r}_1\rangle_1 \, \langle 100|_2 \, |\mathbf{r}_2\rangle_2 \, \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \, \langle \mathbf{r}_1|_1 \, |100\rangle_1 \, \langle \mathbf{r}_2|_2 \, |2lm\rangle_2$$

$$= \int d\mathbf{r}_1 d\mathbf{r}_2 \varphi^*_{2lm}(\mathbf{r}_1) \varphi^*_{100}(\mathbf{r}_2) \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \varphi_{100}(\mathbf{r}_1) \varphi_{2lm}(\mathbf{r}_2)$$

which corresponds to the exchange term in 7.17

A.25 Some proofs for Chap. 8

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Equivalence of 8.5 and 8.4

Using a discrete version of the derivative $u'_i = \frac{u_i - u_{i-1}}{\Delta x}$ together with 8.6 , we have for the r.h.s. of 8.5 [2]

$$\frac{1}{\Delta x} \frac{\partial \mathscr{L}}{\partial u_i} = \frac{\partial \ell_i}{\partial u_i} + \frac{1}{\Delta x} \frac{\partial \ell_i}{\partial u'_i} - \frac{1}{\Delta x} \frac{\partial \ell_{i+1}}{\partial u'_{i+1}} \underset{\Delta x \to 0}{\Rightarrow} \frac{\partial \ell}{\partial u} - \frac{d}{dx} \frac{\partial \ell}{\partial u'} \tag{A.39}$$

where $\ell_i \equiv \ell(u_i, u'_i, \dot{u}_i, x_i, t)$. This gives 8.4 . An alternative derivation is by partial integration.

Canonical commutation rules for the $\hat{p}_m$, $\hat{q}_m$

$$\begin{aligned}
[\hat{q}_m, \hat{p}_{m'}] &= \int_0^L dx \int_0^L dx' \, U_m(x) \, U_{m'}(x') \, [\hat{u}(x), \hat{\pi}(x')] \\
&= i\hbar \int_0^L dx \int_0^L dx' \, U_m(x) \, U_{m'}(x') \, \delta(x - x') \\
&= i\hbar \int_0^L dx \, U_m(x) \, U_{m'}(x) \\
&= i\hbar \delta_{m,m'} \, .
\end{aligned} \tag{A.40}$$

---

[2] Strictly speaking for all i but the last one.

Hamiltonian 8.11 in terms of $\hat{p}_m$, $\hat{q}_m$.

$$\begin{aligned}
\hat{H} &= \frac{1}{2}\sum_{n,m}\int_0^L \left[\frac{1}{\rho}U_n(x)U_m(x)\hat{p}_n\hat{p}_m + c^2\ \rho\ U_n'(x)U_m'(x)\ \hat{q}_n\hat{q}_m\right]\ dx \\
&= \frac{1}{2\rho}\sum_{n,m}\underbrace{\int_0^L U_n(x)U_m(x)\ dx}_{\delta_{n,m}}\hat{p}_n\hat{p}_m + \frac{c^2\ \rho}{2}\sum_{n,m}\underbrace{\int_0^L U_n'(x)U_m'(x)\ dx}_{k_n^2\delta_{n,m}}\ \hat{q}_n\hat{q}_m \\
&= \frac{1}{2}\sum_n\left(\frac{1}{\rho}\hat{p}_n^2 + \rho\ (c\ k_n)^2\ \hat{q}_n^2\right) .
\end{aligned}$$

We have used the fact that

$$\int_0^L U_n'(x)U_m'(x)\ dx = k_n^2\ \delta_{n,m} \tag{A.41}$$

proof:

$$\begin{aligned}
\int_0^L U_n'(x)U_m'(x)\ dx &= \underbrace{U_n'(x)U_m(x)\Big|_0^L}_{=0} - \int_0^L \underbrace{U_n''(x)}_{=-k_n^2U_n(x)}\ U_m(x)\ dx \\
&= k_n^2\int_0^L U_n(x)U_m(x)\ dx = k_n^2\delta_{n,m} .
\end{aligned}$$

A.26 Proof of 9.3

back to pag. 126 First we transform the Lagrangian a little bit. We exploit the fact that

$$\boldsymbol{\nabla}\left(\Psi^*\boldsymbol{\nabla}\Psi - (\boldsymbol{\nabla}\Psi^*)\Psi\right) = \left(\Psi^*\boldsymbol{\nabla}^2\Psi - (\boldsymbol{\nabla}^2\Psi^*)\Psi\right) .$$

After integration over the volume the first term gives a surface integral (Gauss' law), which vanishes in an infinite volume. Then 9.1 becomes

$$\mathscr{L} = \int\left[i\hbar\Psi^*\dot{\Psi} + \frac{\hbar^2}{2m}(\boldsymbol{\nabla}^2\Psi^*)\Psi - V(\mathbf{x})\Psi^*\Psi\right]\ d^3x . \tag{A.42}$$

So that

$$\begin{aligned}
\pi(\mathbf{x},t) &= \frac{\delta\mathscr{L}}{\delta\dot{\Psi}} = i\hbar\Psi^*(\mathbf{x},t) \\
\frac{\delta\mathscr{L}}{\delta\Psi} &= -V(\mathbf{x})\Psi^*(\mathbf{x},t) + \frac{\hbar^2}{2m}\boldsymbol{\nabla}^2\Psi^*
\end{aligned}$$

Lagrange II:

$$-i\hbar\dot{\Psi}^*(\mathbf{x},t) = V(\mathbf{x})\Psi^*(\mathbf{x},t) - \frac{\hbar^2}{2m}\boldsymbol{\nabla}^2\Psi^*$$

A.27 Gauge transformation for the wave function

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For simplicity, we work in units in which $\hbar = c = 1$. Using 4.11, we can rewrite 4.13 as

$$i\overline{\partial_t}\Psi' = \frac{1}{2m}\left(\overline{\mathbf{p}} - q\mathbf{A}\right)^2\Psi' + q\varphi\,\Psi' \tag{A.43}$$

with

$$\overline{\mathbf{p}} \equiv \mathbf{p} - q\boldsymbol{\nabla}\chi \qquad i\overline{\partial}_t \equiv i\partial_t + q\partial_t\chi \tag{A.44}$$

Applying these to the transformed wave function 4.12, we observe that

$$\begin{aligned}\overline{\mathbf{p}}\,\Psi' &= -i\boldsymbol{\nabla}\Psi' - \Psi'\,q\boldsymbol{\nabla}\chi = \Psi'\,q\boldsymbol{\nabla}\chi + e^{iq\chi(\mathbf{r},t)}(-i\boldsymbol{\nabla}\Psi) - \Psi'\,q\boldsymbol{\nabla}\chi\\ &= e^{iq\chi(\mathbf{r},t)}\mathbf{p}\,\Psi \end{aligned}\tag{A.45}$$

similarly

$$i\overline{\partial_t}\,\Psi' = -\Psi'\,q\,\partial_t\chi + e^{iq\chi(\mathbf{r},t)}\,i\partial_t\Psi + \Psi'\,q\,\partial_t\chi = e^{iq\chi(\mathbf{r},t)}\,i\partial_t\Psi \tag{A.46}$$

In other words,

$$\overline{\mathbf{p}}\,e^{iq\chi(\mathbf{r},t)} = e^{iq\chi(\mathbf{r},t)}\,\mathbf{p} \qquad \overline{\partial_t}\,e^{iq\chi(\mathbf{r},t)} = e^{iq\chi(\mathbf{r},t)}\,\partial_t \tag{A.47}$$

Therefore, when applying the differential operators $\overline{p}$ and $\overline{\partial}_t$, they "move" the $e^{iq\chi(\mathbf{r},t)}$ to the left and "lose" the $\overline{\cdots}$. Therefore, A.43 becomes

$$e^{iq\chi(\mathbf{r},t)}\,i\partial_t\Psi = e^{iq\chi(\mathbf{r},t)}\left(\frac{1}{2m}\left(\mathbf{p} - q\mathbf{A}\right)^2\Psi + q\varphi\Psi\right)$$

which is equivalent to 4.8.

A.28 Commutators and relation for the Schrödinger field quantisation

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We consider a more general case, namely 9.15, of which 9.9 is a special case. First of all one can invert the 9.15 in the usual way by scalar multiplication with the wave functions: e.g. $\int \chi_m^*(\mathbf{y})\,d\mathbf{y}\cdots$. The first term gives

$$\hat{c}_m = \int \chi_m^*(\mathbf{y})\,d\mathbf{y}\,\hat{\Psi}(\mathbf{y}) \tag{A.48}$$

the other one is the hermitian conjugate

$$\hat{c}_n^\dagger = \int \chi_n(\mathbf{z})\, d\mathbf{z}\, \hat{\Psi}^\dagger(\mathbf{z})$$

so that the commutation rules become

$$[c_m, c_n^\dagger] = \int d\mathbf{y}\, d\mathbf{z}\, \chi_m^*(\mathbf{y})\chi_n(\mathbf{z})\delta(\mathbf{y}-\mathbf{z}) = \delta_{m,n}$$

The above proof have simply made use of the fact that the χ_m are a complete, orthogonal basis set, so this holds obviously for the b_n and 9.9 as well.
We now consider the Hamiltonian 9.11a , using 9.15 . But this is easily generalizable for arbitrary single particle operators:

$$\hat{H}_{ZQ} = \int \hat{\Psi}^\dagger(\mathbf{x}) \left[-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V(x)\right] \hat{\Psi}(\mathbf{x})\, d\mathbf{x} =$$

$$= \sum_n \hat{c}_n^\dagger \sum_m \hat{c}_m \underbrace{\int d^3x\, \chi_n^*(\mathbf{x}) \left[-\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + V(x)\right] \chi_m(\mathbf{x})}_{h_{n,m}}$$

For the case in which χ_n are replaced by the φ_n, the eigenfunctions of the Hamiltonian, then clearly $h_{n,m} = E_n\delta_{n,m}$.

A.29 Normalisation of two-particle state

back to pag. 135 Wir wollen zunächst die Normierung des Vektors bestimmen. Für $\nu = \mu$ kennen wir die Normierung schon $Z_{\nu\nu} = \sqrt{2!}$. Für $\nu \neq \mu$ erhalten wir

$$Z_{\nu\mu}^2 = \langle 0|b_\mu b_\nu b_\nu^\dagger b_\mu^\dagger|0\rangle\ .$$

Wir bringen den Vernichter b_ν ganz nach rechts, da dann $b_\nu|0\rangle$ verschwindet.

$$b_\nu b_\nu^\dagger b_\mu^\dagger|0\rangle = b_\nu^\dagger b_\nu b_\mu^\dagger|0\rangle + b_\mu^\dagger|0\rangle$$

$$\overset{\mu\neq\nu}{=} b_\nu^\dagger b_\mu^\dagger \underbrace{b_\nu|0\rangle}_{=0} + b_\mu^\dagger|0\rangle = b_\mu^\dagger|0\rangle\ .$$

Nun multiplizieren wir noch von links mit dem Vernichter b_μ und bringen ihn ebenfalls nach rechts

$$b_\mu b_\nu b_\nu^\dagger b_\mu^\dagger|0\rangle = b_\mu b_\mu^\dagger|0\rangle = b_\mu^\dagger \underbrace{b_\mu|0\rangle}_{=0} + |0\rangle = |0\rangle$$

und die gesuchte Normierung ist

$$Z_{\nu\mu}^2 = \langle 0|0\rangle = 1\ .$$

A.30 Commutations rules

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$$[a\, b, c] = abc - cab$$

$$a[b,c] + [a,c]b = abc - acb + acb - cab = abc - cab$$

$$a\{b,c\} - \{a,c\}b = abc + acb - acb - cab = abc - cab$$

which proves 9.30 .
9.31 is proven by observing that all terms are just minus the ones occurring in 9.30

A.31 Lagrangian for electromagnetic field

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First, observe that

$$2(\nabla \times \mathbf{A})^2 = \sum_{ij} \left(\partial_i A_j - \partial_j A_i\right)^2 = 2\sum_{ij} \left(\partial_i A_j\right)\left(\partial_i A_j - \partial_j A_i\right) =$$

The first equality is because in the sum over i, j only terms $i \neq j$ contribute. Consider the case $i = 1, j = 2$, this gives $(\nabla \times \mathbf{A})_z^2$, the same for $i = 2, j = 1$, which gives a factor 2. Then, similarly $2,3$ gives the x component, and $3,1$ the y component. The second equality is obtained by expanding and interchanging indices One can, thus, write

$$(\nabla \times \mathbf{A})^2 = \sum_{ij} \partial_i \left(A_j \left(\partial_i A_j - \partial_j A_i\right)\right) - \sum_{ij} A_j \partial_i \left(\partial_i A_j - \partial_j A_i\right)$$

The first term on the r.h.s. is a divergence, which, integrated over a volume, can be transformed into a surface integral. Taking the surface at infinity, this term can be made to vanish. The second term can be simplified due to te fact that from 10.2 $\partial_i A_i = 0$. Thus the only contribution left is

$$-\sum_{ij} A_j \partial_i^2 A_j$$

giving for 10.4

$$\mathscr{L} = \mu \int d^3\mathbf{r} \frac{1}{2} \left(\dot{\mathbf{A}}^2 + \sum_i A_i \nabla^2 A_i\right) \tag{A.49}$$

We thus have the two terms of the Lagrange equation (cf. 10.5)

$$\frac{d}{dt}\Pi_i = \mu \ddot{A}_i$$

$$\frac{\delta \mathscr{L}}{\delta A_i} = \mu \boldsymbol{\nabla}^2 A_i \, .$$

Setting then equal gives indeed 10.3

A.32 Integrals vs sums

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We use the fact that

$$\frac{1}{\Omega}\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} = \delta(\mathbf{r}-\mathbf{r}')$$

which is due to the **completeness** of the basis $\frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{\sqrt{\Omega}}$.
Alternatively a convenient proof is obtained in the infinite volume $\Omega \to \infty$ limit. Here, one can convert the sum over $\mathbf{k}$ into an integral. The discrete $\mathbf{k}$ are due to the finite "box" as $\mathbf{k} = \frac{2\pi}{L}(n_1, n_2, n_3)$ (cf. 10.12). Therefore in the $L \to \infty$ limit, each point $\mathbf{k}$ can be replaced by the small cube of volume $\Delta k^3 = \left(\frac{2\pi}{L}\right)^3$ around it. Thus,

$$\Delta k^3 \sum_{\mathbf{k}} \cdots \to \int d^3k \cdots$$

which gives

$$\frac{1}{\Omega}\sum_{\mathbf{k}} \cdots = \frac{1}{\Omega \Delta k^3}\int d^3k \, \cdots = \frac{1}{\Omega}\left(\frac{L}{2\pi}\right)^3 \int d^3k \, \cdots = \int \frac{d^3k}{(2\pi)^3} \, \cdots \, . \tag{A.50}$$

Therefore, one has

$$\frac{1}{\Omega}\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} \to \int \frac{d^3k}{(2\pi)^3} e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')} = \delta(\mathbf{r}-\mathbf{r}')$$

A.33 Commutators and transversality condition

back to pag. 156 The commutation rules 10.8 and 10.14 are in contradiction with the transversality condition 10.2 .
To see this, just take the divergence

$$[\underbrace{\partial_n \cdot \hat{A}_n(\mathbf{r})}_{\boldsymbol{\nabla}\cdot\mathbf{A}=0}, \hat{\Pi}_m(\mathbf{r}')] = i\hbar \, \delta_{n,m}\partial_n \delta(\mathbf{r}-\mathbf{r}')$$

The left-hand side vanishes identically, while the right hand side does not.
This holds equivalently for 10.14 , which is its Fourier transform. Multiply 10.14 with $k_n k'_m$ and sum over n, m:

$$[\underbrace{\sum_n k_n \hat{A}_{n\mathbf{k}}}_{\mathbf{k}\cdot\hat{\mathbf{A}}_{\mathbf{k}}=0}, \sum_m \hat{\Pi}_{m-\mathbf{k}'} k'_m] = i\hbar \sum_{nm} k_n k'_m \delta_{nm}\ \delta_{\mathbf{k}\mathbf{k}'} = i\hbar\ |\mathbf{k}|^2\ \delta_{\mathbf{k}\mathbf{k}'}$$

A.34 Commutators of fields

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The completeness of the triplet $\{\mathbf{u}_{\mathbf{k},-1}, \mathbf{u}_{,k1}, \frac{\mathbf{k}}{k}\}$ gives

$$\sum_s u_{n\mathbf{k},s} u_{m\mathbf{k},s} + \frac{k_n k_m}{k^2} = \delta_{n,n}$$

Therefore, the commutator

$$\begin{aligned}[\hat{A}_{n\mathbf{k}}, \hat{\Pi}_{m-\mathbf{k}'}] &= \sum_{ss'} u_{n\mathbf{k},s} u_{m-\mathbf{k}',-s'} [\hat{q}_{\mathbf{k}s}, \hat{p}_{-\mathbf{k}'-s'}] \\ &= \sum_s u_{n\mathbf{k},s} u_{m\mathbf{k},s} = \delta_{n,m} - \frac{k_n k_m}{k^2} \ .\end{aligned}$$

A.35 Fourier transform of Coulomb potential

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$$\begin{aligned}V(\Delta\mathbf{q}) &= \frac{-Ze^2}{\Omega} \int \frac{e^{i\mathbf{x}\Delta\mathbf{q}}}{r}\, d^3\mathbf{x} \\ &= \frac{-Ze^2}{\Omega} \int_0^{2\pi} d\varphi \int_{-1}^{1} d\xi \int_0^{\infty} r^2 dr \frac{e^{ir|\Delta\mathbf{q}|\xi}}{r} \\ &= \frac{-2\pi Ze^2}{\Omega} \int_0^{\infty} dr r \int_{-1}^{1} d\xi\, e^{ir|\Delta\mathbf{q}|\xi} \\ &= \frac{-2\pi Ze^2}{\Omega} \int_0^{\infty} dr r \frac{e^{ir|\Delta\mathbf{q}|} - e^{-ir|\Delta\mathbf{q}|}}{ir|\Delta\mathbf{q}|}\end{aligned}$$

$$
\begin{aligned}
&= \frac{-2\pi Ze^2}{i\Omega|\Delta q|}\int_0^\infty dr\left(e^{ir|\Delta\mathbf{q}|}-e^{-ir|\Delta\mathbf{q}|}\right)\\
&= \frac{-2\pi Ze^2}{i\Omega|\Delta q|}\left(\frac{-1}{i|\Delta\mathbf{q}|}-\frac{-1}{-i|\Delta\mathbf{q}|}\right)\\
&= \frac{-2\pi Ze^2}{i\Omega|\Delta q|^2}
\end{aligned}
$$

Der Beitrag von der oberen Integrationsgrenze führt zu einer unendlich stark oszillierenden Funktion, die verschwindet bereits, wenn man über ein infinitesimales $\Delta\mathbf{q}$ integriert. Integrale über $\mathbf{q}$ werden in der weiteren Rechnung noch auftreten und somit ist $V(\mathbf{q})$ bewiesen.

A.36 (No) energy conservation for the first-order process 11.34

back to pag. 175 To show that momentum and energy cannot be simultaneously conserved in the process 11.34 , let us work in the reference frame in which the initial electron is at rest $\mathbf{q}_i = 0$. Then, the initial energy $E_i = 0$ is also zero. By momentum conservation, then $\mathbf{q}_f = -\mathbf{k}$. Since $\mathbf{k}$ cannot be zero, the final energy $E_f > 0$, which is incompatible with energy conservation.

A.37 Green's function for scattering

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We prove that 12.10 is a solution of 12.9 . We take $\mathbf{r} = \mathbf{x} - \mathbf{x}'$. We start with an

A.37.1 Euristic proof:

$$-\boldsymbol{\nabla}^2 \frac{e^{ikr}}{r} = -(\boldsymbol{\nabla}^2_{reg} + \boldsymbol{\nabla}^2_{sing})\frac{e^{ikr}}{r} =$$

We have divided the Laplace operator here in a regular and in a singular part, the latter due to the singularity at $r = 0$, and, accordingly, nonzero only close to $r = 0$. For the singularity part we have

$$\boldsymbol{\nabla}^2_{sing}\frac{e^{ikr}}{r} = \boldsymbol{\nabla}^2_{sing}\frac{1}{r} = -4\pi\delta^3(\mathbf{r})$$

where the last equality is a well-known result of electrostatics (cf. potential of a point charge), and the first is due to the fact that we are close to $r = 0$.

For the regular part, we can use the Laplace operator in polar coordinates

$$\nabla^2_{reg} f(r) = \frac{1}{r}\frac{\partial^2}{\partial r^2}(rf(r)) = \frac{1}{r}(-k^2)e^{ikr}$$

So that in total we have

$$-(\nabla^2_{reg} + \nabla^2_{sing})\frac{e^{ikr}}{r} = k^2\,\frac{e^{ikr}}{r} + 4\pi\delta^3(\mathbf{r})$$

i.e. 12.9 :

$$(\nabla^2 + k^2)\frac{e^{ikr}}{r} = -4\pi\delta^3(\mathbf{r})$$

A more rigorous proof:

A.37.2 Proof via residue's theorem

TODO

A.38 Green's function in 1D

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$$\frac{d}{dx}e^{ik|x|} = ike^{ik|x|}\mathrm{sign}x \tag{A.51}$$

$$\frac{d^2}{dx^2}e^{ik|x|} = ik\frac{d}{dx}(e^{ik|x|}\mathrm{sign}x) = ik(ike^{ik|x|} + e^{ik|x|}2\delta(x)) = -k^2e^{ik|x|} + 2ik\delta(x)$$

$$-\frac{i}{2k}\left(k^2 + \frac{d^2}{dx^2}\right)e^{ik|x|} = \delta(x)$$