

Quantum Mechanics 2
Lecture notes
(without Relativistic Quantum Mechanics)

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1 Addition of angular momenta

Let \vec{J}_1 and \vec{J}_2 be two angular momentum operators acting on different Hilbert spaces,

$$\vec{J}_i : \mathcal{H}_i \rightarrow \mathcal{H}_i \quad (i = 1, 2), \quad (1)$$

which satisfy the angular momentum algebra,

$$\vec{J}_i \times \vec{J}_i = i\hbar\vec{J}_i. \quad (2)$$

The common eigenvector of $J_{i,z}$ and J^2 is denoted by $|j_i, m_i\rangle \in \mathcal{H}_i$, where $j_i = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots$ and $m_i \in [-j_i, -j_i + 1, \dots, j_i - 1, j_i]$,

$$J_{i,z} |j_i, m_i\rangle = \hbar m_i |j_i, m_i\rangle \quad (3)$$

$$J_i^2 |j_i, m_i\rangle = \hbar^2 j_i(j_i + 1) |j_i, m_i\rangle \quad (4)$$

$$J_{i,\pm} |j_i, m_i\rangle = \hbar \sqrt{j_i(j_i + 1) - m_i(m_i \pm 1)} |j_i, m_i \pm 1\rangle, \quad (5)$$

where the raising and lowering operators, $J_{i,+}$ and $J_{i,-}$, are defined as $J_{i,\pm} = J_{i,x} \pm iJ_{i,y}$.

We extend these operators to the tensor product Hilbert space $\mathcal{H}_1 \otimes \mathcal{H}_2$ as

$$\vec{J}_i : \mathcal{H}_1 \otimes \mathcal{H}_2 \rightarrow \mathcal{H}_1 \otimes \mathcal{H}_2, \quad (6)$$

$$\vec{J}_1 \rightarrow \vec{J}_1 \otimes \mathbb{I}_2, \quad \vec{J}_2 \rightarrow \mathbb{I}_1 \otimes \vec{J}_2, \quad (7)$$

where \mathbb{I}_i is the identity operator on the Hilbert space \mathcal{H}_i . This means that \vec{J}_i acts in \mathcal{H}_i as in Eqs. (3), (4), and (5), while it keeps the vectors of other Hilbert space unchanged. Accordingly, the action of the operator \vec{J}_1 on a vector $|j_1, m_1\rangle \otimes |j_2, m_2\rangle \in \mathcal{H}_1 \otimes \mathcal{H}_2$ is (from now neglecting the notation \otimes from the tensor product vectors):

$$J_{1,z} |j_1, m_1\rangle |j_2, m_2\rangle = \hbar m_1 |j_1, m_1\rangle |j_2, m_2\rangle, \quad (8)$$

$$J_1^2 |j_1, m_1\rangle |j_2, m_2\rangle = \hbar^2 j_1(j_1 + 1) |j_1, m_1\rangle |j_2, m_2\rangle, \quad (9)$$

$$J_{1,\pm} |j_1, m_1\rangle |j_2, m_2\rangle = \hbar \sqrt{j_1(j_1 + 1) - m_1(m_1 \pm 1)} |j_1, m_1 \pm 1\rangle |j_2, m_2\rangle, \quad (10)$$

and similar for \vec{J}_2 . Obviously, the operators \vec{J}_1 and \vec{J}_2 commute and their sum $\vec{J} = \vec{J}_1 + \vec{J}_2$ is also an angular momentum operator. Namely,

$$\begin{aligned} \vec{J} \times \vec{J} &= (\vec{J}_1 + \vec{J}_2) \times (\vec{J}_1 + \vec{J}_2) \\ &= \vec{J}_1 \times \vec{J}_1 + \underbrace{\vec{J}_1 \times \vec{J}_2 + \vec{J}_2 \times \vec{J}_1}_0 + \vec{J}_2 \times \vec{J}_2 \\ &= i\hbar\vec{J}_1 + i\hbar\vec{J}_2 = i\hbar\vec{J}. \end{aligned} \quad (11)$$

Note that the second and third terms in the second row cancel each other because the vector product is antisymmetric. Consequently, the common eigenvector of J_z and J^2 , $|j, m\rangle \in \mathcal{H}_1 \otimes \mathcal{H}_2$, satisfy

$$J_z |j, m\rangle = \hbar m |j, m\rangle \quad (12)$$

$$J^2 |j, m\rangle = \hbar^2 j(j + 1) |j, m\rangle \quad (13)$$

$$J_{\pm} |j, m\rangle = \hbar \sqrt{j(j + 1) - m(m \pm 1)} |j, m \pm 1\rangle. \quad (14)$$

We will demonstrate how the above eigenvectors $|j, m\rangle$ can be constructed for *given values* of j_1 and j_2 as a linear combination of the $|j_1, m_1\rangle |j_2, m_2\rangle$ tensor product states,

$$|j, m\rangle = \sum_{m_1, m_2} C(j_1 m_1, j_2 m_2 | j, m) |j_1, m_1\rangle |j_2, m_2\rangle . \quad (15)$$

The $C(j_1 m_1, j_2 m_2 | j, m)$ coefficients, or with other famous notation $\langle j_1 m_1, j_2 m_2 | j, m \rangle$, are called the Clebsch–Gordan coefficients. According to the usual convention, we choose them to be real. Note that the dimension of the subspace in $\mathcal{H}_1 \otimes \mathcal{H}_2$ spanned by the states $|j_1, m_1\rangle |j_2, m_2\rangle$ is $(2j_1 + 1)(2j_2 + 1)$, which - as shown by representation theory - can be decomposed as a direct sum of the eigensubspaces (irreducible representations) of J_z and J^2 . From this it also follows that on this subspace we can combine $(2j_1 + 1)(2j_2 + 1)$ common eigenvectors of J_z and J^2 .

The action of J_z on the state in (15) can be expressed as

$$\begin{aligned} J_z |j, m\rangle &= (J_{1,z} + J_{2,z}) \sum_{m_1, m_2} C(j_1 m_1, j_2 m_2 | j, m) |j_1, m_1\rangle |j_2, m_2\rangle \\ &= \sum_{m_1, m_2} \hbar(m_1 + m_2) C(j_1 m_1, j_2 m_2 | j, m) |j_1, m_1\rangle |j_2, m_2\rangle \\ &= \hbar(m_1 + m_2) |j, m\rangle , \end{aligned} \quad (16)$$

which together with Eq. (12) leads to

$$\sum_{m_1, m_2} \hbar(m_1 + m_2 - m) C(j_1 m_1, j_2 m_2 | j, m) |j_1, m_1\rangle |j_2, m_2\rangle = 0 . \quad (17)$$

Since the states $|j_1, m_1\rangle |j_2, m_2\rangle$ are orthonormal, therefore, also linearly independent,

$$(m_1 + m_2 - m) C(j_1 m_1, j_2 m_2 | j, m) = 0 , \quad (18)$$

from which we conclude that $C(j_1 m_1, j_2 m_2 | j, m) = 0$ if $m \neq m_1 + m_2$. This condition is usually written as the first rule for the Clebsch-Gordan coefficients,

$$m = m_1 + m_2 . \quad (19)$$

This also implies that, for *given* j_1 and j_2 , the maximum of the possible m quantum numbers is $j_1 + j_2$, therefore j can not be larger than $j_1 + j_2$, i.e., for $j > j_1 + j_2$ $C(j_1 m_1, j_2 m_2 | j, m) = 0$.

Statement:

$$|j_1 + j_2, j_1 + j_2\rangle = |j_1, j_1\rangle |j_2, j_2\rangle , \quad (20)$$

i.e.

$$C(j_1 j_1, j_2 j_2 | j_1 + j_2, j_1 + j_2) = 1 . \quad (21)$$

Proof:

On the one hand,

$$\begin{aligned} J_z |j_1, j_1\rangle |j_2, j_2\rangle &= (J_{1,z} + J_{2,z}) |j_1, j_1\rangle |j_2, j_2\rangle \\ &= \hbar(j_1 + j_2) |j_1, j_1\rangle |j_2, j_2\rangle . \end{aligned} \quad (22)$$

On the other hand,

$$\begin{aligned} J^2 &= \left(\vec{J}_1 + \vec{J}_2 \right)^2 = J_1^2 + J_2^2 + 2\vec{J}_1 \vec{J}_2 = J_1^2 + J_2^2 + 2J_{1,x} J_{2,x} + 2J_{1,y} J_{2,y} + 2J_{1,z} J_{2,z} \\ &= J_1^2 + J_2^2 + 2J_{1,z} J_{2,z} + J_{1,+} J_{2,-} + J_{1,-} J_{2,+} , \end{aligned} \quad (23)$$

therefore, using the actions of the tensor product operators (8), (9), and (10),

$$\begin{aligned} J^2 |j_1, j_1\rangle |j_2, j_2\rangle &= \hbar^2 (j_1(j_1 + 1) + j_2(j_2 + 1) + 2j_1j_2) |j_1, j_1\rangle |j_2, j_2\rangle \\ &\quad + \underbrace{J_{1,+} |j_1, j_1\rangle}_{|0\rangle_1} J_{2,-} |j_2, j_2\rangle + J_{1,-} |j_1, j_1\rangle \underbrace{J_{2,+} |j_2, j_2\rangle}_{|0\rangle_2} \\ &= \hbar^2 (j_1 + j_2) (j_1 + j_2 + 1) |j_1, j_1\rangle |j_2, j_2\rangle , \end{aligned} \quad (24)$$

where $|0\rangle_i$ is the zero vector of the Hilbert space, \mathcal{H}_i .

Let us introduce the notation $j_{\max} = j_1 + j_2$. It is obvious that the successive action of the lowering operator $J_- = J_{1,-} + J_{2,-}$ starting from the state $|j_{\max}, j_{\max}\rangle$ generates the states $|j_{\max}, m\rangle$, $m \in [-j_{\max}, -j_{\max} + 1, \dots, j_{\max} - 1]$. This procedure yields $2j_{\max} + 1$ eigenstates of J_z and J^2 .

Example: The calculation of the Clebsch–Gordan coefficients for $|j_{\max}, j_{\max} - 1\rangle$. Acting on both sides of Eq. (20) with J_- ,

$$J_- |j_1 + j_2, j_1 + j_2\rangle = \hbar\sqrt{2(j_1 + j_2)} |j_1 + j_2, j_1 + j_2 - 1\rangle \quad (25)$$

$$(J_{1,-} + J_{2,-}) |j_1, j_1\rangle |j_2, j_2\rangle = \hbar\sqrt{2j_1} |j_1, j_1 - 1\rangle |j_2, j_2\rangle + \hbar\sqrt{2j_2} |j_1, j_1\rangle |j_2, j_2 - 1\rangle , \quad (26)$$

it immediately follows that

$$|j_1 + j_2, j_1 + j_2 - 1\rangle = \sqrt{\frac{j_1}{j_1 + j_2}} |j_1, j_1 - 1\rangle |j_2, j_2\rangle + \sqrt{\frac{j_2}{j_1 + j_2}} |j_1, j_1\rangle |j_2, j_2 - 1\rangle , \quad (27)$$

i.e. the corresponding Clebsch–Gordan coefficients are:

$$C(j_1, j_1 - 1; j_2, j_2 | j_1 + j_2, j_1 + j_2 - 1) = \sqrt{\frac{j_1}{j_1 + j_2}} \quad (28)$$

$$C(j_1, j_1; j_2, j_2 - 1 | j_1 + j_2, j_1 + j_2 - 1) = \sqrt{\frac{j_2}{j_1 + j_2}} . \quad (29)$$

Obviously,

$$(2j_1 + 1)(2j_2 + 1) = 2(j_1 + j_2) + 1 \quad (30)$$

only holds if one of j_1 and j_2 is zero. For these trivial cases, we have found all of the eigenstates of J^2 and J_z that satisfy (15). For all other cases, we can find further eigenstates corresponding to the quantum numbers $j < j_{\max} = j_1 + j_2$. Next we have to construct the eigenstates $|j_1 + j_2 - 1, m\rangle$. The state $|j_1 + j_2 - 1, j_1 + j_2 - 1\rangle$ should have the form,

$$|j_1 + j_2 - 1, j_1 + j_2 - 1\rangle = c_1 |j_1, j_1 - 1\rangle |j_2, j_2\rangle + c_2 |j_1, j_1\rangle |j_2, j_2 - 1\rangle , \quad (31)$$

which follows from Eq. (19). This state can be calculated if we utilize the orthogonality of the eigenstates $|j_1 + j_2 - 1, j_1 + j_2 - 1\rangle$ and $|j_1 + j_2, j_1 + j_2 - 1\rangle$, see in (27), being the linear combinations of the same tensor product vectors. From the orthogonality of the eigenstates of J^2 and J_z we obtain,

$$c_1 \sqrt{\frac{j_1}{j_1 + j_2}} + c_2 \sqrt{\frac{j_2}{j_1 + j_2}} = 0 .$$

Normalizing the eigenstates to one implies,

$$c_1^2 + c_2^2 = 1 . \quad (32)$$

Up to a multiplicative factor ± 1 , the solutions of the above two equations is

$$c_1 = C(j_1, j_1 - 1; j_2, j_2 | j_1 + j_2 - 1, j_1 + j_2 - 1) = \sqrt{\frac{j_2}{j_1 + j_2}} , \quad (33)$$

$$c_2 = C(j_1, j_1 - 1; j_2, j_2 | j_1 + j_2 - 1, j_1 + j_2 - 1) = \sqrt{\frac{j_1}{j_1 + j_2}} , \quad (34)$$

i.e.,

$$|j_1 + j_2 - 1, j_1 + j_2 - 1\rangle = \sqrt{\frac{j_2}{j_1 + j_2}} |j_1, j_1 - 1\rangle |j_2, j_2\rangle - \sqrt{\frac{j_1}{j_1 + j_2}} |j_1, j_1\rangle |j_2, j_2 - 1\rangle . \quad (35)$$

Starting from this state, by successive actions of J_- , we can generate the states $|j_1 + j_2 - 1, m\rangle$ for $m \in [-j_1 - j_2 + 1, \dots, j_1 + j_2 - 2]$. If the total number of the eigenstates $|j, m\rangle$ is still less than $(2j_1 + 1)(2j_2 + 1)$, we proceed with generating the subspace corresponding to $j = j_1 + j_2 - 2$. First, we find the state $|j_1 + j_2 - 2, j_1 + j_2 - 2\rangle$ by orthogonalizing it to the states, $|j_1 + j_2, j_1 + j_2 - 2\rangle$ and $|j_1 + j_2 - 1, j_1 + j_2 - 2\rangle$, obtained previously and then applying again J_- until we get the state $|j_1 + j_2 - 2, -(j_1 + j_2 - 2)\rangle$ (see Practical course).

The question naturally arises how long we can continue this process. In other words, what is the minimal quantum number j_{\min} , the eigensubspace of which can be generated from the states $|j_1, m_1\rangle |j_2, m_2\rangle$? As we mentioned before, the dimension of the subspace in $\mathcal{H}_1 \otimes \mathcal{H}_2$ spanned by the states $|j_1, m_1\rangle |j_2, m_2\rangle$ is $(2j_1 + 1)(2j_2 + 1)$, which should be equal to the sum of the dimensions of the eigensubspaces of J^2 and J_z that can be generated on this subspace,

$$(2j_1 + 1)(2j_2 + 1) = \sum_{j=j_{\min}}^{j_{\max}} (2j + 1) . \quad (36)$$

There are two possible cases:

(1) j is integer (or $2j + 1$ is odd):

The sum of the odd numbers up to $j = n$ equals

$$\sum_{j=0}^n (2j + 1) = 2 \sum_{j=0}^n j + n + 1 = 2 \frac{n(n+1)}{2} + n + 1 = (n+1)^2 , \quad (37)$$

from which

$$\sum_{j=j_{\min}}^{j_{\max}} (2j + 1) = (j_{\max} + 1)^2 - j_{\min}^2 = (j_1 + j_2 + 1)^2 - j_{\min}^2 . \quad (38)$$

(2) j is half-integer (or $2j + 1$ is even):

$$\sum_{j=\frac{1}{2}}^{n+\frac{1}{2}} (2j + 1) = n + 1 + \sum_{j=\frac{1}{2}}^{n+\frac{1}{2}} (2j) = n + 1 + \sum_{k=0}^n (2k + 1) = n + 1 + (n + 1)^2 = (n + 1)(n + 2) , \quad (39)$$

where we used the substitution $k = j - 1/2$. Using this identity,

$$\begin{aligned} \sum_{j=j_{\min}}^{j_{\max}} (2j+1) &= (j_{\max} + \frac{1}{2})(j_{\max} + \frac{3}{2}) - (j_{\min} - \frac{1}{2})(j_{\min} + \frac{1}{2}) \\ &= j_{\max}^2 + 2j_{\max} + 1 - j_{\min}^2 = (j_1 + j_2 + 1)^2 - j_{\min}^2, \end{aligned} \quad (40)$$

i.e., we get the same result in both cases. From Eq. (36) we get for j_{\min} ,

$$j_{\min}^2 = (j_1 + j_2 + 1)^2 - (2j_1 + 1)(2j_2 + 1) = (j_1 + j_2)^2 - 4j_1j_2 = (j_1 - j_2)^2 \quad (41)$$

or

$$j_{\min} = |j_1 - j_2|. \quad (42)$$

The possible quantum numbers j are then as follows,

$$j \in [|j_1 - j_2|, |j_1 - j_2| + 1, \dots, j_1 + j_2 - 1, j_1 + j_2], \quad (43)$$

or

$$C(j_1m_1, j_2m_2|j, m) = 0 \text{ if } j < |j_1 - j_2| \text{ or } j > j_1 + j_2, \quad (44)$$

which is usually termed as the second rule for the Clebsch-Gordan coefficients.

We note two important properties of the Clebsch-Gordan coefficients:

Orthonormality

It follows from the orthonormality of the angular momentum eigenstates:

$$\langle jm | j'm' \rangle = \delta_{jj'} \delta_{mm'} \quad (45)$$

Expanding the above scalar product using (15),

$$\langle jm | j'm' \rangle = \sum_{m_1 m_2} \sum_{m'_1 m'_2} C(j_1m_1; j_2m_2|jm) C(j'_1m'_1; j'_2m'_2|j'm') \underbrace{\langle j_1m_1 | j'_1m'_1 \rangle}_{\delta_{j_1j'_1} \delta_{m_1m'_1}} \underbrace{\langle j_2m_2 | j'_2m'_2 \rangle}_{\delta_{j_2j'_2} \delta_{m_2m'_2}} \quad (46)$$

↓

$$\sum_{m_1 m_2} C(j_1m_1; j_2m_2|jm) C(j_1m_1; j_2m_2|j'm') = \delta_{jj'} \delta_{mm'}. \quad (47)$$

Completeness

A second identity follows from the fact that, being an orthonormal set of vectors, the eigenstates $|jm\rangle$ form a complete set of the subspace $\{|j_1m_1\rangle |j_2m_2\rangle : -j_1 \leq m_1 \leq j_1, -j_2 \leq m_2 \leq j_2\}$:

$$\sum_{j=|j_1-j_2|}^{j_1+j_2} \sum_{m=-j}^j |jm\rangle \langle jm| = \sum_{m_1 m_2} |j_1m_1\rangle |j_2m_2\rangle \otimes \langle j_1m_1| \langle j_2m_2| \quad (48)$$

$$\equiv \sum_{m_1 m_2} |j_1m_1\rangle \langle j_1m_1| \otimes |j_2m_2\rangle \langle j_2m_2|. \quad (49)$$

Expanding the projectors on left-hand side of the identity using again (15),

$$\sum_{j=j_{\min}}^{j_{\max}} \sum_{m=-j}^j |jm\rangle \langle jm| = \sum_{j=j_{\min}}^{j_{\max}^+} \sum_{m=-j}^j \sum_{m_1 m_2} \sum_{m'_1 m'_2} C(j_1 m_1; j_2 m_2 | jm) C(j_1 m'_1; j_2 m'_2 | jm) |j_1 m_1\rangle \langle j_1 m'_1| \otimes |j_2 m_2\rangle \langle j_2 m'_2| \quad (50)$$

$$= \sum_{m_1 m_2} \sum_{m'_1 m'_2} \left(\sum_{j=j_{\min}}^{j_{\max}} \sum_{m=-j}^j C(j_1 m_1; j_2 m_2 | jm) C(j_1 m'_1; j_2 m'_2 | jm) \right) |j_1 m_1\rangle \langle j_1 m'_1| \otimes |j_2 m_2\rangle \langle j_2 m'_2| , \quad (51)$$

which, as compared with

$$\sum_{j=j_{\min}}^{j_{\max}} \sum_{m=-j}^j |jm\rangle \langle jm| = \sum_{m_1 m_2} |j_1 m_1\rangle \langle j_1 m_1| \otimes |j_2 m_2\rangle \langle j_2 m_2| ,$$

implies

$$\sum_{j=j_{\min}}^{j_{\max}} \sum_{m=-j}^j C(j_1 m_1; j_2 m_2 | jm) C(j_1 m'_1; j_2 m'_2 | jm) = \delta_{m_1 m'_1} \delta_{m_2 m'_2} . \quad (52)$$

2 The Helium atom

The Helium atom displays a prototypical system for two interacting electrons. The two-electron Hamilton operator can be decomposed into two parts,

$$H(1, 2) = H^0(1, 2) + V(1, 2) , \quad (53)$$

where $H^0(1, 2)$ is the Hamilton operator of the independent electrons, while $V(1, 2)$ describes the interaction between the two electrons. $H^0(1, 2)$ can be written as the sum of one-electron Hamilton operators,

$$H^0(1, 2) = H_1(1) + H_1(2) , \quad (54)$$

where H_1 is a hydrogen type of Hamilton operator with $Z = 2$,

$$H_1(i) = -\frac{\hbar^2}{2m}\Delta_i - \frac{2ke^2}{r_i} \quad (i = 1, 2) . \quad (55)$$

The interaction is the Coulomb repulsion between the two electrons,

$$V(1, 2) = \frac{ke^2}{|\vec{r}_1 - \vec{r}_2|} . \quad (56)$$

As we learned in the course Quantum Mechanics 1, the eigenstates of $H_1(i)$ are labelled by the principal quantum number $n = 1, 2, 3, \dots$, the angular momentum quantum number $\ell = 0, 1, \dots, n - 1$, the magnetic quantum number $m = -\ell, -\ell + 1, \dots, \ell$ and the spin quantum number $m_s = \pm\frac{1}{2}$, $\phi_{n\ell m m_s}(i) = \phi_{n\ell m}(\vec{r}_i) \left| \frac{1}{2}, m_s \right\rangle_i$,

$$H_1(i) \phi_{n\ell m m_s}(i) = E_n \phi_{n\ell m m_s}(i) \quad (57)$$

$$E_n = -4 \frac{m (ke^2)^2}{\hbar^2} \frac{1}{n^2} = -\frac{4}{n^2} \text{Ryd} . \quad (58)$$

2.1 Ground state

The lowest energy one-particle states are the 1s states,

$$\phi_{1,0,0,+\frac{1}{2}}(i) = \phi_{100}(\vec{r}_i) \left| \frac{1}{2}, +\frac{1}{2} \right\rangle_i = \phi_{1s}(\vec{r}_i) \left| \frac{1}{2}, +\frac{1}{2} \right\rangle_i \quad (59)$$

$$\phi_{1,0,0,-\frac{1}{2}}(i) = \phi_{100}(\vec{r}_i) \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_i = \phi_{1s}(\vec{r}_i) \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_i . \quad (60)$$

The tensor product space generated by these wavefunctions is four-dimensional, but only one of them is antisymmetric, i.e., describes a two-fermion state:

$$\psi_{1s,1s}(1, 2) = \phi_{1s}(\vec{r}_1)\phi_{1s}(\vec{r}_2) |0, 0\rangle . \quad (61)$$

where the spatial part, $\phi_{1s}(\vec{r}_1)\phi_{1s}(\vec{r}_2)$, is symmetric and the spin part,

$$|0, 0\rangle = \frac{1}{\sqrt{2}} \left(\left| \frac{1}{2}, +\frac{1}{2} \right\rangle_1 \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_2 - \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_1 \left| \frac{1}{2}, +\frac{1}{2} \right\rangle_2 \right) \quad (62)$$

is the antisymmetric singlet two-spin state ($S = 0$, $m_S = 0$). This is the ground state of the unperturbed (non-interacting) Helium atom, called parahelium, which has the energy,

$$H^0(1, 2)\psi_{1s,1s}(1, 2) = E_{1s,1s}^{(0)} \psi_{1s,1s}(1, 2) \quad (63)$$

$$E_{1s,1s}^{(0)} = -8 \text{Ryd} . \quad (64)$$

What is the energy of the ground state in first order of the perturbation theory?

$$\Delta E_{1s,1s}^{(1)} = \langle \psi_{1s,1s}(1, 2) | V(1, 2) | \psi_{1s,1s}(1, 2) \rangle \quad (65)$$

$$= \underbrace{\langle 00 | 00 \rangle}_{=1} k e^2 \int \int \frac{\phi_{1s}^*(\vec{r}_1) \phi_{1s}^*(\vec{r}_2) \phi_{1s}(\vec{r}_1) \phi_{1s}(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d^3 r_1 d^3 r_2 \quad (66)$$

$$= k e^2 \int \int \frac{\varrho_{1s}(\vec{r}_1) \varrho_{1s}(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d^3 r_1 d^3 r_2 = C_{1s,1s} > 0. \quad (67)$$

Obviously, $C_{1s,1s}$ is the Coulomb interaction energy of the classical charge distribution, $\varrho_{1s}(\vec{r}) = \phi_{1s}^*(\vec{r}) \phi_{1s}(\vec{r})$. The result of the calculation is,

$$C_{1s,1s} = \frac{5 Z m (k e^2)^2}{4 \hbar^2} = 2.5 \text{ Ryd} , \quad (68)$$

so that the first-order ground-state energy of the He atom equals to

$$E_{1s,1s}^{(1)} = E_{1s,1s} + \Delta E_{1s,1s}^{(1)} = -5.5 \text{ Ryd} . \quad (69)$$

Actually, this is a good approximation of the exact ground state energy, $-5.807 \text{ Ryd} .$

2.2 Excited states

From the $1s$ and $2s$ states we can generate four antisymmetric two-electron wavefunctions by using the orthonormal eigenstates of the S_z and S^2 operators,

$$|00\rangle = \frac{1}{\sqrt{2}} \left(\left| \frac{1}{2}, +\frac{1}{2} \right\rangle_1 \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_2 - \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_1 \left| \frac{1}{2}, +\frac{1}{2} \right\rangle_2 \right) \quad \text{singlet} \quad (70)$$

$$\left. \begin{aligned} |1-1\rangle &= \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_1 \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_2 \\ |10\rangle &= \frac{1}{\sqrt{2}} \left(\left| \frac{1}{2}, +\frac{1}{2} \right\rangle_1 \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_2 + \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_1 \left| \frac{1}{2}, +\frac{1}{2} \right\rangle_2 \right) \\ |11\rangle &= \left| \frac{1}{2}, +\frac{1}{2} \right\rangle_1 \left| \frac{1}{2}, +\frac{1}{2} \right\rangle_2 \end{aligned} \right\} \quad \text{triplet} \quad (71)$$

and the orthonormal symmetric and antisymmetric spatial components,

$$\phi_{1s,2s}^+(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} (\phi_{1s}(\vec{r}_1) \phi_{2s}(\vec{r}_2) + \phi_{2s}(\vec{r}_1) \phi_{1s}(\vec{r}_2)) \quad (72)$$

$$\phi_{1s,2s}^-(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} (\phi_{1s}(\vec{r}_1) \phi_{2s}(\vec{r}_2) - \phi_{2s}(\vec{r}_1) \phi_{1s}(\vec{r}_2)) . \quad (73)$$

The antisymmetric combinations are as follows,

$$\psi_{1s,2s}^1(1, 2) = \phi_{1s,2s}^+(\vec{r}_1, \vec{r}_2) |00\rangle \quad (74)$$

$$\psi_{1s,2s}^2(1, 2) = \phi_{1s,2s}^-(\vec{r}_1, \vec{r}_2) |1-1\rangle \quad (75)$$

$$\psi_{1s,2s}^3(1, 2) = \phi_{1s,2s}^-(\vec{r}_1, \vec{r}_2) |10\rangle \quad (76)$$

$$\psi_{1s,2s}^4(1, 2) = \phi_{1s,2s}^-(\vec{r}_1, \vec{r}_2) |11\rangle . \quad (77)$$

These states are degenerate eigenfunctions of the unperturbed Hamiltonian, $H^0(1, 2)$,

$$H^0(1, 2)\psi_{1s,2s}^\alpha(1, 2) = E_{1s,2s}\psi_{1s,2s}^\alpha(1, 2) \quad (\alpha = 1, 2, 3, 4) \quad (78)$$

$$E_{1s,2s} = -4 \left(1 + \frac{1}{4}\right) \text{Ryd} = -5 \text{Ryd} . \quad (79)$$

In principle, we have to apply degenerate first-order perturbation theory, but the Coulomb interaction is independent of the spin and we work with orthonormal spin states, therefore, the matrix of the Coulomb interaction is diagonal on the basis $\{\psi_{1s,2s}^\alpha\}$. We then obtain the following energy corrections,

$$\Delta E_{1s,2s}^{(1),1} = \langle \psi_{1s,2s}^1(1, 2) | V(1, 2) | \psi_{1s,2s}^1(1, 2) \rangle \quad (80)$$

$$= \int \int \phi_{1s,2s}^+(\vec{r}_1, \vec{r}_2)^* \frac{ke^2}{|\vec{r}_1 - \vec{r}_2|} \phi_{1s,2s}^+(\vec{r}_1, \vec{r}_2) d^3r_1 d^3r_2 , \quad (81)$$

and for $\alpha \in \{2, 3, 4\}$

$$\Delta E_{1s,2s}^{(1),\alpha} = \langle \psi_{1s,2s}^\alpha(1, 2) | V(1, 2) | \psi_{1s,2s}^\alpha(1, 2) \rangle \quad (82)$$

$$= \int \int \phi_{1s,2s}^-(\vec{r}_1, \vec{r}_2)^* \frac{ke^2}{|\vec{r}_1 - \vec{r}_2|} \phi_{1s,2s}^-(\vec{r}_1, \vec{r}_2) d^3r_1 d^3r_2 . \quad (83)$$

The triplet states are still degenerate but the degeneracy between the triplet and singlet states is lifted. Let's see the meaning of the energy corrections:

$$\int \int \phi_{1s,2s}^\pm(\vec{r}_1, \vec{r}_2)^* \frac{ke^2}{|\vec{r}_1 - \vec{r}_2|} \phi_{1s,2s}^\pm(\vec{r}_1, \vec{r}_2) d^3r_1 d^3r_2 = \quad (84)$$

$$= \frac{1}{2} \int \int \phi_{1s}(\vec{r}_1)^* \phi_{2s}(\vec{r}_2)^* \frac{ke^2}{|\vec{r}_1 - \vec{r}_2|} \phi_{1s}(\vec{r}_1) \phi_{2s}(\vec{r}_2) d^3r_1 d^3r_2 \quad (85)$$

$$+ \frac{1}{2} \int \int \phi_{2s}(\vec{r}_1)^* \phi_{1s}(\vec{r}_2)^* \frac{ke^2}{|\vec{r}_1 - \vec{r}_2|} \phi_{2s}(\vec{r}_1) \phi_{1s}(\vec{r}_2) d^3r_1 d^3r_2 \quad (86)$$

$$\pm \frac{1}{2} \int \int \phi_{1s}(\vec{r}_1)^* \phi_{2s}(\vec{r}_2)^* \frac{ke^2}{|\vec{r}_1 - \vec{r}_2|} \phi_{2s}(\vec{r}_1) \phi_{1s}(\vec{r}_2) d^3r_1 d^3r_2 \quad (87)$$

$$\pm \frac{1}{2} \int \int \phi_{2s}(\vec{r}_1)^* \phi_{1s}(\vec{r}_2)^* \frac{ke^2}{|\vec{r}_1 - \vec{r}_2|} \phi_{1s}(\vec{r}_1) \phi_{2s}(\vec{r}_2) d^3r_1 d^3r_2 . \quad (88)$$

The first two terms yield the classical Coulomb energy term,

$$C_{1s,2s} = ke^2 \int \int \frac{\rho_{1s}(\vec{r}_1) \rho_{2s}(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d^3r_1 d^3r_2 , \quad (89)$$

but the other two terms have no classical analogues. Since they contain two different wavefunctions with the same coordinate argument, we call these terms the *exchange integral*,

$$K_{1s,2s} = ke^2 \int \int \frac{\phi_{1s}(\vec{r}_1)^* \phi_{2s}(\vec{r}_2)^* \phi_{2s}(\vec{r}_1) \phi_{1s}(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d^3r_1 d^3r_2 \in \mathbb{R} \quad (90)$$

which gives the energy splitting between the singlet and triplet states,

$$\Delta E_{1s,2s}^{(1),\text{singlet}} = C_{1s,2s} + K_{1s,2s} , \quad (91)$$

$$\Delta E_{1s,2s}^{(1),\text{triplet}} = C_{1s,2s} - K_{1s,2s} . \quad (92)$$

For the investigation of the excited states of the Helium atom we have to consider also the Slater determinants formed by the $1s$ and $2p$ states, because they are eigenfunctions of the unperturbed Hamiltonian with the same energy, $E = -5$ Ryd. So, in principle, we have to work on a $4 \times 4 = 16$ -dimensional subspace of two-fermion wavefunctions and employ first-order degenerate perturbation theory on this space. In order to avoid this high dimensional problem we can make use that the two-electron orbital angular momentum operator, $\vec{L} = \vec{L}_1 + \vec{L}_2$, commutes with the Hamiltonian $H(1, 2)$, so we can look for the eigenstates of the Hamiltonian being simultaneously common eigenstates of the operators \vec{L}_z and L^2 . Based on the addition of the angular momenta, it is obvious that the $(1s, 2s)$ states correspond to the two-electron orbital quantum number $L = 0$, while the $(1s, 2p)$ states correspond to $L = 1$. From the $(1s, 2p)$ states related to $M_L = -1, 0, 1$ the valid two-electron states can be constructed as (74)-(77), thus they span a 12-dimensional subspace. Obviously, the matrix of $V(1, 2)$ is again diagonal and the degeneracies are lifted as above,

$$\Delta E_{1s,2p}^{(1),\text{singlet}} = C_{1s,2p} + K_{1s,2p} \quad (93)$$

$$\Delta E_{1s,2p}^{(1),\text{triplet}} = C_{1s,2p} - K_{1s,2p} \quad (94)$$

where $C_{1s,2p}$ is the Coulomb integral and $K_{1s,2p}$ is the exchange integral defined in (89) and (90), respectively, we only have to replace ϕ_{2s} by ϕ_{2p_m} with $m = -1, 0, 1$. It is easy to show that the integrals $C_{1s,2p}$ and $K_{1s,2p}$ are independent of m by symmetry. The tensor product space of the $(1s, 2s)$ and $(1s, 2p)$ states split then into four energy levels, as shown in the below figure.

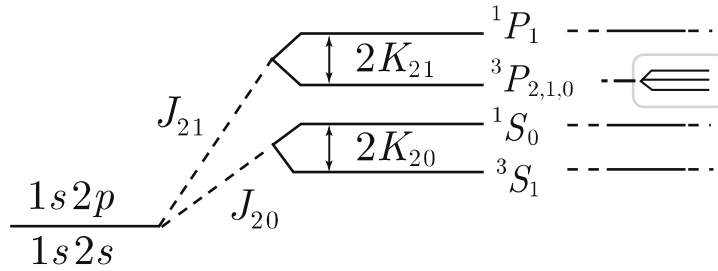


Figure 1: The energy levels of low-energy excited states in the He atom. The notations are as follows: $J_{20} = C_{1s,2s}$, $J_{21} = C_{1s,2p}$, $K_{20} = K_{1s,2s}$, $K_{21} = K_{1s,2p}$.

For the description of the two-electron states of the He atom we use the notation $^{2S+1}L_J$, where $\vec{J} = \vec{J}_1 + \vec{J}_2$ with $\vec{J}_i = \vec{L}_i + \vec{S}_i$ being the total angular momentum. Instead of $L = 0, 1, 2, 3, \dots$ we use the conventional notation is S, P, D, F , respectively. Due to the addition rules of angular momenta, for the singlet states $S = 0$ ($2S + 1 = 1$), J is unambiguously defined, $J = L$. In case of the 3S_1 triplet states, where $L = 0$, J is also defined unambiguously, $J = S = 1$. These levels are $2J + 1$ times degenerate. The 3P_J states, or in other words, the $L = 1$ and $S = 1$ states can have $J = 0, 1, 2$, so this level is $1 + 3 + 5 = 9$ times degenerate. We will see later that this level is going to split according to the three different values of J due to spin-orbit coupling as noted in the Figure.

Remark: Effective spin Hamiltonian for the spin singlet and triplet states. The energy of the singlet and triplet states,

$$E(S = 0) = C + K \quad (95)$$

$$E(S = 1) = C - K \quad (96)$$

can be written as

$$E(S) = C - (S(S + 1) - 1)K . \quad (97)$$

In the above expression we recognize the eigenvalue of the S^2 operator, so we define the effective Hamiltonian, which describes the interaction of the spins of the two electrons,

$$H_{\text{spin}}(\vec{S}_1, \vec{S}_2) = C + K - \frac{1}{\hbar^2}(\vec{S}_1 + \vec{S}_2)^2 K = C - \frac{1}{2}K - \frac{2K}{\hbar^2} \vec{S}_1 \vec{S}_2 \quad (98)$$

$$= H_0 - J \vec{S}_1 \vec{S}_2 . \quad (99)$$

This is a prototype of the so-called isotropic Heisenberg interaction with the so-called exchange coupling J related to the exchange integral K as

$$J = \frac{2K}{\hbar^2} . \quad (100)$$

3 Scattering theory

In this section, we investigate the propagation of particles through a scattering medium termed as the target. The scattered particles are detected far from the target. As in the case of one-dimensional scattering, we use plane-wave states for the incoming particle,

$$i\hbar\partial_t\psi_0(\vec{r},t) = H_0\psi_0(\vec{r},t) = -\frac{\hbar^2\Delta}{2m}\psi_0(\vec{r},t), \quad (101)$$

$$\psi_0(\vec{r},t) = A e^{i(\vec{k}\vec{r} - \frac{E}{\hbar}t)} \quad (102)$$

$$E = \frac{\hbar^2 k^2}{2m}. \quad (103)$$

In case of a particle described by a wave packet localized both in coordinate and momentum space we have to consider the superposition of the corresponding plane waves.

3.1 Lippmann–Schwinger equation, Green’s function, Born series

The scattering process is described by the time dependent Schrödinger equation,

$$i\hbar\partial_t\psi(\vec{r},t) = (H_0 + V(\vec{r}))\psi(\vec{r},t) \quad (104)$$

where $V(\vec{r})$ is the interaction potential between the scattered particle and the target. Since the potential is time independent, the energy of the particle is a conserved quantity (*elastic scattering*), so we can switch to the time independent Schrödinger equation:

$$\psi(\vec{r},t) = \psi(\vec{r}) e^{-i\frac{E}{\hbar}t} \quad (105)$$

↓

$$(H_0 + V(\vec{r}))\psi(\vec{r}) = E\psi(\vec{r}). \quad (106)$$

Without loss of generality it is worth to take the steady solution $\psi(\vec{r})$ as the sum of the incident wave $\psi_0(\vec{r})$ and a *scattered wave* $\psi_{sc}(\vec{r})$:

$$\psi(\vec{r}) = \psi_0(\vec{r}) + \psi_{sc}(\vec{r}). \quad (107)$$

As the detectors are far from the target, we will need to express the scattered wave for large $r = |\vec{r}|$, called the asymptotic limit.

Substituting (107) into the Schrödinger equation (106),

$$(H_0 + V(\vec{r}))(\psi_0(\vec{r}) + \psi_{sc}(\vec{r})) = E(\psi_0(\vec{r}) + \psi_{sc}(\vec{r})), \quad (108)$$

we proceed as

$$(H_0 + V(\vec{r}))\psi_{sc}(\vec{r}) + V(\vec{r})\psi_0(\vec{r}) = E\psi_{sc}(\vec{r}) \quad (109)$$

$$(H_0 - E)\psi_{sc}(\vec{r}) = -V(\vec{r})(\psi_0(\vec{r}) + \psi_{sc}(\vec{r})) \quad (110)$$

and obtain the following equation for the scattered wave,

$$(H_0 - E)\psi_{sc}(\vec{r}) = \left(-\frac{\hbar^2}{2m}\Delta - E\right)\psi_{sc}(\vec{r}) = -V(\vec{r})\psi(\vec{r}). \quad (111)$$

The above equation can be solved by Green's function technique. The Green's function of the free particles is defined as

$$\left(-\frac{\hbar^2}{2m}\Delta - E \right) G_0(\vec{r}, \vec{r}'; E) = -\delta(\vec{r} - \vec{r}'). \quad (112)$$

It is then straightforward to show that the solution of (111) is

$$\psi_{\text{sc}}(\vec{r}) = \int G_0(\vec{r}, \vec{r}', E) V(\vec{r}') \psi(\vec{r}') d^3r', \quad (113)$$

consequently, the stationary solution of (107) can be written as

$$\psi(\vec{r}) = \psi_0(\vec{r}) + \int G_0(\vec{r}, \vec{r}'; E) V(\vec{r}') \psi(\vec{r}') d^3r', \quad (114)$$

which is called the *Lippmann–Schwinger equation*. The Lippmann–Schwinger equation is an integral equation that provides the solution of the time-independent Schrödinger equation including the boundary conditions for the solution by a suitable choice of the Green's function $G_0(\vec{r}, \vec{r}'; E)$. In the scattering case, we expect spherical outgoing wave solutions far away from the target.

In order to determine the Green's function we introduce the *resolvent operator*, $G_0(z)$,

$$(H_0 - zI) G_0(z) = -I \quad (115)$$

where I is the unit operator of the Hilbert space and $z \in \mathbb{C}$ is a complex energy argument. Taking the coordinate representation of the above operator equation,

$$\langle \vec{r} | (H_0 - zI) G_0(z) | \vec{r}' \rangle = -\langle \vec{r} | \vec{r}' \rangle = -\delta(\vec{r} - \vec{r}') \quad (116)$$

↓

$$\int d^3r'' \langle \vec{r} | (H_0 - zI) | \vec{r}'' \rangle \langle \vec{r}'' | G_0(z) | \vec{r}' \rangle = (H_0(\vec{r}) - z) G_0(\vec{r}, \vec{r}'; z) = -\delta(\vec{r} - \vec{r}'), \quad (117)$$

where we used that H_0 is diagonal in coordinate representation,

$$\langle \vec{r} | H_0 | \vec{r}' \rangle = H_0(\vec{r}, \vec{r}') = H_0(\vec{r}) \delta(\vec{r} - \vec{r}'). \quad (118)$$

It is then obvious that the coordinate representation of the resolvent operator, $\langle \vec{r} | G_0(z) | \vec{r}' \rangle = G_0(\vec{r}, \vec{r}'; z)$, is the required Green's function.

Let's recall the spectral resolution of H_0 ,

$$H_0 = \sum_n \varepsilon_n |n\rangle \langle n|, \quad (119)$$

where ε_n and $|n\rangle$ are the eigenvalues and eigenvectors of H_0 , and they form an orthonormal basis on the Hilbert space. Note that in the case of a continuous spectrum, instead of the summation we have to take an integral over generalized eigenvalues. From Eq. (115) it follows,

$$\langle n | (zI - H_0) G_0(z) | m \rangle = (z - \varepsilon_n) \langle n | G_0(z) | m \rangle = \delta_{nm} \quad (120)$$

from which we get

$$\langle n | G_0(z) | m \rangle = \delta_{nm} \frac{1}{z - \varepsilon_n}, \quad (121)$$

and the spectral resolution of the resolvent,

$$G_0(z) = \sum_n \frac{|n\rangle \langle n|}{z - \varepsilon_n \pm i0}. \quad (122)$$

Since ε_n can take only real values, in order to avoid the division by zero, for real values of z we take the limits when the imaginary part goes to zero. Depending on whether this limit is taken from the upper or lower complex semiplane, we define $G_0^+(E)$ and $G_0^-(E)$ as

$$G_0^\pm(E) = G_0(E \pm i0).$$

Obviously $G_0^+(E)$ and $G_0^-(E)$ are the adjoint operators of each other, and identical only if E is not an eigenvalue of H_0 .

The Green's function can be written as

$$G_0^\pm(\vec{r}', \vec{r}; z) = \sum_n \frac{\langle \vec{r}' | n \rangle \langle n | \vec{r} \rangle}{z - \varepsilon_n \pm i0} = \sum_n \frac{\varphi_n(\vec{r}') \varphi_n(\vec{r})^*}{z - \varepsilon_n \pm i0}, \quad (123)$$

where $\varphi_n(\vec{r})$ denote the eigenfunctions of H_0 .

Taking into account that the properly normalized generalized eigenfunctions of H_0 are $\varphi_{\vec{p}}(\vec{r}) = \frac{1}{h^{3/2}} e^{i\vec{p}\vec{r}}$ with the generalized eigenvalues $\varepsilon_{\vec{p}} = \frac{p^2}{2m}$, and writing the energy variable of the Green's function as $z = \frac{\hbar^2 k^2}{2m}$, we get the following expression:

$$G_0(\vec{r}', \vec{r}; z) = \frac{1}{h^3} \int \frac{e^{i\vec{p}(\vec{r}' - \vec{r})}}{\frac{\hbar^2 k^2}{2m} - \frac{p^2}{2m}} d^3 p = \frac{2m}{h^3} \int \frac{e^{i\vec{p}(\vec{r}' - \vec{r})}}{\hbar^2 k^2 - p^2} d^3 p \quad (124)$$

$$= \frac{4\pi m}{h^3} \int_0^\infty \frac{p^2 dp}{\hbar^2 k^2 - p^2} \int_{-1}^1 dx e^{i\frac{1}{2} p |\vec{r}' - \vec{r}| x} \quad (125)$$

$$= \frac{2m}{ih^2 |\vec{r}' - \vec{r}'|} \int_0^\infty p dp \frac{e^{i\frac{1}{2} p |\vec{r}' - \vec{r}'|} - e^{-i\frac{1}{2} p |\vec{r}' - \vec{r}'|}}{\hbar^2 k^2 - p^2} \quad (126)$$

$$= \frac{m}{ih^2 |\vec{r}' - \vec{r}'|} \left[\int_{-\infty}^\infty dp \frac{p e^{i\frac{1}{2} p |\vec{r}' - \vec{r}'|}}{\hbar^2 k^2 - p^2} - \int_{-\infty}^\infty dp \frac{p e^{-i\frac{1}{2} p |\vec{r}' - \vec{r}'|}}{\hbar^2 k^2 - p^2} \right]. \quad (127)$$

The integrals can be calculated by using the residue theorem. Obviously, the first and second integrals can be closed in the upper and lower complex semiplane, respectively. Thus by choosing $\text{Re } z > 0$ and $\text{Im } z > 0 \rightarrow \text{Im } k > 0$ yields

$$G_0(\vec{r}', \vec{r}; z) = -\frac{2\pi m}{h^2 |\vec{r}' - \vec{r}'|} \left[\text{Res}\left(\frac{p e^{i\frac{1}{2} p |\vec{r}' - \vec{r}'|}}{(p - \hbar k)(p + \hbar k)}, \hbar k\right) - \text{Res}\left(\frac{p e^{-i\frac{1}{2} p |\vec{r}' - \vec{r}'|}}{(p - \hbar k)(p + \hbar k)}, -\hbar k\right) \right] \\ = -\frac{2m}{\hbar^2} \frac{e^{ik|\vec{r}' - \vec{r}'|}}{4\pi |\vec{r}' - \vec{r}'|}, \quad (128)$$

while by choosing $\text{Re } z > 0$ and $\text{Im } z < 0 \rightarrow \text{Im } k < 0$,

$$G_0(\vec{r}', \vec{r}; z) = -\frac{2\pi m}{h^2 |\vec{r}' - \vec{r}'|} \left[\text{Res}\left(\frac{p e^{i\frac{1}{2} p |\vec{r}' - \vec{r}'|}}{(p - \hbar k)(\hbar k + p)}, -\hbar k\right) - \text{Res}\left(\frac{p e^{-i\frac{1}{2} p |\vec{r}' - \vec{r}'|}}{(p - \hbar k)(\hbar k + p)}, \hbar k\right) \right] \\ = -\frac{2m}{\hbar^2} \frac{e^{-ik|\vec{r}' - \vec{r}'|}}{4\pi |\vec{r}' - \vec{r}'|}, \quad (129)$$

↓

$$E > 0 : G_0^\pm(\vec{r}', \vec{r}; E) = -\frac{2m}{\hbar^2} \frac{e^{\pm ik|\vec{r}-\vec{r}'|}}{4\pi|\vec{r}-\vec{r}'|}. \quad (130)$$

In order to derive the asymptotic form of the scattered wave, we will use $G_0^+(\vec{r}', \vec{r}; E)$ providing outgoing spherical waves as mentioned already. We also should mention that for $E < 0$, $E \pm i0 = (\pm ik)^2$ with $k = \sqrt{-E}$, therefore,

$$G_0^\pm(\vec{r}', \vec{r}; E) = -\frac{2m}{\hbar^2} \frac{e^{-k|\vec{r}-\vec{r}'|}}{4\pi|\vec{r}-\vec{r}'|}, \quad (131)$$

being identical for both side-limits.

Choosing the positive side limit of the free Green's function, the abstract form of the Lippmann–Schwinger equation reads as

$$|\psi\rangle = |\psi_0\rangle + G_0^+ V |\psi\rangle, \quad (132)$$

where we dropped the energy argument. The above equation can be solved by successive approximation,

$$|\psi^{(0)}\rangle = |\psi_0\rangle \quad (133)$$

$$|\psi^{(1)}\rangle = |\psi_0\rangle + G_0^+ V |\psi_0\rangle = |\psi_0\rangle + G_0^+ V |\psi_0\rangle \quad (134)$$

$$|\psi^{(2)}\rangle = |\psi_0\rangle + G_0^+ V |\psi^{(1)}\rangle = |\psi_0\rangle + G_0^+ V |\psi_0\rangle + (G_0^+ V)^2 |\psi_0\rangle \quad (135)$$

$$|\psi^{(3)}\rangle = |\psi_0\rangle + G_0^+ V |\psi^{(2)}\rangle = |\psi_0\rangle + G_0^+ V |\psi_0\rangle + (G_0^+ V)^2 |\psi_0\rangle + (G_0^+ V)^3 |\psi_0\rangle \quad (136)$$

...

what we call the *Born series*. It is easy to see, that the complete solution is:

$$|\psi\rangle = |\psi_0\rangle + G_0^+ \sum_{n=0}^{\infty} (V G_0^+)^n V |\psi_0\rangle. \quad (137)$$

If $\|V G_0^+\| < 1$, that is the scattering potential is weak, we can use the sum of the Neumann-series,

$$\sum_{n=0}^{\infty} (V G_0^+)^n = (I - V G_0^+)^{-1} \quad (138)$$

and the solution of the Lippmann–Schwinger equation is

$$|\psi\rangle = |\psi_0\rangle + G_0^+ (I - V G_0^+)^{-1} V |\psi_0\rangle. \quad (139)$$

Further manipulations,

$$\begin{aligned} G_0^+ (I - V G_0^+)^{-1} &= \left((G_0^+)^{-1} - V \right)^{-1} = (E + i0 - H_0 - V)^{-1} \\ &= (E + i0 - H)^{-1} = G^+(E) \end{aligned} \quad (140)$$

lead to the resolvent operator of the scattering target. The Lippmann–Schwinger equation with this resolvent reads as

$$|\psi\rangle = |\psi_0\rangle + G^+ V |\psi_0\rangle \quad (141)$$

or in coordinate representation,

$$\psi(\vec{r}) = \psi_0(\vec{r}) + \int G^+(\vec{r}, \vec{r}'; E) V(\vec{r}') \psi_0(\vec{r}') d^3r'. \quad (142)$$

3.2 Scattering amplitudes and cross sections

In this section we are going to use the first term of the Born series called the *Born approximation*:

$$\psi(\vec{r}) \simeq \psi^{(1)}(\vec{r}) = \psi_0(\vec{r}) + \int G_0^+(\vec{r}, \vec{r}'; E) V(\vec{r}') \psi_0(\vec{r}') d^3r'. \quad (143)$$

Putting the origin of the coordinate system into the compact domain of the potential $V(\vec{r}')$ (target) we get the asymptotic form of the scattered wave by determining the Green's function in the limit of $r \gg r'$. In the denominator of Eq. (131) we can take the approximation $|\vec{r} - \vec{r}'| \simeq r$, because higher order terms in the expansion $1/|\vec{r} - \vec{r}'|$ lead to contributions to $\psi(\vec{r})$ proportional with $1/r^2$ or $1/r^3$ etc., which decay faster than the leading term proportional with $1/r$. On the contrary, in the numerator we have to go further in the expansion of $|\vec{r} - \vec{r}'|$ in order to obtain an asymptotic form for the scattered wave that depends on the direction of the detector,

$$k|\vec{r} - \vec{r}'| \underset{\vec{e}_r = \frac{\vec{r}}{r}}{=} kr \sqrt{\left(\vec{e}_r - \frac{\vec{r}'}{r}\right)^2} = kr \sqrt{1 - \frac{2\vec{r}\vec{r}'}{r^2} + \frac{r'^2}{r^2}} \underset{r \gg r'}{\rightarrow} kr \left(1 - \frac{\vec{r}\vec{r}'}{r^2}\right) \quad (144)$$

from which the asymptotic form of the Green's function reads as

$$G_0^\pm(\vec{r}', \vec{r}; E) \rightarrow -\frac{2m}{\hbar^2} \frac{e^{\pm ikr}}{4\pi r} e^{\mp i\vec{k}'\vec{r}'}, \quad (145)$$

where

$$\vec{k}' = k\vec{e}_r = k\frac{\vec{r}}{r} \quad (146)$$

denotes the wavevector for the particle propagating towards the detector at the position \vec{r} .

Considering the time dependent phase factor $e^{-i\frac{E}{\hbar}t}$ involved in the wavefunction, the function e^{ikr}/r describes a spherical wave propagating outwards (away from the target), while e^{-ikr}/r stands for a spherical wave propagating inwards (towards the target). This is why we choose the Green's function $G_0^+(\vec{r}, \vec{r}'; E)$ for the solution of the scattering problem,

$$\psi_{sc}(\vec{r}) \simeq -\frac{e^{ikr}}{r} \frac{m}{2\pi\hbar^2} \int e^{-i\vec{k}'\vec{r}'} V(\vec{r}') e^{i\vec{k}\vec{r}'} d^3r'. \quad (147)$$

The asymptotic wavefunction can then be written in the following form,

$$\psi(\vec{r}) \simeq A \left(e^{i\vec{k}\vec{r}} + f(\vec{q}) \frac{e^{ikr}}{r} \right), \quad (148)$$

where we introduced the so called *scattering amplitude*

$$f(\vec{q}) = -\frac{m}{2\pi\hbar^2} \int V(\vec{r}') e^{-i\vec{q}\vec{r}'} d^3r', \quad (149)$$

with

$$\vec{q} = \vec{k}' - \vec{k} = k\frac{\vec{r}}{r} - \vec{k} = k(\vec{e}_r - \vec{e}_k). \quad (150)$$

It seems to be a natural to choose the z axis of our coordinate system parallel to the direction of the incoming wave, $\vec{e}_k = \vec{e}_z$. In general, the \vec{q} vector depends on the polar and azimuth angles of \vec{e}_r , namely

$$f(\vec{q}) = f(\vartheta, \varphi), \quad (151)$$

but the length of \vec{q} depends only on ϑ ,

$$\vec{q}^2 = 2k^2 (1 - \vec{e}_z \vec{e}_r) = 2k^2 (1 - \cos \vartheta) = 4k^2 \sin^2 \frac{\vartheta}{2} \rightarrow q = 2k \sin \frac{\vartheta}{2}. \quad (152)$$

In case of spherically symmetric (central) potentials the scattering amplitude depends just on q , i.e., on the polar angle ϑ ,

$$\begin{aligned} f(q) &= -\frac{m}{\hbar^2} \int_0^\infty r'^2 dr' V(r') \int_{-1}^1 dx e^{-iqr'x} \\ &= -\frac{2m}{q\hbar^2} \int_0^\infty r' dr' V(r') \sin(qr'), \end{aligned} \quad (153)$$

where we choose the z' axis along the direction of the \vec{q} vector.

As we mentioned before, the condition for the Born approximation is that scattering potential should be weak. In the denominator of the above expression, q is proportional to the square-root of the energy, which suggests that the scattering amplitude is going to be small for *high energies*, making the *Born approximation applicable*. We note that the Born approximation works also for infinitely extended potentials in case of sufficiently fast spatial decay. An example is given by the Yukawa potential, where in case of the limit of zero screening length we get correct scattering amplitude for the Coulomb potential (Rutherford scattering).

In the scattering experiments we measure cross sections, i.e., the current density (number of particles per unit area and per unit time) at the detector divided by the current density of the incoming particles. The probability current density of the incoming plane wave is

$$\vec{j}_0 = |A|^2 \frac{\hbar \vec{k}}{m},$$

being obviously proportional with the current density of the incoming particles. The radial current density of the scattered wave is,

$$\begin{aligned} \vec{j}_{sc}(\vec{r}) \vec{e}_r &= \frac{\hbar}{2m} (\psi_{sc}^*(\vec{r}) \partial_r \psi_{sc}(\vec{r}) - \psi_{sc}(\vec{r}) \partial_r \psi_{sc}^*(\vec{r})) \\ &= \text{Re} \left(\frac{\hbar}{im} \psi_{sc}^*(\vec{r}) \partial_r \psi_{sc}(\vec{r}) \right). \end{aligned} \quad (154)$$

Making the following approximation,

$$\partial_r \psi_{sc}(\vec{r}) = f(\vartheta, \varphi) \partial_r \frac{e^{ikr}}{r} = -f(\vartheta, \varphi) \frac{e^{ikr}}{r^2} + ikf(\vartheta, \varphi) \frac{e^{ikr}}{r} \xrightarrow{r \rightarrow \infty} ikf(\vartheta, \varphi) \frac{e^{ikr}}{r}, \quad (155)$$

the radial current density can be expressed as

$$\vec{j}_{sc}(\vec{r}) \vec{e}_r \simeq |A|^2 \frac{\hbar k}{m} \frac{|f(\vartheta, \varphi)|^2}{r^2} = j_0 \frac{|f(\vartheta, \varphi)|^2}{r^2}. \quad (156)$$

The number of the scattered particles flowing through the area of the detector $d\vec{A} = \vec{e}_r r^2 d\Omega$ per unit time is then given by,

$$\frac{dN(\vartheta, \varphi)}{dt} = \vec{j}_{sc} d\vec{A} = (\vec{j}_{sc} \vec{e}_r) r^2 d\Omega = j_0 |f(\vartheta, \varphi)|^2 d\Omega. \quad (157)$$

This expression should be compared with

$$\frac{dN(\vartheta, \varphi)}{dt} = \sigma(\vartheta, \varphi) j_0 d\Omega, \quad (158)$$

where $\sigma(\vartheta, \varphi)$ is the *differential cross section*. Obviously, we obtained a simple relationship between the differential cross section and the scattering amplitude,

$$\sigma(\vartheta, \varphi) = |f(\vartheta, \varphi)|^2. \quad (159)$$

In the Born approximation this yields,

$$\sigma(\vartheta, \varphi) = \frac{m^2}{4\pi^2 \hbar^4} \left| \int V(\vec{r}) e^{-i\vec{q}\vec{r}} d^3r \right|^2. \quad (160)$$

The total cross section is defined as

$$\sigma = \int d\Omega \sigma(\Omega). \quad (161)$$

Note, however, that the calculation of the total cross section within the Born approximation could be misleading because the result does not satisfy the optical theorem (see later).

The scattering cross section of a composite target

If the scattering medium consists of identical atomic potentials $V_0(\vec{r})$ centered at the lattice points \vec{R}_i , then the potential energy of the system can be written as

$$V(\vec{r}) = \sum_i V_0(\vec{r} - \vec{R}_i), \quad (162)$$

where we also supposed that the atomic potentials are of compact, non-overlapping domains Ω_i . In this case the following expression enters the scattering amplitude in Born approximation,

$$\int V(\vec{r}) e^{-i\vec{q}\vec{r}} d^3r = \sum_i \int_{\Omega_i} V_0(\vec{r} - \vec{R}_i) e^{-i\vec{q}\vec{r}} d^3r = \sum_i \int_{\Omega_0} V_0(\vec{r}) e^{-i\vec{q}(\vec{r} + \vec{R}_i)} d^3r \quad (163)$$

$$= \left(\int_{\Omega_0} V_0(\vec{r}) e^{-i\vec{q}\vec{r}} d^3r \right) \sum_i e^{-i\vec{q}\vec{R}_i}. \quad (164)$$

The differential cross section can then be written in the following form,

$$\sigma(\vec{q}) = \sigma_0(\vec{q}) S(\vec{q}), \quad (165)$$

where the cross section corresponding to the atomic potential is called the *form factor*,

$$\sigma_0(\vec{q}) = \frac{m^2}{4\pi^2 \hbar^4} \left| \int_{\Omega_0} V_0(\vec{r}) e^{-i\vec{q}\vec{r}} d^3r \right|^2, \quad (166)$$

and the information about the atomic positions is included in the *structure constant*,

$$S(\vec{q}) = \sum_{i,j} e^{-i\vec{q}(\vec{R}_j - \vec{R}_i)}. \quad (167)$$

Note that the structure constant is usually defined by normalizing the above expression to one atom, i.e., divided by the number of atoms N .

3.3 The method of partial waves

We have learned that for *spherically symmetric potentials* the wavefunctions,

$$\psi_{\ell m}(E, \vec{r}) = \frac{R_{\ell}(E, r)}{r} Y_{\ell}^m(\vartheta, \varphi) \quad (168)$$

are solutions of the Schrödinger equation, where $R_{\ell}(E, r)$ is the solution of the radial Schrödinger equation,

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dr^2} + \frac{\hbar^2}{2m} \frac{\ell(\ell+1)}{r^2} + V(r) - E \right) R_{\ell}(E, r) = 0, \quad (169)$$

and $Y_{\ell}^m(\vartheta, \varphi)$ are the (complex) spherical harmonics.

Let us investigate first the free electron solutions! Introducing the wavenumber $k = \sqrt{\frac{2mE}{\hbar^2}}$ ($E > 0$), the radial Schrödinger equation can be transformed to the second order differential equation,

$$\left(\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} + k^2 \right) R_{\ell}(r) = 0. \quad (170)$$

The solutions, being finite at the origin, termed as *regular solutions* are given by

$$R_{\ell}^{\text{reg}}(r) = r j_{\ell}(kr), \quad (171)$$

where $j_{\ell}(x)$ are the so-called spherical Bessel functions. They exhibit the following boundary conditions,

$$j_{\ell}(x) \xrightarrow{x \rightarrow 0} \frac{x^{\ell}}{(2\ell+1)!!} \quad j_{\ell}(x) \xrightarrow{x \rightarrow \infty} \frac{1}{x} \sin\left(x - \ell\frac{\pi}{2}\right). \quad (172)$$

The *irregular solutions* (diverging at the origin) are,

$$R_{\ell}^{\text{irreg}}(r) = r n_{\ell}(kr), \quad (173)$$

where $n_{\ell}(x)$ are the spherical Neumann functions with the following limits,

$$n_{\ell}(x) \xrightarrow{x \rightarrow 0} -\frac{(2\ell-1)!!}{x^{\ell+1}} \quad n_{\ell}(x) \xrightarrow{x \rightarrow \infty} -\frac{1}{x} \cos\left(x - \ell\frac{\pi}{2}\right). \quad (174)$$

Far from the target ($V = 0$) a solution of the Schrödinger equation with cylindrical symmetry can be taken in the following form,

$$\psi(\vec{r}) = \sum_{\ell m} [A_{\ell} j_{\ell}(kr) - B_{\ell} n_{\ell}(kr)] Y_{\ell}^0(\vartheta) \quad (175)$$

$$\simeq \sum_{\ell m} \frac{1}{kr} \left[A_{\ell} \sin\left(kr - \ell\frac{\pi}{2}\right) + B_{\ell} \cos\left(kr - \ell\frac{\pi}{2}\right) \right] Y_{\ell}^0(\vartheta). \quad (176)$$

Here we omitted the contributions containing $Y_{\ell}^m(\vartheta, \varphi)$ with $m \neq 0$, since they break the cylindrical symmetry of the asymptotic wavefunction. Up to a complex phase, the radial wavefunctions can be chosen as real functions. This means that the coefficients A_{ℓ} and B_{ℓ} have the same complex phase,

$$\frac{A_{\ell}}{B_{\ell}} \in \mathbb{R},$$

thus $\exists C_\ell \in \mathbb{C}$ $|C_\ell|^2 = |A_\ell|^2 + |B_\ell|^2$ such that

$$\begin{aligned} A_\ell &= C_\ell \cos \delta_\ell, \\ B_\ell &= C_\ell \sin \delta_\ell, \end{aligned}$$

where $\delta_\ell \in \mathbb{R}$ are called the *partial phase shifts*. The asymptotic form of the wavefunction can then be written as,

$$\psi(\vec{r}) = \sum_{\ell m} \frac{C_\ell}{kr} \left[\cos \delta_\ell \sin \left(kr - \ell \frac{\pi}{2} \right) + \sin \delta_\ell \cos \left(kr - \ell \frac{\pi}{2} \right) \right] Y_\ell^0(\vartheta) \quad (177)$$

$$= \sum_{\ell m} \frac{C_\ell}{kr} \sin \left(kr - \ell \frac{\pi}{2} + \delta_\ell \right) Y_\ell^0(\vartheta). \quad (178)$$

The incoming plane wave with a wave vector along the z direction can be expanded with respect to the spherical Bessel functions (Bauer's identity),

$$e^{ikz} = e^{ikr \cos \vartheta} = \sum_{\ell} \sqrt{4\pi(2\ell+1)} i^\ell j_\ell(kr) Y_\ell^0(\vartheta). \quad (179)$$

Recalling the asymptotic form of the wavefunction (148),

$$\begin{aligned} \psi(\vec{r}) &= Ae^{ikz} + \psi_{sc}(\vec{r}) \\ &= \sum_{\ell} \frac{A}{kr} \sqrt{4\pi(2\ell+1)} i^\ell \sin \left(kr - \ell \frac{\pi}{2} \right) Y_\ell^0(\vartheta) + Af(\vartheta, \varphi) \frac{e^{ikr}}{r} \end{aligned} \quad (180)$$

$$= \sum_{\ell} \frac{A}{kr} \sqrt{4\pi(2\ell+1)} i^\ell \frac{e^{i(kr - \ell \frac{\pi}{2})} - e^{-i(kr - \ell \frac{\pi}{2})}}{2i} Y_\ell^0(\vartheta) + Af(\vartheta, \varphi) \frac{e^{ikr}}{r} \quad (181)$$

$$\begin{aligned} &= \frac{e^{ikr}}{r} \left(Af(\vartheta, \varphi) + \sum_{\ell} \frac{A}{2k\ell} \sqrt{4\pi(2\ell+1)} Y_\ell^0(\vartheta) \right) \\ &- \frac{e^{-ikr}}{r} \left(\sum_{\ell} \frac{A(-1)^\ell}{2k\ell} \sqrt{4\pi(2\ell+1)} Y_\ell^0(\vartheta) \right), \end{aligned} \quad (182)$$

which is the superposition of an incoming and an outgoing spherical wave.

We have to compare the expression (182) with the function in (178):

$$\psi(\vec{r}) = \sum_{\ell} \frac{C_\ell}{kr} \frac{e^{i(kr - \ell \frac{\pi}{2} + \delta_\ell)} - e^{-i(kr - \ell \frac{\pi}{2} + \delta_\ell)}}{2i} Y_\ell^0(\vartheta) \quad (183)$$

$$= \frac{e^{ikr}}{r} \left(\sum_{\ell} \frac{C_\ell e^{i\delta_\ell} i^{-\ell}}{2k\ell} Y_\ell^0(\vartheta) \right) - \frac{e^{-ikr}}{r} \left(\sum_{\ell} \frac{C_\ell e^{-i\delta_\ell} i^\ell}{2k\ell} Y_\ell^0(\vartheta) \right). \quad (184)$$

Matching of the coefficients of the incoming spherical wave we obtain,

$$\sum_{\ell} \frac{A(-1)^\ell}{2k\ell} \sqrt{4\pi(2\ell+1)} Y_\ell^0(\vartheta) = \sum_{\ell} \frac{C_\ell e^{-i\delta_\ell} i^\ell}{2k\ell} Y_\ell^0(\vartheta) \quad (185)$$

↓

$$\frac{A(-1)^\ell}{2k\iota} \sqrt{4\pi(2\ell+1)} = \frac{C_\ell e^{-i\delta_\ell} \iota^\ell}{2k\iota} \quad (186)$$

↓

$$C_\ell = A e^{i\delta_\ell} \iota^\ell \sqrt{4\pi(2\ell+1)}. \quad (187)$$

From the matching of the coefficient of the outgoing spherical wave in (182),

$$\begin{aligned} Af(\vartheta) + \sum_\ell \frac{A}{2k\iota} \sqrt{4\pi(2\ell+1)} Y_\ell^0(\vartheta) &= \sum_\ell \frac{C_\ell e^{i\delta_\ell} \iota^{-\ell}}{2k\iota} Y_\ell^0(\vartheta) \\ &= \sum_\ell \frac{A e^{2i\delta_\ell}}{2k\iota} \sqrt{4\pi(2\ell+1)} Y_\ell^0(\vartheta), \end{aligned} \quad (188)$$

we derive the partial wave expansion of the scattering amplitude,

$$\begin{aligned} f(\vartheta) &= \sum_\ell \frac{e^{2i\delta_\ell} - 1}{2k\iota} \sqrt{4\pi(2\ell+1)} Y_\ell^0(\vartheta) \\ &= \sum_\ell \frac{\sqrt{4\pi(2\ell+1)}}{k} e^{i\delta_\ell} \sin \delta_\ell Y_\ell^0(\vartheta). \end{aligned} \quad (189)$$

It is then straightforward to calculate the total (integrated) cross section,

$$\begin{aligned} \sigma_{\text{tot}} &= \int d\Omega \sigma(\vartheta) = \int d\Omega |f(\vartheta)|^2 \\ &= \frac{4\pi}{k^2} \sum_{\ell, \ell'} \sqrt{(2\ell+1)(2\ell'+1)} e^{i\delta_\ell} e^{-i\delta_{\ell'}} \sin \delta_\ell \sin \delta_{\ell'} \underbrace{\int d\Omega Y_\ell^0(\vartheta)^* Y_{\ell'}^0(\vartheta)}_{\delta_{\ell\ell'}} \\ &= \frac{4\pi}{k^2} \sum_\ell (2\ell+1) \sin^2 \delta_\ell, \end{aligned} \quad (190)$$

where we used that the spherical harmonics $Y_\ell^m(\vartheta)$ are orthonormal.

The above expression of the total cross section is, in principle, exact, but the evaluation of the sum of infinite partial contributions is obviously a hard task. The square of the angular momentum of a particle in the ℓ^{th} partial wave state can be given as

$$L^2 = \hbar^2 \ell(\ell+1). \quad (191)$$

By analogy with classical mechanics, the angular momentum of the particle moving parallel to the z axis can be expressed as $L = pa$, where the so-called *impact parameter* a is ascribed to the distance of the particle from the z axis. If the scattering potential is zero beyond a radius R , then we don't expect scattering for $a \gg R$, so the partial waves with

$$\begin{aligned} a = \frac{L}{p} \gg R &\rightarrow \frac{L^2}{p^2} \gg R^2 \rightarrow \frac{L^2}{2mE} \gg R^2 \\ &\rightarrow E \ll \frac{L^2}{2mR^2} = \frac{\hbar^2 \ell(\ell+1)}{2mR^2}, \end{aligned}$$

do not give a significant contribution to the scattering. This implies that for small energies we have to consider only a few scattering channel (ℓ) in the calculation of (190). *So the method of*

partial waves can usually be applied for small energies and for central potentials with compact support.

For very small energies, scattering happens in the partial channel $\ell = 0$. In 1921 C. Ramsauer and J.S. Townsend investigated independently the scattering of the very slow electrons on noble gases like Ar, Kr and Xe. They found that at $E \approx 0.7$ eV the electron propagates through the medium essentially without scattering. The reason for this is that around this energy the $\ell = 0$ phase shift passes π , $\delta_0(E) \approx \pi$, making the total cross section nearly zero.

We note that for $\delta_\ell(E) = (n + \frac{1}{2})\pi$ the partial cross section has a maximum, $\sigma_\ell = \frac{4\pi(2\ell+1)}{k^2}$. For large ℓ this maximum can be sharp (as a function of the energy) which is called a *resonant scattering*.

3.4 Optical theorem

Based on Eqs. (189) and (190) there is a direct connection between the scattering amplitude and the total cross section. Namely

$$\text{Im } f(\vartheta) = \sum_{\ell} \frac{\sqrt{4\pi(2\ell+1)}}{k} \sin^2 \delta_{\ell} Y_{\ell}^0(\vartheta) \quad (192)$$

and using the identity $Y_{\ell}^0(\vartheta = 0) = \sqrt{\frac{2\ell+1}{4\pi}}$, we get,

$$\text{Im } f(\vartheta = 0) = \frac{1}{k} \sum_{\ell} (2\ell+1) \sin^2 \delta_{\ell}, \quad (193)$$

implying

$$\sigma_{\text{tot}} = \frac{4\pi}{k} \text{Im } f(\vartheta = 0), \quad (194)$$

that means, the imaginary part of the forward scattering is proportional to the total cross section. This is the so-called *optical theorem*. In a very general sense, it is related to the conservation of the number of particles in scattering processes, so it follows from the continuity equation. The probability current (i.e. the flux of the probability current density) of the incoming plane wave is zero for a closed surface, while the probability current of the scattered wave (outgoing spherical wave) is proportional to the total scattering cross section. However, the probability current for a stationary wavefunction has to vanish on a closed surface. So, the probability current arising due to the superposition of the incoming plane wave and the scattered wave (interference term) has to eliminate the probability current of the scattered wave. This leads to the optical theorem (194) being valid for both elastic and inelastic scattering.

Proof for elastic scattering:

The wavefunction is the sum of the incoming wavefunction and the scattered wave,

$$\psi(\vec{r}) = \psi_0(\vec{r}) + \psi_{\text{sc}}(\vec{r}). \quad (195)$$

The probability current density can then be expressed as

$$\begin{aligned} \vec{j} &= \frac{\hbar}{2mi} \left(\psi^* \vec{\nabla} \psi - \psi \vec{\nabla} \psi^* \right) \\ &= \frac{\hbar}{2mi} \left[(\psi_0^* + \psi_{\text{sc}}^*) \vec{\nabla} (\psi_0 + \psi_{\text{sc}}) - (\psi_0 + \psi_{\text{sc}}) \vec{\nabla} (\psi_0^* + \psi_{\text{sc}}^*) \right] \end{aligned} \quad (196)$$

$$\begin{aligned} & \Downarrow \\ \vec{j} &= \vec{j}_0 + \vec{j}_{\text{sc}} + \vec{j}_{\text{int}}, \end{aligned} \quad (197)$$

with the current density of the incoming wave,

$$\vec{j}_0 = \frac{\hbar}{2m\lambda} \left(\psi_0^* \vec{\nabla} \psi_0 - \psi_0 \vec{\nabla} \psi_0^* \right), \quad (198)$$

the current density of the scattered wave,

$$\vec{j}_{\text{sc}} = \frac{\hbar}{2m\lambda} \left(\psi_{\text{sc}}^* \vec{\nabla} \psi_{\text{sc}} - \psi_{\text{sc}} \vec{\nabla} \psi_{\text{sc}}^* \right), \quad (199)$$

and the current density from the superposition of the two waves (the interference term),

$$\vec{j}_{\text{int}} = \frac{\hbar}{2m\lambda} \left[\psi_0^* \vec{\nabla} \psi_{\text{sc}} + \psi_{\text{sc}}^* \vec{\nabla} \psi_0 - \psi_0 \vec{\nabla} \psi_{\text{sc}}^* - \psi_{\text{sc}} \vec{\nabla} \psi_0^* \right]. \quad (200)$$

The asymptotic form of the radial component of the interference term,

$$\vec{j}_{\text{int}} \vec{e}_r = \frac{\hbar}{2m\lambda} \left[\psi_0^* \partial_r \psi_{\text{sc}} + \psi_{\text{sc}}^* \partial_r \psi_0 - \psi_0 \partial_r \psi_{\text{sc}}^* - \psi_{\text{sc}} \partial_r \psi_0^* \right], \quad (201)$$

can be formulated by the below approximations,

$$\psi_0(\vec{r}) = e^{i k r \cos \vartheta} \rightarrow \partial_r \psi_0(\vec{r}) = i k \cos \vartheta e^{i k r \cos \vartheta} \quad (202)$$

$$\psi_{\text{sc}}(\vec{r}) = f(\vartheta, \varphi) \frac{e^{i k r}}{r} \rightarrow \partial_r \psi_{\text{sc}}(\vec{r}) = i k f(\vartheta, \varphi) \frac{e^{i k r}}{r} + o\left(\frac{1}{r^2}\right), \quad (203)$$

yielding

$$\begin{aligned} \vec{j}_{\text{int}} \vec{e}_r &\simeq \frac{\hbar k}{2mr} \left[e^{i k r (1 - \cos \vartheta)} f(\vartheta, \varphi) + e^{-i k r (1 - \cos \vartheta)} \cos \vartheta f^*(\vartheta, \varphi) \right. \\ &\quad \left. + e^{-i k r (1 - \cos \vartheta)} f^*(\vartheta, \varphi) + e^{i k r (1 - \cos \vartheta)} \cos \vartheta f(\vartheta, \varphi) \right] \end{aligned} \quad (204)$$

$$\simeq \frac{\hbar k}{2mr} \left[e^{i k r (1 - \cos \vartheta)} (1 + \cos \vartheta) f(\vartheta, \varphi) + e^{-i k r (1 - \cos \vartheta)} (1 + \cos \vartheta) f^*(\vartheta, \varphi) \right] \quad (205)$$

$$= \frac{\hbar k}{mr} \text{Re} \left(e^{i k r (1 - \cos \vartheta)} (1 + \cos \vartheta) f(\vartheta, \varphi) \right). \quad (206)$$

If $\vartheta \neq 0$, then $1 - \cos \vartheta \neq 0$, so because of $kr \gg 1$ the function $e^{i k r (1 - \cos \vartheta)}$ oscillates rapidly as a function of ϑ . Since the function $(1 + \cos \vartheta) f(\vartheta, \varphi)$ varies slowly, the integral of the interference current density vanishes out of a small region around $\vartheta = 0$, so we are going to get a contribution to the interference current only from a cone given by $0 \leq \vartheta \leq \delta\vartheta$ and $0 \leq \varphi \leq 2\pi$, where $\delta\vartheta$ is small non-zero value. In this region we can approximate the interference term of the current density as:

$$\lim_{\vartheta \rightarrow 0} \vec{j}_{\text{int}} \vec{e}_r \simeq \frac{2\hbar k}{mr} \text{Re} \left(e^{i k r \vartheta^2 / 2} f(\vartheta = 0) \right) \quad (207)$$

and the corresponding flux is,

$$\begin{aligned} \int d\Omega \vec{j}_{\text{int}} \vec{e}_r &\simeq \frac{2\hbar k}{mr} \text{Re} \left(f(0) \int_0^{2\pi} d\varphi \int_0^{\delta\vartheta} d\vartheta \sin \vartheta e^{i k r \vartheta^2 / 2} \right) \\ &\simeq \frac{4\pi \hbar k}{mr} \text{Re} \left(f(0) \int_0^{\delta\vartheta} d\vartheta \vartheta e^{i k r \vartheta^2 / 2} \right) \\ &= \frac{4\pi \hbar k}{mr} \text{Re} \left(f(0) \int_0^{\delta x} dx e^{i k r x} \right) \\ &= \frac{4\pi \hbar k}{mr} \text{Re} \left(\frac{f(0)}{i k r} (e^{i k r \delta x} - 1) \right) \end{aligned} \quad (208)$$

where we used the substitution $\delta x = (\delta\vartheta)^2/2$. In the Lippmann–Schwinger equation we used the Green’s function of the outgoing wave, that can be determined from contour integration and given by the following limit,

$$\lim_{\alpha \rightarrow +0} G_0(\vec{r}', \vec{r}, E + i\alpha) = -\frac{2m}{\hbar^2} \lim_{\beta \rightarrow +0} \frac{e^{i(k+i\beta)|\vec{r}'-\vec{r}|}}{4\pi|\vec{r}'-\vec{r}|}, \quad (209)$$

where $E + i\alpha = \frac{\hbar^2(k+i\beta)^2}{2m}$. For arbitrary small positive β ,

$$e^{i(k+i\beta)r\delta x} = e^{ikr\delta x} e^{-\beta r\delta x} \xrightarrow{r \rightarrow \infty} 0, \quad (210)$$

this way we can neglect the oscillating term from the intrference current,

$$\int d\Omega \vec{j}_{\text{int}} \vec{e}_r \simeq \frac{4\pi\hbar k}{mr} \text{Re} \left(-\frac{f(0)}{ikr} \right) \simeq -\frac{4\pi}{r^2} \frac{\hbar}{m} \text{Im} f(0). \quad (211)$$

The probability current of the incoming wave vanishes,

$$\int d\Omega \vec{j}_0 \vec{e}_r = \frac{\hbar\vec{k}}{m} \int d\Omega \vec{e}_r = 0, \quad (212)$$

while the probability current of the outgoing wave is given by

$$r^2 \int d\Omega \vec{j}_s \vec{e}_r = \frac{\hbar k}{m} \sigma_{\text{tot}}. \quad (213)$$

The total probability current of the stationary wavefunction is zero,

$$r^2 \int d\Omega \vec{j} \vec{e}_r = \frac{\hbar k}{m} \sigma_{\text{tot}} - 4\pi \frac{\hbar}{m} \text{Im} f(0) = 0, \quad (214)$$

leading to the optical theorem,

$$\sigma_{\text{tot}} = \frac{4\pi}{k} \text{Im} f(0). \quad (215)$$

4 The pictures of quantum mechanics

In quantum mechanics we can use three different view points (pictures) to describe the time evolution of the states and the operators. As we will see they are related to each other in terms of unitary transformations, thus, we have the freedom to use either one according to the Hamilton operator of the system.

4.1 The Schrödinger picture

All we we have learned in quantum mechanics so far is related to the so-called Schrödinger picture. For sake of simplicity we consider a time independent Hamilton operator,

$$\partial_t H^S(t) = 0, \quad (216)$$

where the superscript S notes that the Hamilton operator considered in the Schrödinger picture. This picture is defined by the time dependent Schrödinger equation valid for the physical states,

$$i\hbar\partial_t\psi^S(t) = H^S\psi^S(t), \quad (217)$$

where the initial condition for the wavefunction is fixed by,

$$\psi^S(t_0) = \varphi. \quad (218)$$

Let us introduce the time evolution operator $U(t, t_0)$ as

$$\psi^S(t) = U(t, t_0)\psi^S(t_0), \quad (219)$$

with the obvious boundary condition,

$$U(t_0, t_0) = I. \quad (220)$$

Substituting the right-hand side of Eq. (219) into the Schrödinger equation (217), we get

$$i\hbar\frac{d}{dt}U(t, t_0) = H^S U(t, t_0), \quad (221)$$

or after integration,

$$U(t, t_0) = I - \frac{i}{\hbar} \int_{t_0}^t H^S U(t', t_0) dt'. \quad (222)$$

This equation can be solved by successive approximation,

$$U^{(k+1)}(t, t_0) = I - \frac{i}{\hbar} \int_{t_0}^t H^S U^{(k)}(t', t_0) dt', \quad (223)$$

↓

$$U^{(0)}(t, t_0) = I \quad (224)$$

$$U^{(1)}(t, t_0) = I - \frac{i}{\hbar} \int_{t_0}^t H^S dt' = I - \frac{i}{\hbar} H^S (t - t_0) \quad (225)$$

$$U^{(2)}(t, t_0) = I - \frac{i}{\hbar} H^S (t - t_0) + \left(-\frac{i}{\hbar}\right)^2 \frac{(H^S)^2 (t - t_0)^2}{2} \quad (226)$$

$$U^{(3)}(t, t_0) = I - \frac{i}{\hbar} H^S (t - t_0) + \left(-\frac{i}{\hbar}\right)^2 \frac{(H^S)^2 (t - t_0)^2}{2} + \left(-\frac{i}{\hbar}\right)^3 \frac{(H^S)^3 (t - t_0)^3}{3!} \quad (227)$$

$$(228)$$

$$\Downarrow$$

$$U^{(k)}(t, t_0) = \sum_{l=0}^k \frac{1}{l!} \left(-\frac{i}{\hbar} H^S(t-t_0) \right)^l .$$

We can realize that this is the Taylor expansion of the exponential function, so the final solution can be written as

$$U(t, t_0) = e^{-\frac{i}{\hbar} H^S(t-t_0)} , \quad (229)$$

satisfying the commutation relation,

$$[U(t, t_0), H^S] = 0 . \quad (230)$$

Statement: The time evolution operator is unitary.

Proof:

$$i\hbar \frac{d}{dt} U^\dagger(t, t_0) = -U^\dagger(t, t_0) H^S \quad (231)$$

\Downarrow

$$\frac{d}{dt} [U^\dagger(t, t_0) U(t, t_0)] = \frac{1}{i\hbar} (-U^\dagger(t, t_0) H U(t, t_0) + U^\dagger(t, t_0) H U(t, t_0)) = 0 . \quad (232)$$

Since

$$U^\dagger(t_0, t_0) U(t_0, t_0) = I \quad (233)$$

\Downarrow

$$U^\dagger(t, t_0) U(t, t_0) = I \implies U^\dagger(t, t_0) = U(t, t_0)^{-1} . \quad (234)$$

Note that the inverse of $U(t, t_0)$ describes a reversed time evolution:

$$U(t, t_0)^{-1} = e^{-\frac{i}{\hbar} H^S(t_0-t)} = U(t_0, t) . \quad (235)$$

For two arbitrary states, $\psi_i^S(t)$ and $\psi_j^S(t)$, the matrix element of the hermitian operator $A^S(t)$, that can have explicit time dependence, is defined as

$$a_{ij}^S(t) = \langle \psi_i^S(t) | A^S(t) | \psi_j^S(t) \rangle = \langle \varphi_i | U^\dagger(t, t_0) A^S(t) U(t, t_0) | \varphi_j \rangle . \quad (236)$$

The time evolution of this matrix element can be expressed as

$$\begin{aligned} \frac{d}{dt} a_{ij}^S(t) &= -\frac{1}{i\hbar} \langle \psi_i^S(t) | H^S A^S(t) | \psi_j^S(t) \rangle + \frac{1}{i\hbar} \langle \psi_i^S(t) | A^S(t) H^S | \psi_j^S(t) \rangle \\ &\quad + \langle \psi_i^S(t) | \partial_t A^S(t) | \psi_j^S(t) \rangle \\ &= \langle \psi_i^S(t) | \frac{1}{i\hbar} [A^S(t), H^S] + \partial_t A^S(t) | \psi_j^S(t) \rangle . \end{aligned} \quad (237)$$

As we learned already, the quantum mechanical time derivative $\frac{1}{i\hbar} [A^S(t), H^S]$ enters the above identity.

4.2 The Heisenberg picture

The wavefunctions in the Heisenberg picture are defined as,

$$\psi^H(t) = U^\dagger(t, t_0) \psi^S(t) = \psi^S(t_0) = \varphi, \quad (238)$$

used to be tipified such that the states are stopped. This fixes the transformation of the operators:

$$\varphi^S(t) = A\psi^S(t) \rightarrow \varphi^H(t) = U^\dagger(t, t_0) (A^S(t) \psi^S(t)) \quad (239)$$

$$= U^\dagger(t, t_0) (A^S(t) U(t, t_0) U^\dagger(t, t_0) \psi^S(t)) \quad (240)$$

$$= U^\dagger(t, t_0) A^S(t) U(t, t_0) \psi^H(t) \quad (241)$$

$$= A^H(t) \psi^H(t) \rightarrow A^H(t) = U^\dagger(t, t_0) A^S(t) U(t, t_0). \quad (242)$$

This means that even the operators being time independent in the Schrödinger picture become time dependent (i.e. move) in the Heisenberg picture.

The equation of motion for the operators reads as

$$\begin{aligned} \frac{d}{dt} A^H(t) &= \frac{1}{i\hbar} (-U^\dagger(t, t_0) H^S A^S(t) U(t, t_0) + U^\dagger(t, t_0) A^S(t) H^S U(t, t_0)) \\ &\quad + U^\dagger(t, t_0) \partial_t A^S(t) U(t, t_0) \end{aligned} \quad (243)$$

$$= \frac{1}{i\hbar} [A^H(t), H^H(t)] + \partial_t A^H(t), \quad (244)$$

where

$$H^H(t) = U^\dagger(t, t_0) H^S U(t, t_0) \quad (245)$$

and

$$\partial_t A^H(t) \equiv U^\dagger(t, t_0) \partial_t A^S(t) U(t, t_0). \quad (246)$$

It is easy to prove that the Hamilton operator is independent of time in the Heisenberg picture if it is independent of time in the Schrödinger picture:

$$\frac{d}{dt} H^H(t) = \frac{1}{i\hbar} \left(-U^\dagger(t, t_0) (H^S)^2 U(t, t_0) + U^\dagger(t, t_0) (H^S)^2 U(t, t_0) \right) = 0 \quad (247)$$

↓

$$H^H(t) = H^S. \quad (248)$$

The matrix element of the observables are identical in the Heisenberg and Schrödinger pictures:

$$a_{ij}^H(t) = \langle \psi_i^H | A^H(t) | \psi_j^H \rangle = \langle \psi_i^S(t) | A^S(t) | \psi_j^S(t) \rangle = a_{ij}^S(t), \quad (249)$$

while its time dependence can also be expressed as in the Schrödinger picture:

$$\frac{d}{dt} a_{ij}^H(t) = \langle \psi_i^H | \frac{1}{i\hbar} [A^H(t), H^H(t)] + \partial_t A^H(t) | \psi_j^H \rangle \quad (250)$$

4.3 The Dirac (interaction) picture

We consider a Hamilton operator, which in Schrödinger picture is composed as the sum of a time independent part, H_0^S , and a time dependent perturbation, $V^S(t)$,

$$H^S(t) = H_0^S + V^S(t) . \quad (251)$$

Within the Dirac picture, the operators evolve in time according to the time evolution operator related to H_0^S ,

$$U(t, t_0) = e^{-\frac{i}{\hbar} H_0^S (t-t_0)} \quad (252)$$

↓

$$\psi^D(t) = U^\dagger(t, t_0) \psi^S(t) , \quad (253)$$

with the boundary condition,

$$\psi^D(t_0) = \psi^S(t_0) = \varphi . \quad (254)$$

and

$$A^D(t) = U^\dagger(t, t_0) A^S(t) U(t, t_0) . \quad (255)$$

The equation of motion of the operators looks formally similar as in the Heisenberg picture:

$$\begin{aligned} \frac{d}{dt} A^D(t) &= -\frac{1}{i\hbar} U^\dagger(t, t_0) H_0^S A^S(t) U(t, t_0) + \frac{1}{i\hbar} U^\dagger(t, t_0) A^S(t) H_0^S U(t, t_0) \\ &\quad + U^\dagger(t, t_0) \partial_t A^S(t) U(t, t_0) \end{aligned} \quad (256)$$

$$= \frac{1}{i\hbar} [A^D(t), H_0^D(t)] + \partial_t A^D(t) , \quad (257)$$

where

$$\partial_t A^D(t) \equiv U^\dagger(t, t_0) \partial_t A^S(t) U(t, t_0) . \quad (258)$$

In particular, the time independent part of the Hamilton operator remains time independent,

$$\frac{d}{dt} H_0^D(t) = 0 \implies H_0^D(t) = H_0^S . \quad (259)$$

Equation of motion for the wavefunction within the Dirac picture,

$$i\hbar \partial_t \psi^D(t) = i\hbar \partial_t U^\dagger(t, t_0) \psi^S(t) + i\hbar U^\dagger(t, t_0) \partial_t \psi^S(t) \quad (260)$$

$$= -U^\dagger(t, t_0) H_0^S \psi^S(t) + U^\dagger(t, t_0) (H_0 + V^S(t)) \psi^S(t) \quad (261)$$

$$= U^\dagger(t, t_0) V^S(t) \psi^S(t) \quad (262)$$

$$= V^D(t) \psi^D(t) , \quad (263)$$

where

$$V^D(t) = U^\dagger(t, t_0) V^S(t) U(t, t_0) \quad (264)$$

is the perturbation operator in the Dirac picture.

The time dependence of the matrix elements of observables,

$$a_{ij}(t) = \langle \psi_i^D(t) | A^D(t) | \psi_j^D(t) \rangle \quad (265)$$

↓

$$\frac{d}{dt} a_{ij}(t) = -\frac{1}{i\hbar} \langle \psi_i^D(t) | V^D(t) A^D(t) | \psi_j^D(t) \rangle + \frac{1}{i\hbar} \langle \psi_i^D(t) | A^D(t) V^D(t) | \psi_j^D(t) \rangle \quad (266)$$

$$+ \frac{1}{i\hbar} \langle \psi_i^D(t) | [A^D(t), H_0^D] | \psi_j^D(t) \rangle + \langle \psi_i^D(t) | \partial_t A^D(t) | \psi_j^D(t) \rangle \quad (267)$$

$$= \frac{1}{i\hbar} \langle \psi_i^D(t) | [A^D(t), H^D(t)] | \psi_j^D(t) \rangle + \langle \psi_i^D(t) | \partial_t A^D(t) | \psi_j^D(t) \rangle \quad (268)$$

which is formally the same as in the Schrödinger and Heisenberg pictures.

The time dependence of the wavefunction can be expressed in terms of a new time evolution operator:

$$\psi^D(t) = U^D(t, t_0) \psi^D(t_0) = U^D(t, t_0) \varphi, \quad (269)$$

with

$$U^D(t_0, t_0) = I. \quad (270)$$

Using Eq. (263) we get the differential equation for the time evolution operator in the Dirac picture,

$$\frac{d}{dt} U^D(t, t_0) = -\frac{i}{\hbar} V^D(t) U^D(t, t_0), \quad (271)$$

which yields by integration,

$$U^D(t, t_0) = I - \frac{i}{\hbar} \int_{t_0}^t V^D(t') U^D(t', t_0) dt'. \quad (272)$$

This integral equation can be solved by successive approximation as we discussed before,

$$U^{D(0)}(t, t_0) = I$$

$$U^{D(k+1)}(t, t_0) = I - \frac{i}{\hbar} \int_{t_0}^t V^D(t') U^{D(k)}(t', t_0) dt' \quad (k = 0, 1, 2, \dots) \quad (273)$$

↓

$$U^D(t, t_0) = \sum_{k=0}^{\infty} \left(-\frac{i}{\hbar}\right)^k \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \dots \int_{t_0}^{t_{k-1}} dt_k V^D(t_1) V^D(t_2) \dots V^D(t_k) \quad (274)$$

$$= \sum_{k=0}^{\infty} \frac{1}{k!} \left(-\frac{i}{\hbar}\right)^k \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \dots \int_{t_0}^{t_{k-1}} dt_k \mathbb{T} [V^D(t_1) V^D(t_2) \dots V^D(t_k)] \quad (275)$$

$$:= \mathbb{T} \exp \left(-\frac{i}{\hbar} \int_{t_0}^t dt_1 V^D(t_1) \right), \quad (276)$$

where we introduced the time ordered product of the operators:

$$\mathbb{T} [V^D(t_1) V^D(t_2) \dots V^D(t_k)] = V^D(t_{i_1}) V^D(t_{i_2}) \dots V^D(t_{i_k}) \quad (277)$$

$$t_{i_l} \in \{t_1, t_2, \dots, t_k\} \quad (l = 1, 2, \dots, k) \quad (278)$$

$$t_{i_1} > t_{i_2} > t_{i_3} \dots > t_{i_{k-1}} > t_k \quad (279)$$

Statement: Using the notation,

$$f(t_1, t_2, \dots, t_k) = V^D(t_1) V^D(t_2) \dots V^D(t_k),$$

$$\int_{t_0}^t dt_1 \int_{t_0}^t dt_2 \dots \int_{t_0}^t dt_k \mathbb{T}f(t_1, t_2, \dots, t_k) = k! \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \dots \int_{t_0}^{t_{k-1}} dt_k f(t_1, t_2, \dots, t_k) . \quad (280)$$

Proof: $k = 2$

$$\begin{aligned} \int_{t_0}^t dt_1 \int_{t_0}^t dt_2 \mathbb{T}f(t_1, t_2) &= \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 f(t_1, t_2) + \int_{t_0}^t dt_2 \int_{t_0}^{t_2} dt_1 f(t_2, t_1) \\ &= 2 \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 f(t_1, t_2) , \end{aligned} \quad (281)$$

$k = 3$:

$$\begin{aligned} \int_{t_0}^t dt_1 \int_{t_0}^t dt_2 \int_{t_0}^t dt_3 \mathbb{T}f(t_1, t_2, t_3) &= \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \int_{t_0}^{t_2} dt_3 f(t_1, t_2, t_3) \\ &+ \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_3 \int_{t_0}^{t_3} dt_2 f(t_1, t_3, t_2) \\ &+ \int_{t_0}^t dt_2 \int_{t_0}^{t_2} dt_1 \int_{t_0}^{t_1} dt_3 f(t_2, t_1, t_3) \\ &+ \int_{t_0}^t dt_2 \int_{t_0}^{t_2} dt_3 \int_{t_0}^{t_3} dt_1 f(t_2, t_3, t_1) \\ &+ \int_{t_0}^t dt_3 \int_{t_0}^{t_3} dt_1 \int_{t_0}^{t_1} dt_2 f(t_3, t_1, t_2) \\ &+ \int_{t_0}^t dt_3 \int_{t_0}^{t_3} dt_2 \int_{t_0}^{t_2} dt_1 f(t_3, t_2, t_1) \\ &= 6 \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \int_{t_0}^{t_2} dt_3 f(t_1, t_2, t_3) . \end{aligned} \quad (282)$$

In general: On the left hand side of Eq. (280) we divide the integration domain to $k!$ peaces, where the variables t_1, t_2, \dots, t_k are time ordered: we have k choices for the smallest one, $k-1$ for the next one etc. By redefining the variables to t_1, t_2, \dots, t_k , it turns out that all off them are identical with the integral that appears on the right hand side of Eq. (280).

Connection with time dependent perturbation theory:

We take the time evolution operator up to first order in the Dirac picture:

$$U^{D(1)}(t, t_0) = I - \frac{i}{\hbar} \int_{t_0}^t V^D(t') dt' = I - \frac{i}{\hbar} \int_{t_0}^t e^{\frac{i}{\hbar} H_0^S(t'-t_0)} V^S(t') e^{-\frac{i}{\hbar} H_0^S(t'-t_0)} dt' , \quad (283)$$

and the wave function in the Dirac picture reads as,

$$|\psi^{D(1)}(t)\rangle = |\varphi\rangle - \frac{i}{\hbar} \int_{t_0}^t e^{\frac{i}{\hbar} H_0^S(t'-t_0)} V^S(t') e^{-\frac{i}{\hbar} H_0^S(t'-t_0)} |\varphi\rangle dt' . \quad (284)$$

The wavefunction in the Schrödinger picture can be written as,

$$|\psi^{S(1)}(t)\rangle = e^{-\frac{i}{\hbar} H_0^S(t-t_0)} |\psi^{D(1)}(t)\rangle \quad (285)$$

$$= e^{-\frac{i}{\hbar} H_0^S(t-t_0)} |\varphi\rangle - \frac{i}{\hbar} e^{-\frac{i}{\hbar} H_0^S(t-t_0)} \int_{t_0}^t e^{\frac{i}{\hbar} H_0^S(t'-t_0)} V^S(t') e^{-\frac{i}{\hbar} H_0^S(t'-t_0)} |\varphi\rangle dt' . \quad (286)$$

As before (in the course Quantum Mechanics 1), we assume that the initial state at t_0 is an eigenstate of H_0^S ,

$$|\psi(t_0)\rangle = |\varphi\rangle = |k\rangle, \quad (287)$$

and we will use the spectral resolution of H_0^S ,

$$H_0^S = \sum_n \varepsilon_n |n\rangle \langle n|. \quad (288)$$

The wave function can then be evaluated as

$$|\psi^{S(1)}(t)\rangle = e^{-\frac{i}{\hbar}H_0^S(t-t_0)} |k\rangle - \frac{i}{\hbar} \sum_n e^{-\frac{i}{\hbar}H_0^S(t-t_0)} \times \int_{t_0}^t e^{\frac{i}{\hbar}H_0^S(t'-t_0)} |n\rangle \langle n| V^S(t') e^{-\frac{i}{\hbar}H_0^S(t'-t_0)} |k\rangle dt' \quad (289)$$

$$= e^{-\frac{i}{\hbar}\varepsilon_k(t-t_0)} |k\rangle - \frac{i}{\hbar} \sum_n e^{-\frac{i}{\hbar}\varepsilon_n(t-t_0)} |n\rangle \int_{t_0}^t e^{i\omega_{nk}(t'-t_0)} V_{nk}^S(t') dt' \quad (290)$$

where

$$\omega_{nk} = \frac{\varepsilon_n - \varepsilon_k}{\hbar} \quad (291)$$

and

$$V_{nk}^S(t) = \langle n| V^S(t) |k\rangle.$$

Thus, the wave function in first order in $V^S(t)$ reads as

$$|\psi^{S(1)}(t)\rangle = \sum_n c_n^{(1)}(t) e^{-\frac{i}{\hbar}\varepsilon_n(t-t_0)} |n\rangle, \quad (292)$$

where

$$c_k^{(1)}(t) = 1 - \frac{i}{\hbar} \int_{t_0}^t V_{kk}^S(t') dt' \simeq 1 \quad (293)$$

and for $n \neq k$

$$c_n^{(1)}(t) = -\frac{i}{\hbar} \int_{t_0}^t e^{i\omega_{nk}(t'-t_0)} V_{nk}^S(t') dt'. \quad (294)$$

The above expressions are identical with the results we obtained in first order of the time dependent perturbation theory in the course QM1.

5 Motion in electromagnetic field

According to special relativity the Hamiltonian of a particle with rest mass m and electric charge q in an external electromagnetic field is given by

$$H(\vec{r}, \vec{p}) = \sqrt{m^2 c^4 + c^2 \left(\vec{p} - q \vec{A}(\vec{r}) \right)^2} + q\phi(\vec{r}), \quad (295)$$

where \vec{p} is the *canonical momentum*, while $\phi(\vec{r})$ and $\vec{A}(\vec{r})$ are the scalar and the vector potentials, respectively. Note that the electric field \vec{E} and the magnetic field (B-field) \vec{B} are related to the potentials as

$$\vec{E} = -\vec{\nabla}\phi - \frac{\partial \vec{A}}{\partial t} \text{ and } \vec{B} = \vec{\nabla} \times \vec{A}. \quad (296)$$

Using the approximation,

$$mc^2 \sqrt{1 + \frac{1}{m^2 c^2} \left(\vec{p} - q \vec{A}(\vec{r}) \right)^2} \simeq mc^2 + \frac{\left(\vec{p} - q \vec{A}(\vec{r}) \right)^2}{2m}$$

in the nonrelativistic limit we use the following form for the Hamiltonian,

$$H(\vec{r}, \vec{p}) = \frac{\left(\vec{p} - q \vec{A}(\vec{r}) \right)^2}{2m} + V(\vec{r}), \quad (297)$$

where we have dropped the rest energy and introduced the potential energy, $V(\vec{r}) = q\phi(\vec{r})$. The *kinetic momentum* is defined as,

$$\vec{K} = \vec{p} - q\vec{A} = m\vec{v}. \quad (298)$$

5.1 The commutation relations of the kinetic momentum

We extend quantum mechanics to the case of electromagnetic field, described by the Hamiltonian (297), by keeping the commutator relation between the position and the canonical momentum operators,

$$[p_i, x_j] = \frac{\hbar}{i} \delta_{ij}. \quad (299)$$

In coordinate representation, the position operators being the multiplication with the coordinates, the canonical momentum operator is defined as,

$$\vec{p} = \frac{\hbar}{i} \vec{\nabla}, \quad (300)$$

and for the kinetic momentum as

$$\vec{K} = \frac{\hbar}{i} \vec{\nabla} - q\vec{A}. \quad (301)$$

The components of the canonical momentum operator commute with each other, but this is not necessarily true for the kinetic momentum operators:

$$\begin{aligned} [K_i, K_j] &= i\hbar q ([\partial_i, A_j] + [A_i, \partial_j]) \\ &= i\hbar q (\partial_i A_j - A_j \partial_i + A_i \partial_j - \partial_j A_i) \\ &= i\hbar q ((\partial_i A_j) - (\partial_j A_i)), \end{aligned} \quad (302)$$

where $(\partial_i A_j)$ means the multiplication with the function $\frac{\partial A_j}{\partial x_i}$. Since $\vec{B} = \text{rot } \vec{A}$,

$$\varepsilon_{ijk} B_k = \varepsilon_{ijk} \varepsilon_{lmk} (\partial_l A_m) = (\delta_{il} \delta_{jm} - \delta_{im} \delta_{jl}) (\partial_l A_m) = (\partial_i A_j) - (\partial_j A_i), \quad (303)$$

therefore,

$$[K_i, K_j] = i\hbar q \varepsilon_{ijk} B_k,$$

which can also be expressed as (see the angular momentum operators):

$$\vec{K} \times \vec{K} = i\hbar q \vec{B}. \quad (304)$$

This means that the kinetic energy operators commute with each other only in absence of magnetic field. We note the commutator relations of the position and the kinetic momentum operators,

$$[K_i, x_j] = [p_i, x_j] = \frac{\hbar}{i} \delta_{ij}. \quad (305)$$

5.2 The Hamilton operator

As what follows, we investigate the coordinate representation of the Hamiltonian (297). To this end, we expand the square of the kinetic momentum operator,

$$\left(\frac{\hbar}{i} \vec{\nabla} - q\vec{A} \right)^2 = -\hbar^2 \Delta + q^2 A^2 - \frac{\hbar q}{i} \left(\vec{\nabla} \vec{A} + \vec{A} \vec{\nabla} \right). \quad (306)$$

Inferring the action of the last term on a wavefunction ψ ,

$$\partial_i A_i \psi + A_i \partial_i \psi = (\partial_i A_i) \psi + 2A_i (\partial_i \psi), \quad (307)$$

or

$$\vec{\nabla} \vec{A} + \vec{A} \vec{\nabla} = \text{div} \vec{A} + 2\vec{A} \vec{\nabla}, \quad (308)$$

yields the Hamilton operator

$$H = -\frac{\hbar^2}{2m} \Delta + V + \frac{q^2}{2m} A^2 + \frac{i\hbar q}{2m} \text{div} \vec{A} + \frac{i\hbar q}{m} \vec{A} \vec{\nabla}. \quad (309)$$

Using *Coulomb gauge* for the vector potential, $\text{div} \vec{A} = 0$, the Hamilton operator reduces to

$$H = \underbrace{-\frac{\hbar^2}{2m} \Delta + V}_{H_0} + \frac{i\hbar q}{m} \vec{A} \vec{\nabla} + \frac{q^2}{2m} A^2. \quad (310)$$

As what follows, we will investigate the third and fourth terms in the above Hamilton operator.

5.3 Para- and diamagnetism

In homogeneous static magnetic field, the vector potential can be written using the so-called *symmetric gauge*,

$$\vec{A} = \frac{1}{2} \vec{B} \times \vec{r}. \quad (311)$$

This is a Coulomb gauge,

$$\operatorname{div}\vec{A} = \partial_i A_i = \frac{1}{2} \varepsilon_{ijk} B_j \partial_i x_k = \frac{1}{2} \varepsilon_{ijk} \delta_{ik} B_j = \frac{1}{2} \varepsilon_{kjk} B_j = 0, \quad (312)$$

and, indeed,

$$\begin{aligned} (\vec{\nabla} \times \vec{A})_i &= \frac{1}{2} \varepsilon_{ijk} \varepsilon_{klm} \partial_j x_m B_l \\ &= \frac{1}{2} (\delta_{il} \delta_{jm} - \delta_{im} \delta_{jl}) \delta_{jm} B_l \\ &= \frac{1}{2} (\delta_{il} \delta_{jj} - \delta_{il}) B_l \\ &= \frac{1}{2} (3B_i - B_i) = B_i. \end{aligned} \quad (313)$$

For the case of $\vec{B} = (0, 0, B)$, this gives $\vec{A} = \frac{1}{2}(-By, Bx, 0)$. It is easy to see that the asymmetric gauges $\vec{A} = (-By, 0, 0)$ and $\vec{A} = (0, Bx, 0)$ also reproduce the desired magnetic field. The action of the third term of the Hamiltonian in Eq. (310) can be expressed as

$$\begin{aligned} \frac{i\hbar q}{m} \vec{A} \vec{\nabla} \psi &= \frac{i\hbar q}{2m} (\vec{B} \times \vec{r}) (\vec{\nabla} \psi) = \frac{i\hbar q}{2m} (\vec{r} \times (\vec{\nabla} \psi)) \vec{B} \\ &= \frac{i\hbar q}{2m} (\vec{r} \times \vec{\nabla}) \vec{B} \psi, \end{aligned} \quad (314)$$

where we took into account that the spatial derivatives of \vec{B} disappear. Employing the coordinate representation of the momentum operator, $\vec{p} = \frac{\hbar}{i} \vec{\nabla}$, this term can then be written as

$$\frac{i\hbar q}{m} \vec{A} \vec{\nabla} = -\frac{q}{2m} (\vec{r} \times \vec{p}) \vec{B} = -\frac{q}{2m} \vec{L} \vec{B} = -\vec{M}_L \vec{B}, \quad (315)$$

where for electrons, $q = -e$,

$$\vec{M}_L = \frac{q}{2m} \vec{L} = -\mu_B \frac{\vec{L}}{\hbar}, \quad (316)$$

e being the unit charge, m the electron mass and $\mu_B = \frac{e\hbar}{2m} = 9.27 \times 10^{-24}$ J/T the Bohr magneton. Together with the coupling of the spin with the magnetic field, the *Pauli paramagnetic term* reads as,

$$H_{\text{para}} = -(\vec{M}_L + 2\vec{M}_S) \vec{B} = \frac{\mu_B}{\hbar} (\vec{L} + 2\vec{S}) \vec{B}. \quad (317)$$

The ordinary Zeemann effect

The energy levels of the hydrogen atom in a homogeneous magnetic field along the z direction split as

$$E_{n\ell m_\ell m_s} = E_n^{(0)} + \mu_B (m_\ell + 2m_s) B. \quad (318)$$

Interestingly, the level spacing corresponds to the Larmour frequency $\omega_L = \mu_B B / \hbar = \frac{qB}{2m}$ known from classical electrodynamics. The original level is $2\ell + 1$ times degenerate in the angular momentum and 2 times degenerate in the spin, so there is an overall degeneracy of $2(2\ell + 1)$. If we consider the combinations $m_\ell + 2m_s$ with $m_\ell \in \{-\ell, -\ell + 1, \dots, \ell - 1, \ell\}$ and $m_s \in \{-1/2, 1/2\}$, then we get $2\ell + 3$ different combinations. The levels with the energies $E_n^{(0)} + \mu_B B \{-\ell - 1, -\ell, \ell, \ell + 1\}$ are nondegenerate, while the ones with energies $E_n^{(0)} + \mu_B B \{-\ell + 1, -\ell + 2, \dots, \ell - 2, \ell - 1\}$ are doubly degenerate, so the total number of levels is retained, $4 + 2(2\ell - 1) = 2(2\ell + 1)$. (In fact, the relativistic spin-orbit coupling can strongly modify the above level splittings.)

The second term in the Hamiltonian in Eq. (310) is the so called *Langevin diamagnetic term*. Using the symmetric gauge again,

$$\frac{q^2}{2m} A^2 = \frac{q^2}{8m} (\vec{B} \times \vec{r})^2 = \frac{q^2}{8m} (r^2 B^2 - (\vec{r} \vec{B})^2) = \frac{q^2 B^2}{8m} (x^2 + y^2) , \quad (319)$$

where for the final expression we assumed that the magnetic field points to the z direction. In atoms this term is usually negligible as compared to the paramagnetic term:

$$\frac{\delta E_{\text{dia}}}{\delta E_{\text{para}}} = \frac{e^2 B^2}{8m} \left(\frac{eB}{2m} \right)^{-1} \frac{|\langle x^2 + y^2 \rangle|}{|\langle L_z + 2S_z \rangle|} \simeq \frac{e a_0^2}{4\hbar} B .$$

In the estimate above we used $|\langle x^2 + y^2 \rangle| \sim a_0^2$ and $|\langle L_z + 2S_z \rangle| \sim \hbar$. If the magnetic field is measured in Tesla, the above ratio equals

$$\begin{aligned} & \frac{2\pi \times 1.602177 \times 10^{-19} \times (5.2917721 \times 10^{-11})^2}{4 \times 6.62607 \times 10^{-34}} B \left[\frac{C m^2 kg}{J s s^2 A} \right] \\ & = 1.0636 \times 10^{-6} B . \end{aligned}$$

However, if the paramagnetic term vanishes, $\langle L_z + 2S_z \rangle = 0$, the effect of the magnetic field arises from the diamagnetic term.

The paramagnetic term appears because the atomic magnetic moment $\vec{\mu} = -\frac{\mu_B}{\hbar} \langle \vec{L} + 2\vec{S} \rangle$ interacts with the external magnetic field and it turns along \vec{B} . On the contrary, the Langevin diamagnetism is related to the induced magnetic moment created by the external field,

$$\begin{aligned} \vec{\mu}_{\text{dia}} &= -\frac{\partial E_{\text{dia}}}{\partial \vec{B}} = -\frac{e^2}{8m} \frac{\partial \langle (\vec{B} \times \vec{r})^2 \rangle}{\partial \vec{B}} \\ &= -\frac{e^2}{4m} \left(\langle r^2 \rangle \vec{B} - \langle \vec{r} (\vec{r} \vec{B}) \rangle \right)_{\vec{B} \parallel \vec{e}_z} = -\frac{e^2 B}{4m} \langle x^2 + y^2 \rangle \vec{e}_z , \end{aligned} \quad (320)$$

being proportional to the external magnetic field and pointing along the opposite direction. This is indeed in agreement with Lenz's law. In the framework of linear response theory, we can introduce the diamagnetic susceptibility tensor as

$$\underline{\chi}_{\text{dia}} = -\frac{e^2}{4m} \left(\langle r^2 \rangle \underline{I} - \langle \vec{r} \circ \vec{r} \rangle \right) , \quad (321)$$

where \underline{I} is the 3×3 unit matrix, such that

$$\vec{\mu}_{\text{dia}} = \underline{\chi}_{\text{dia}} \vec{B} \quad (322)$$

and

$$\delta E_{\text{dia}} = -\frac{1}{2} \vec{B} \underline{\chi}_{\text{dia}} \vec{B} = \frac{e^2}{8m} \langle (\vec{B} \times \vec{r})^2 \rangle . \quad (323)$$

5.4 Probability current densities in electromagnetic field

Similarly as we discussed earlier, in the presence of electromagnetic field we can derive a continuity equation that provides the probability interpretation of the wavefunction. The initial point of the calculation is the time dependent Pauli–Schrödinger equation,

$$\begin{aligned} i\hbar \partial_t \psi &= -\frac{\hbar^2}{2m} \Delta \psi + \frac{q^2}{2m} \vec{A}^2 \psi + \frac{i\hbar q}{2m} (\text{div } \vec{A} + 2 \vec{A} \vec{\nabla}) \psi \\ &+ V \psi + \mu_B \vec{B} \vec{\sigma} \psi , \end{aligned} \quad (324)$$

where we considered the interaction between the magnetic field and the spin of the electron, so we have a spinor wavefunction:

$$\psi = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} . \quad (325)$$

In terms of components, the Pauli-Schrödinger equation reads as

$$\begin{aligned} i\hbar\partial_t\psi_r &= -\frac{\hbar^2}{2m}\Delta\psi_r + \frac{q^2}{2m}\vec{A}^2\psi_r + \frac{i\hbar q}{2m}(\text{div}\vec{A} + 2\vec{A}\vec{\nabla})\psi_r \\ &+ V\psi_r + \mu_B B_i \sigma_i^{rs} \psi_s \quad (r, s \in \{1, 2\}) , \end{aligned} \quad (326)$$

where σ_i^{rs} denotes the matrix elements of the i th Pauli matrix, $i \in \{x, y, z\}$. Note the hermiticity of the Pauli matrices, $\sigma_i^{rs} = (\sigma_i^{sr})^*$. From the conjugation of the above equation we get

$$\begin{aligned} -i\hbar\partial_t^*\psi_r &= -\frac{\hbar^2}{2m}\Delta\psi_r^* + \frac{q^2}{2m}\vec{A}^2\psi_r^* - \frac{i\hbar q}{2m}(\text{div}\vec{A} + 2\vec{A}\vec{\nabla})\psi_r^* \\ &+ V\psi_r^* + \mu_B B_i \psi_s^* \sigma_i^{sr} \quad (r, s \in \{1, 2\}) , \end{aligned} \quad (327)$$

which can compactly be written as,

$$\begin{aligned} -i\hbar\partial_t\psi^\dagger &= -\frac{\hbar^2}{2m}\Delta\psi^\dagger + \frac{q^2}{2m}\vec{A}^2\psi^\dagger - \frac{i\hbar q}{2m}(\text{div}\vec{A} + 2\vec{A}\vec{\nabla})\psi^\dagger \\ &+ V\psi^\dagger + \mu_B \psi^\dagger \vec{B}\vec{\sigma} , \end{aligned} \quad (328)$$

where

$$\psi^\dagger = \begin{pmatrix} \psi_1^* & \psi_2^* \end{pmatrix} . \quad (329)$$

From Eqs. (324) and (328) we get,

$$\begin{aligned} i\hbar(\psi^\dagger(\partial_t\psi) + (\partial_t\psi^\dagger)\psi) &= -\frac{\hbar^2}{2m}(\psi^\dagger\Delta\psi - (\Delta\psi^\dagger)\psi) \\ &+ \frac{i\hbar q}{mc}\left((\vec{\nabla}\vec{A})\psi^\dagger\psi + \vec{A}\psi^\dagger(\vec{\nabla}\psi) + \vec{A}(\vec{\nabla}\psi^\dagger)\psi\right) , \end{aligned} \quad (330)$$

where the inner rounded brackets explicitly mark on which functions the differential operators act. Remarkably, the Pauli paramagnetic part of Eq. (324) containing the Pauli matrices don't contribute to the right-hand side of the above equation. After manipulating both sides of the equation above:

$$\psi^\dagger\partial_t\psi + (\partial_t\psi^\dagger)\psi = \partial_t(\psi^\dagger\psi) \quad (331)$$

$$\psi^\dagger\Delta\psi - (\Delta\psi^\dagger)\psi = \vec{\nabla}\left(\psi^\dagger\vec{\nabla}\psi - (\vec{\nabla}\psi^\dagger)\psi\right) , \quad (332)$$

and

$$(\vec{\nabla}\vec{A})\psi^\dagger\psi + \vec{A}\psi^\dagger(\vec{\nabla}\psi) + \vec{A}(\vec{\nabla}\psi^\dagger)\psi = \vec{\nabla}(\vec{A}\psi^\dagger\psi) , \quad (333)$$

we arrive at the following continuity equation,

$$\partial_t\rho + \vec{\nabla}\vec{j} = 0 \quad , \quad (334)$$

where

$$\rho = \psi^\dagger\psi \quad (335)$$

and

$$\vec{j} = \frac{\hbar}{2mi}\left(\psi^\dagger(\vec{\nabla}\psi - (\vec{\nabla}\psi^\dagger)\psi)\right) - \frac{q}{m}\vec{A}\psi^\dagger\psi \quad . \quad (336)$$

We thus see that the result for the finding probability density is the same as in case without electromagnetic field (vector potential), but the finding probability current density is extended by a term containing explicitly the vector potential. We can understand this if we relate the *probability current density* with the *kinetic momentum* instead of the canonical momentum,

$$\vec{j} = \frac{1}{m} \operatorname{Re}(\psi^\dagger \vec{K} \psi) = \frac{1}{m} \operatorname{Re}(\psi^\dagger (\vec{p} - \frac{q}{c} \vec{A}) \psi) \quad (337)$$

$$= \frac{\hbar}{2mi} \left\{ \psi^\dagger (\vec{\nabla} \psi) - (\vec{\nabla} \psi^\dagger) \psi \right\} - \frac{q}{m} \vec{A} \psi^\dagger \psi . \quad (338)$$

We note that the continuity equation remains valid, if we add a magnetisation term with zero divergence to the probability current density. The calculation showed here doesn't give any information about the spin magnetisation current density,

$$\vec{j}_M = -\frac{1}{e} \operatorname{rot}(\psi^\dagger \vec{M}_S \psi) = \frac{1}{m} \operatorname{rot}(\psi^\dagger \vec{S} \psi) = \frac{\hbar}{2m} \operatorname{rot}(\psi^\dagger \vec{\sigma} \psi) . \quad (339)$$

We shall come back to this problem in details when we discuss the nonrelativistic limit of the Dirac equation.

5.5 Gauge transformation

As mentioned already the electric and the magnetic field are related to the scalar and vector potentials as

$$\vec{E} = -\vec{\nabla} \phi - \frac{\partial \vec{A}}{\partial t} \quad \text{and} \quad \vec{B} = \vec{\nabla} \times \vec{A} . \quad (340)$$

We can introduce the following gauge transformation of the potentials,

$$\vec{A}'(\vec{r}, t) = \vec{A}(\vec{r}, t) + \vec{\nabla} \Lambda(\vec{r}, t) \quad \phi'(\vec{r}, t) = \phi(\vec{r}, t) - \partial_t \Lambda(\vec{r}, t) , \quad (341)$$

since the fields remain unchanged.

Since the time dependent Schrödinger equation contains the potentials instead of the fields, which manifest physical observables,

$$i\hbar \partial_t \psi(\vec{r}, t) = \left[\frac{1}{2m} \left(\frac{\hbar}{i} \vec{\nabla} - q \vec{A}(\vec{r}, t) \right)^2 + q\phi(\vec{r}, t) \right] \psi(\vec{r}, t) , \quad (342)$$

it is mandatory to look for the solutions $\psi'(\vec{r}, t)$ when substituting the gauge transformed potentials in Eq. (342),

$$\begin{aligned} i\hbar \partial_t \psi'(\vec{r}, t) &= \left[\frac{1}{2m} \left(\frac{\hbar}{i} \vec{\nabla} - q \vec{A}'(\vec{r}, t) \right)^2 + q\phi'(\vec{r}, t) \right] \psi'(\vec{r}, t) \\ &= \left[\frac{1}{2m} \left(\frac{\hbar}{i} \vec{\nabla} - q \vec{A}(\vec{r}, t) - q \vec{\nabla} \Lambda(\vec{r}, t) \right)^2 + q\phi(\vec{r}, t) - q \partial_t \Lambda(\vec{r}, t) \right] \psi'(\vec{r}, t) . \end{aligned} \quad (343)$$

Statement: The solution of Eq. (343) is

$$\psi'(\vec{r}, t) = \psi(\vec{r}, t) \exp\left(\frac{iq}{\hbar} \Lambda(\vec{r}, t)\right) . \quad (344)$$

Proof: Substituting the expression,

$$i\hbar\partial_t \left[\exp\left(\frac{iq}{\hbar}\Lambda(\vec{r}, t)\right) \psi(\vec{r}, t) \right] = \exp\left(\frac{iq}{\hbar}\Lambda(\vec{r}, t)\right) (i\hbar\partial_t - q\partial_t\Lambda(\vec{r}, t)) \psi(\vec{r}, t) , \quad (345)$$

into the left-hand side of Eq. (343), after trivial manipulations we get

$$i\hbar\partial_t\psi(\vec{r}, t) = \left[\frac{1}{2m} e^{-\frac{iq}{\hbar}\Lambda(\vec{r}, t)} \left(\frac{\hbar}{i}\vec{\nabla} - q\vec{A}(\vec{r}, t) - q\vec{\nabla}\Lambda(\vec{r}, t) \right)^2 e^{\frac{iq}{\hbar}\Lambda(\vec{r}, t)} + q\phi(\vec{r}, t) \right] \psi(\vec{r}, t) . \quad (346)$$

Using the following identity,

$$e^{-\frac{i}{\hbar}f(\vec{r})} \left(\frac{\hbar}{i}\vec{\nabla} + g(\vec{r}) - \vec{\nabla}f(\vec{r}) \right) e^{\frac{i}{\hbar}f(\vec{r})}\psi(\vec{r}, t) = \left(\frac{\hbar}{i}\vec{\nabla} + g(\vec{r}) \right) \psi(\vec{r}, t) \quad (347)$$

or generalized for arbitrary $n \in \mathbb{N}$,

$$e^{-\frac{i}{\hbar}f(\vec{r})} \left(\frac{\hbar}{i}\vec{\nabla} + g(\vec{r}) - \vec{\nabla}f(\vec{r}) \right)^n e^{\frac{i}{\hbar}f(\vec{r})}\psi(\vec{r}, t) = \left(\frac{\hbar}{i}\vec{\nabla} + g(\vec{r}) \right)^n \psi(\vec{r}, t) , \quad (348)$$

and substituting the functions $f(\vec{r}) = q\Lambda(\vec{r}, t)$ and $g(\vec{r}) = -q\vec{A}(\vec{r}, t)$, Eq. (346) trivially transforms to the Schrödinger equation (342).

5.6 The Aharonov–Bohm effect

For static (time independent) electromagnetic fields, the potentials are also time independent, thus we can choose a time independent gauge function $\Lambda(\vec{r})$. Integrating the gauge transformed vector potential along a path between the points \vec{r}_0 and \vec{r} , we obtain

$$\int_{\vec{r}_0}^{\vec{r}} \vec{A}'(\vec{s}) d\vec{s} = \int_{\vec{r}_0}^{\vec{r}} \vec{A}(\vec{s}) d\vec{s} + \Lambda(\vec{r}) - \Lambda(\vec{r}_0) . \quad (349)$$

In zero magnetic field we can choose the gauge such that the vector potential $\vec{A}'(\vec{r})$ becomes zero,

$$\Lambda(\vec{r}) = - \int_{\vec{r}_0}^{\vec{r}} \vec{A}(\vec{s}) d\vec{s} , \quad (350)$$

where, by choosing a suitable additive constant for $\Lambda(\vec{r})$, we fixed $\Lambda(\vec{r}_0) = 0$. Obviously the above construction only provides a unique $\Lambda(\vec{r})$ for a curl-free vector potential, i.e., for zero magnetic field, which ensures that the integral of the vector potential between \vec{r}_0 and \vec{r} is independent of the path chosen. Furthermore, we have to assume that the domain where $\vec{B} = 0$, which we will denote by Ω_0 , is simply connected. On the other hand, if we have a compact region Ω_B , where $\vec{B} \neq 0$, surrounded by Ω_0 then $\Lambda(\vec{r})$ for $\vec{r} \in \Omega_0$ is determined only up to the enclosed magnetic flux,

$$\Phi_B = \oint \vec{A}(\vec{s}) d\vec{s} . \quad (351)$$

It is then a fundamental question whether the change of the magnetic field in domain Ω_B does have any effect on the motion of a charged particle moving in the region where the magnetic field is zero. According to the gauge transformation of the wavefunction (344) the magnetic field can have a nonlocal effect through the vectorpotential. We, however, know that only the

magnetic field is measurable and, in classical electrodynamics, the fields are introduced as a mathematical concept. In addition, the change in the magnetic field appears in a phase shift in the wavefunction, so it is also a nontrivial experimental question, how this effect can be measured.

The Aharonov–Bohm effect gives a positive answer to these questions. Imagine a double-slit electron interference experiment, where a perpendicular magnetic field generated by a solenoid is enclosed between the two slits. Let \vec{r}_0 be the position of the source and \vec{r} is a point of the screen. Instead of looking for an exact quantum mechanical solution, i.e., a single-valued wavefunction, the interference pattern at the screen is constructed from the wavefunctions $\psi_1(\vec{r}, t)$ and $\psi_2(\vec{r}, t)$ for the cases when one of the slits is covered (impenetrable). In both cases, the region with zero magnetic field becomes simply connected and the vector potential can be transformed to zero. Denoting the wavefunctions by ψ_A and ψ_0 for vector potential $\vec{A}(\vec{r}) \neq 0$ and $\vec{A}(\vec{r}) = 0$ ($\vec{r} \in \Omega_0$), respectively,

$$\psi_0(\vec{r}, t) = \psi_A(\vec{r}, t) \exp\left(\frac{iq}{\hbar} \Lambda(\vec{r})\right) = \psi_A(\vec{r}, t) \exp\left(-\frac{iq}{\hbar} \int_{\vec{r}_0}^{\vec{r}} \vec{A}(\vec{s}) d\vec{s}\right), \quad (352)$$

or

$$\psi_A(\vec{r}, t) = \psi_0(\vec{r}, t) \exp\left(\frac{iq}{\hbar} \int_{\vec{r}_0}^{\vec{r}} \vec{A}(\vec{s}) d\vec{s}\right). \quad (353)$$

Note that ψ_0 is identical with the wavefunction when the magnetic field is switched off in Ω_B , since in this case a zero vectorpotential can be chosen in all space.

We use this result for the selectively covered slits,

$$\psi_{1A}(\vec{r}, t) = \psi_{10}(\vec{r}, t) \exp\left(\frac{iq}{\hbar} \int_2 \vec{A}(\vec{s}) d\vec{s}\right) \quad (354)$$

and

$$\psi_{2A}(\vec{r}, t) = \psi_{20}(\vec{r}, t) \exp\left(\frac{iq}{\hbar} \int_1 \vec{A}(\vec{s}) d\vec{s}\right), \quad (355)$$

where the paths 1 and 2 conduct through either the first or second slit, respectively. The intensity observed on the screen is proportional to the square of the magnitude of the superposed wavefunctions,

$$\begin{aligned} I &\sim |\psi_{1A}(\vec{r}, t) + \psi_{2A}(\vec{r}, t)|^2 \\ &= \left| \psi_{10}(\vec{r}, t) \exp\left(\frac{iq}{\hbar} \left[\int_2 \vec{A}(\vec{s}) d\vec{s} - \int_1 \vec{A}(\vec{s}) d\vec{s} \right]\right) + \psi_{20}(\vec{r}, t) \right|^2 \\ &= \left| \psi_{10}(\vec{r}, t) \exp\left(\frac{iq}{\hbar} \oint \vec{A}(\vec{s}) d\vec{s}\right) + \psi_{20}(\vec{r}, t) \right|^2 \end{aligned} \quad (356)$$

$$= \left| \psi_{10}(\vec{r}, t) \exp\left(\frac{iq}{\hbar} \Phi_B\right) + \psi_{20}(\vec{r}, t) \right|^2. \quad (357)$$

If we assume plane waves for the wavefunctions we can give a qualitative estimate for the positions of the interference pattern,

$$\begin{aligned} I &\sim \left| \exp\left(ik\ell_1 + \frac{iq}{\hbar} \Phi_B\right) + \exp(ik\ell_2) \right|^2 \\ &= \left| 1 + \exp\left(i \left[k\ell_1 - k\ell_2 + \frac{q}{\hbar} \Phi_B \right] \right) \right|^2 \\ &= 2 + 2 \cos\left(k\ell_1 - k\ell_2 + \frac{q}{\hbar} \Phi_B\right), \end{aligned} \quad (358)$$

where ℓ_1 and ℓ_2 denote the lengths of path 1 and 2. The positions of the maxima of the electron interference pattern can be identified from

$$k(\ell_1 - \ell_2) - \frac{e}{\hbar}\Phi_B = 2\pi n \longrightarrow \ell_1 - \ell_2 = \lambda \left(n + \frac{\Phi_B}{h/e} \right) = \lambda \left(n + \frac{\Phi_B}{\Phi_0} \right) , \quad (359)$$

where $n \in \mathbb{Z}$, $k = \frac{2\pi}{\lambda}$ and $\lambda = \frac{h}{mv}$ is the de Broglie wavelength and $\Phi_0 = h/e = 4.135 \cdot 10^{-11} \text{ Tcm}^2$ the flux quantum. This implies that the positions of the interference maxima (minima) can be tuned by the magnetic flux. The shift of the positions of the interference lines is a periodic function of Φ_B and the period is Φ_0 . These theoretical results are confirmed by several experiments.

The explanation of the Aharonov–Bohm effect presented here is rather qualitative. In the experiment both slits are open, so we have to construct the wavefunction in region Ω_0 enclosing a magnetic flux, i.e. Ω_0 being not simply connected. The problem becomes obvious when considering the scattering of plane waves on a solenoid. The interference pattern on the screen shows a similar dependence on Φ_B as in the double-slit experiment, though the transformation of the wavefunction (353) can not be used. Sir Michael V. Berry *et al.* [M.V. Berry *et al.*, *Eur. J. Phys.* **1**, 154 (1980), M.V. Berry, *Eur. J. Phys.* **1**, 240 (1980)] showed that a single-valued (exact) scattering wavefunction can be constructed in the region Ω_0 region and the asymptotic form of this wavefunction provides a good explanation of the experimental observation.

For a simple demonstration of an exact single-valued wavefunction we consider a line flux Φ_B . In cylindrical coordinates (r, ϕ, z) a possible choice for the vector potential can be expressed as

$$A_\phi = \frac{\Phi_B}{2\pi r} , \quad A_r = A_z = 0 . \quad (360)$$

As a further simplification the motion of the charged particle is confined to a circle with radius a . This way the Hamilton operator is given by

$$H = \frac{1}{2m} \left(\frac{\hbar}{i} \frac{1}{a} \frac{\partial}{\partial \phi} - qA_\phi \right)^2 = -\frac{\hbar^2}{2ma^2} \left(\frac{\partial}{\partial \phi} - \frac{iq}{\hbar} \Phi_B \right)^2 \quad (361)$$

$$= -\frac{\hbar^2}{2ma^2} \left(\frac{\partial}{\partial \phi} - i \frac{\Phi_B}{\Phi_0} \right)^2 . \quad (362)$$

The solution of the eigenvalue equation is:

$$E = \frac{\hbar^2 C^2}{2ma^2} , \quad (363)$$

$$\psi(E; \phi) = \frac{1}{\sqrt{2\pi}} \exp \left(i \left[C + \frac{\Phi_B}{\Phi_0} \right] \phi \right) , \quad (364)$$

where the *single-valuedness* of the wavefunction is provided by the condition,

$$C + \frac{\Phi_B}{\Phi_0} = n \in \mathbb{Z} . \quad (365)$$

So the eigenenergies are

$$E_n = \frac{\hbar^2}{2ma^2} \left(n - \frac{\Phi_B}{\Phi_0} \right)^2 , \quad (366)$$

with the wavefunctions,

$$\psi_n(\phi) = \frac{1}{\sqrt{2\pi}} e^{in\phi} . \quad (367)$$

We can interpret this result as:

$$\psi(E; \varphi) = \frac{1}{\sqrt{2\pi}} \exp\left(i \frac{\sqrt{2ma^2E}}{\hbar} \varphi\right) \exp\left(i \frac{\Phi_B}{\Phi_0} \varphi\right), \quad (368)$$

where the wavefunction for a given energy explicitly contains a phase factor known from the Aharanov-Bohm effect.

5.7 Flux quantisation in type-I superconductors

Due to the Meissner–Ochsenfeld effect inside a type-I superconductor the magnetic field the magnetic field is zero. Imagine a superconducting ring where inside the ring there is a perpendicular magnetic field to the plane of the ring. Experiments [B.S.Deaver, Jr. and W.F.Fairbank, *Phys. Rev. Lett.* **7**, 43 (1961); R.Doll and M.Näbauer, *Phys. Rev.Lett.* **7**, 51 (1961)] show that *the closed flux is quantised*.

In order to understand the phenomenon we have to use the specific properties of type-I superconductors. Namely, the superconductor is an ideal diamagnet, i.e. inside the superconductor the magnetic field is zero. In the stationary case, the Maxwell equation,

$$\nabla \times \vec{B} = \mu_0 \left(\vec{j} + \varepsilon_0 \frac{\partial \vec{E}}{\partial t} \right), \quad (369)$$

implies that inside the superconductor the current density \vec{j} is also zero. The current flows only at the surface of the superconductor within the London penetration depth. One can show that in the superconducting phase the charge density is homogeneous, so the wavefunction in the superconducting state can be written as

$$\psi(\vec{r}) = \sqrt{\varrho} e^{i\vartheta(\vec{r})}, \quad (370)$$

where ϱ is the density of the superconducting particles and $\vartheta(\vec{r})$ is the phase of the superconducting state. The current density can then be expressed as

$$\vec{j}(\vec{r}) = \frac{\hbar q}{m} \left(\vec{\nabla} \vartheta(\vec{r}) - \frac{q}{\hbar} \vec{A}(\vec{r}) \right) \varrho. \quad (371)$$

From $\vec{j} = 0$ it follows,

$$\vec{\nabla} \vartheta(\vec{r}) = \frac{q}{\hbar} \vec{A}(\vec{r}). \quad (372)$$

Now we are going to utilize the single valuedness of the wavefunction, namely, travelling along a closed loop in the superconducting ring the wavefunction can just pick up a phase of multiples of 2π :

$$\Delta \vartheta = \oint \vec{\nabla} \vartheta(\vec{s}) d\vec{s} = \frac{q}{\hbar} \oint \vec{A}(\vec{r}) d\vec{s} = \frac{q}{\hbar} \Phi_B = 2\pi n, \quad (373)$$

i.e.

$$\Phi_B = \frac{h}{q} n. \quad (374)$$

Since the superconducting media is a condensate of Cooper pairs with charge $q = -2e$, the magnetic flux closed by the type-I superconductor is multiples of $\Phi_0/2$.

5.8 The motion of free electrons in magnetic field: Landau levels

In *classical electrodynamics*, a charged particle in a homogeneous magnetic field displays a uniform circular motion in the plane perpendicular to the magnetic field with frequency

$$\omega_c = \frac{|q| B}{m} . \quad (375)$$

The energy of the system is

$$E = \frac{1}{2} m R^2 \omega_c^2 , \quad (376)$$

that can be quantised using the *Bohr–Sommerfeld quantisation principle* for the angular momentum as

$$\oint L_z d\varphi = 2\pi m R v = 2\pi m R^2 \omega_c = h n \Rightarrow m R^2 \omega_c = n \hbar \Rightarrow E_n = \frac{1}{2} n \hbar \omega_c . \quad (377)$$

It is tempting that using a proper quantum mechanical treatment the planar motion also leads to quantised energy levels.

Let's consider a homogeneous magnetic field along the z axis, $\vec{B} = (0, 0, B)$. In *symmetric gauge* the vector potential can be expressed as

$$\vec{A} = \left(-\frac{1}{2} B y, \frac{1}{2} B x, 0 \right) , \quad (378)$$

thus, the kinetic momentum is given by

$$\vec{K} = (K_x, K_y, K_z) = \left(p_x - \frac{eB}{2} y, p_y + \frac{eB}{2} x, p_z \right) \quad (379)$$

$$= \left(p_x - \frac{m\omega_c}{2} y, p_y + \frac{m\omega_c}{2} x, p_z \right) . \quad (380)$$

(Note that for electrons $q = -e!$), As we learned, the commutator of K_x and K_y is

$$[K_x, K_y] = \frac{\hbar e}{i} B = \frac{\hbar}{i} m \omega_c . \quad (381)$$

The eigenfunctions of the Hamiltonian,

$$H = \frac{1}{2m} (K_x^2 + K_y^2) + \frac{p_z^2}{2m} , \quad (382)$$

can be written as

$$\psi(\vec{r}) = \varphi_k(x, y) e^{ikz} , \quad (383)$$

where $k \in \mathbb{R}$ and $\varphi_k(x, y)$ satisfies the equation,

$$\frac{1}{2m} (K_x^2 + K_y^2) \varphi_k(x, y) = \left(E - \frac{\hbar^2 k^2}{2m} \right) \varphi_k(x, y) . \quad (384)$$

Now we can introduce the operators,

$$X = \frac{K_y c}{eB} = \frac{K_y}{m\omega_c} \quad \text{és} \quad P = K_x . \quad (385)$$

From Eq. (381) the following commutation relation follows,

$$[P, X] = \frac{\hbar}{i}, \quad (386)$$

and the eigenvalue equation (384) transforms to

$$\left(\frac{P^2}{2m} + \frac{1}{2}m\omega_c^2 X^2 \right) \varphi_k(x, y) = \left(E - \frac{\hbar^2 k^2}{2m} \right) \varphi_k(x, y), \quad (387)$$

which is analogous with the Schrödinger equation of a linear harmonic oscillator. We then introduce the creation and annihilation operators,

$$a = \sqrt{\frac{m\omega_c}{2\hbar}} \left(X + \frac{i}{m\omega_c} P \right) \quad (388)$$

$$= \frac{1}{\sqrt{2}L_H} \frac{1}{m\omega_c} (K_x + iK_y) \quad (389)$$

and

$$a^+ = \sqrt{\frac{m\omega_c}{2\hbar}} \left(X - \frac{i}{m\omega_c} P \right) \quad (390)$$

$$= \frac{1}{\sqrt{2}L_H} \frac{1}{m\omega_c} (K_x - iK_y), \quad (391)$$

where

$$L_H = \sqrt{\frac{\hbar}{m\omega_c}} = \sqrt{\frac{\hbar}{eB}} \quad (392)$$

is the so-called magnetic length. By substituting \hbar and e we get

$$L_H = \frac{25.66}{\sqrt{B [T]}} \text{nm}, \quad (393)$$

where the magnetic field is measured in tesla. For ordinary magnetic fields the magnetic length is orders of magnitude larger than the atomic length scale. The Hamiltonian can obviously be expressed in terms of the ladder operators,

$$H = \frac{1}{2}m\omega_c^2 X^2 + \frac{P^2}{2m} + \frac{p_z^2}{2m} = \hbar\omega_c \left(a^+ a + \frac{1}{2} \right) + \frac{p_z^2}{2m}. \quad (394)$$

Consequently, the eigenenergies are

$$E_{n,k} = \hbar\omega_c \left(n + \frac{1}{2} \right) + \frac{\hbar^2 k^2}{2m}, \quad (395)$$

where the index $n = 0, 1, 2, \dots$ denotes the *Landau levels*.

We can solve the quantum mechanical problem in the *asymmetric* or *Landau gauge*, too

$$\vec{A} = (-By, 0, 0), \quad (396)$$

which leads to the wavefunction (see Practical course),

$$\psi_{n,k_x,k_z}(x, y, z) \sim \exp(ik_z z) \exp(ik_x x) \exp\left(-\frac{1}{2L_H^2} (y - k_x L_H^2)^2\right) H_n\left(\frac{y - k_x L_H^2}{L_H}\right), \quad (397)$$

where H_n denotes the Hermite polynomials. From here we can see that the characteristic length corresponding to the y direction is L_H . Since the energy doesn't depend on k_x , the *Landau levels are degenerate*. If the planar system has finite widths (L_x, L_y) , then k_x becomes quantised,

$$k_x = \frac{2\pi}{L_x} m \quad (m \in \mathbb{N}) . \quad (398)$$

Because the distance between the Landau orbitals is $k_x L_H^2$ in the y direction, only a finite number of these orbitals can occur,

$$L_H^2 \underbrace{\frac{2\pi}{L_x}}_{\max k_x} M = L_y \longrightarrow M = \frac{L_x L_y}{2\pi L_H^2} = \frac{A |q| B}{h} = \frac{\Phi}{\Phi_0} , \quad (399)$$

where M is the degeneracy of a Landau level, A is the surface of the sample and Φ is the flux of the magnetic field.

We can interpret this result as a Landau level stands for a unit flux and the number of the Landau levels in the sample is in linear relationship with the flux. If in a quasiclassical approximation we consider a Landau state as a circular motion on a circle with radius L_H and we include the broadening of the state ($r \simeq \sqrt{2}L_H$), then we get

$$\Phi = 2\pi L_H^2 B = \frac{hB}{m\omega_c} = \frac{h}{e} = \Phi_0 \quad (400)$$

for the flux represented by a Landau state.

Finally, let us note that in symmetric gauge we can construct the b and b^+ ladder operators from the x, y, p_x, p_y operators that correspond to the center of gravity of the particle. These operators commute with the a and a^+ operators, so they also commute with the Hamiltonian. This implies that b and b^+ operators step between degenerate states inside a Landau level.

A Identical (indistinguishable) particles

The wavefunction of a system containing identical particles

The one-particle wavefunction in coordinate-spin representation:

$$\psi_1 \in H_1 = \mathcal{L}^2(\mathbb{R}^3) \otimes \mathbb{C}^{2s+1} \implies \psi_1(\vec{r}_1) \chi_s \equiv \psi_1(\vec{r}_1, s) \equiv \psi_1(1), \quad (401)$$

where $\psi_1(\vec{r}_1)$ is the spatial part of the wavefunction and χ_s is the spin part.

The wavefunction of N identical particles:

$$\psi_N \in H_N = \underbrace{H_1 \otimes H_1 \otimes \dots \otimes H_1}_{N\text{-times}} \implies \psi_N(1, 2, \dots, N). \quad (402)$$

Exchanging two particles: the exchange operator

$$P(i, j) \psi_N(\dots, i, \dots, j, \dots) = \psi_N(\dots, j, \dots, i, \dots). \quad (403)$$

Properties of the exchange operator:

Hermitian

$$\begin{aligned} & \langle \varphi_N(\dots, i, \dots, j, \dots) | P(i, j) \psi_N(\dots, i, \dots, j, \dots) \rangle \\ &= \langle \varphi_N(\dots, i, \dots, j, \dots) | \psi_N(\dots, j, \dots, i, \dots) \rangle \\ &= \langle \varphi_N(\dots, j, \dots, i, \dots) | \psi_N(\dots, i, \dots, j, \dots) \rangle \\ &= \langle P(i, j) \varphi_N(\dots, i, \dots, j, \dots) | \psi_N(\dots, i, \dots, j, \dots) \rangle \end{aligned}$$

Unitary

$$P(i, j)^2 = \mathbb{I} \rightarrow P(i, j) = P(i, j)^{-1} \rightarrow P(i, j)^\dagger = P(i, j)^{-1} \quad (404)$$

Eigenvalues

$$P(i, j) \psi = k \psi \rightarrow k^2 = 1 \rightarrow k = \pm 1 \quad (405)$$

Principle of indistinguishability

The result of any measurement is invariant under the exchange of two identical particles, i.e., for any Hermitian N -particle operator A ,

$$\langle \psi_N | A | \psi_N \rangle = \langle P(i, j) \psi_N | A | P(i, j) \psi_N \rangle. \quad (406)$$

Take $A = \langle \phi | \phi \rangle$, where $\phi \in H_N$. In this case

$$\langle \psi_N | \phi \rangle \langle \phi | \psi_N \rangle = \langle P(i, j) \psi_N | \phi \rangle \langle \phi | P(i, j) \psi_N \rangle, \quad (407)$$

which can be also written as

$$\langle \phi | \psi_N \rangle \langle \psi_N | \phi \rangle = \langle \phi | P(i, j) \psi_N \rangle \langle P(i, j) \psi_N | \phi \rangle. \quad (408)$$

In order to satisfy the above equation for any ϕ , a sufficient condition can be written as

$$|\psi_N\rangle \langle \psi_N| = |P(i, j) \psi_N\rangle \langle P(i, j) \psi_N|, \quad (409)$$

which implies

$$|\psi_N\rangle = \frac{\langle P(i, j) \psi_N | \psi_N \rangle}{\langle \psi_N | \psi_N \rangle} P(i, j) |\psi_N\rangle. \quad (410)$$

This means that ψ_N is eigenfunction of $P(i, j)$,

$$P(i, j) |\psi_N\rangle = k |\psi_N\rangle, \quad (411)$$

where

$$k = \frac{\langle P(i, j) \psi_N | \psi_N \rangle}{\langle \psi_N | \psi_N \rangle} = \pm 1, \quad (412)$$

as we proved already.

Classification:

$$P(i, j) \psi_N = \begin{cases} \psi_N & \text{bosons } (s = 0, 1, \dots) \\ -\psi_N & \text{fermions } (s = \frac{1}{2}, \frac{3}{2}, \dots) \end{cases} \quad (413)$$

Applying the exchange operator to the Schrödinger equation,

$$i\hbar \partial_t \psi_N = H_N \psi_N \quad (414)$$

where H_N is the N -particle Hamilton operator, we obtain.

$$i\hbar \partial_t P(i, j) \psi_N = P(i, j) H_N \psi_N = P(i, j) H_N P(i, j) P(i, j) \psi_N. \quad (415)$$

On the other hand, $P(i, j) \psi_N = \pm \psi_N$ also solves the Schrödinger equation,

$$i\hbar \partial_t P(i, j) \psi_N = H_N P(i, j) \psi_N. \quad (416)$$

Comparing Eqs. (415) and (416), we get

$$(H_N - P(i, j) H_N P(i, j)) \psi_N = 0, \quad (417)$$

thus, we conclude that the Hamilton operator commutes with the exchange operator,

$$[P(i, j), H_N] = 0. \quad (418)$$

What is the meaning of the operator $P(i, j) H_N P(i, j)$?

$$P(i, j) [H_N(i, j) P(i, j) \psi_N(i, j)] = P(i, j) [H_N(i, j) \psi_N(j, i)] = H_N(j, i) \psi_N(i, j) \quad (419)$$

i.e.

$$P(i, j) H_N(i, j) P(i, j) = H_N(j, i) \quad (420)$$

or

$$H_N(i, j) = H_N(j, i), \quad (421)$$

therefore, *the Hamilton operator of identical particles should be invariant under the exchange of two particles.*

Consequently, the symmetry of the N -particle wavefunction is a conserved quantity,

$$\frac{d}{dt} \langle \psi_N | P(i, j) | \psi_N \rangle = \frac{1}{i\hbar} \langle \psi_N | [P(i, j), H_N] | \psi_N \rangle = 0, \quad (422)$$

that means, fermionic particles remain fermionic under the time evolution dictated by the Schrödinger equation and vice versa.

The Pauli principle: The electrons are fermions, therefore, the many-electron wavefunction is antisymmetric against the exchange of two electrons.

Construction of the antisymmetric wavefunctions

First we show the construction of the two-electron wavefunction and then we generalize it for N electrons. Let's choose two one-electron basis functions φ_a and $\varphi_b \in H_1 = \mathcal{L}^2(\mathbb{R}^3) \otimes \mathbb{C}^2$. The tensor product vectors that can be generated from these basis functions are

$$\varphi_a(1) \otimes \varphi_a(2) , \quad \varphi_b(1) \otimes \varphi_b(2) , \quad \varphi_a(1) \otimes \varphi_b(2) , \quad \varphi_b(1) \otimes \varphi_a(2) \quad (423)$$

or, by dropping the notation \otimes ,

$$\varphi_a(1) \varphi_a(2) , \quad \varphi_b(1) \varphi_b(2) , \quad \varphi_a(1) \varphi_b(2) , \quad \varphi_b(1) \varphi_a(2) . \quad (424)$$

The general form of the two-particle wavefunctions is

$$\psi(1, 2) = c_{aa}\varphi_a(1) \varphi_a(2) + c_{bb}\varphi_b(1) \varphi_b(2) + c_{ab}\varphi_a(1) \varphi_b(2) + c_{ba}\varphi_b(1) \varphi_a(2) . \quad (425)$$

After the exchange of the two particles we obtain,

$$\begin{aligned} \psi(2, 1) &= c_{aa}\varphi_a(2) \varphi_a(1) + c_{bb}\varphi_b(2) \varphi_b(1) + c_{ab}\varphi_a(2) \varphi_b(1) + c_{ba}\varphi_b(2) \varphi_a(1) \\ &= c_{aa}\varphi_a(1) \varphi_a(2) + c_{bb}\varphi_b(1) \varphi_b(2) + c_{ab}\varphi_b(1) \varphi_a(2) + c_{ba}\varphi_a(1) \varphi_b(2) \end{aligned} \quad (426)$$

while using that the wavefunction is antisymmetric,

$$\begin{aligned} \psi(2, 1) &= -\psi(1, 2) \\ &= -c_{aa}\varphi_a(1) \varphi_a(2) - c_{bb}\varphi_b(1) \varphi_b(2) - c_{ab}\varphi_a(1) \varphi_b(2) - c_{ba}\varphi_b(1) \varphi_a(2) . \end{aligned} \quad (427)$$

Matching the coefficients from the two last equations yields,

$$c_{aa} = -c_{aa} = 0 \quad (428)$$

$$c_{bb} = -c_{bb} = 0 \quad (429)$$

$$c_{ab} = -c_{ba} \quad (430)$$

i.e.

$$\psi(1, 2) = \frac{1}{\sqrt{2}} (\varphi_a(1) \varphi_b(2) - \varphi_b(1) \varphi_a(2)) , \quad (431)$$

where $\psi(1, 2)$ is normalized to 1. This can be formally written in a determinant form:

$$\psi(1, 2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \varphi_a(1) & \varphi_b(1) \\ \varphi_a(2) & \varphi_b(2) \end{vmatrix} . \quad (432)$$

Generalization for $\varphi_{i_1}, \varphi_{i_2}, \dots, \varphi_{i_N} \in \mathcal{H}_1$ orthonormal functions:

$$\Psi_{i_1, i_2, \dots, i_N}^A(1, \dots, N) = \frac{1}{\sqrt{N!}} \sum_{P(1, \dots, N)} (-1)^P P(1, \dots, N) \varphi_{i_1}(1) \dots \varphi_{i_N}(N) , \quad (433)$$

where $P(1, \dots, N)$ is the permutation of the $(1, \dots, N)$ elements and P is the parity of the given permutation and the summation goes through all possible permutations. This is exactly the expansion of a determinant, called the Slater determinant:

$$\Psi_{\varphi_{i_1}, \varphi_{i_2}, \dots, \varphi_{i_N}}^A(1, \dots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_{i_1}(1) & \varphi_{i_2}(1) & \dots & \varphi_{i_N}(1) \\ \varphi_{i_1}(2) & \varphi_{i_2}(2) & \dots & \varphi_{i_N}(2) \\ \vdots & \vdots & \ddots & \vdots \\ \varphi_{i_1}(N) & \varphi_{i_2}(N) & \dots & \varphi_{i_N}(N) \end{vmatrix} . \quad (434)$$

Pauli extension principle: In the N -fermion wavefunction, constructed as an antisymmetric linear combination of the tensor product of N one-particle wavefunctions, each one-particle wavefunction appears only once. (We used to say that there can not be more than one fermion in the same one-particle state).

The general fermionic wavefunction: if $\{\varphi_n \in \mathcal{H}_1, n \in \mathbb{N}\}$ is a complete orthonormal set,

$$\psi(1, \dots, N) = \sum_{\substack{i_1, i_2, \dots, i_N \in \mathbb{N} \\ (i_l \neq i_k)}} C(i_1, i_2, \dots, i_N) \Psi_{i_1, i_2, \dots, i_N}^A(1, \dots, N) \quad (435)$$

Symmetric wavefunctions

The bosonic wavefunction is symmetric for the interchange of the particles. In the two-boson case the following combinations are symmetric:

$$\varphi_a(1) \varphi_a(2), \quad \varphi_b(1) \varphi_b(2), \quad \frac{1}{\sqrt{2}} (\varphi_a(1) \varphi_b(2) + \varphi_b(1) \varphi_a(2)). \quad (436)$$

Consequently, the bosons do not respect the Pauli extension principle, so there can be more particles in the same one-particle state, or even all of them (see Bose–Einstein condensation in statistical physics).

General construction: if $\{\varphi_n \in \mathcal{H}_1 = \mathcal{L}^2(\mathbb{R}^3) \otimes \mathbb{C}^{2s+1}\}$ ($s = 0, 1, 2, \dots$) is a complete orthonormal set,

$$\Psi_{i_1, i_2, \dots, i_N}^S(1, \dots, N) = \sqrt{\frac{N_1! N_2! \dots}{N!}} \sum_{P'(1, \dots, N)} P'(1, \dots, N) \varphi_{i_1}(1) \dots \varphi_{i_N}(N), \quad (437)$$

where P' contains the permutations between different one-particle states, because the permutation of identical states doesn't give a new N -particle wavefunction. N_1, N_2, \dots stand for the number of identical one-particle states. The general N boson wavefunction is the linear combination of such symmetrized wavefunctions:

$$\psi(1, \dots, N) = \sum_{i_1, i_2, \dots, i_N \in \mathbb{N}} C(i_1, i_2, \dots, i_N) \Psi_{i_1, i_2, \dots, i_N}^S(1, \dots, N). \quad (438)$$

Occupation number representation

On the tensor product space of a complete set of one particle states (called Fock space) the basis functions of the symmetric or antisymmetric N particle state can be uniquely determined by the numbers specifying how many times the one particle states occur, called the occupation numbers,

$$\left\{ \begin{array}{ll} \text{Fermions} & n_i \in \{0, 1\} \\ \text{Bosons} & n_i \in \mathbb{N} \end{array} \right. \quad (439)$$

↓

$$\left. \begin{array}{l} \Psi_{i_1, i_2, \dots, i_N}^A \\ \Psi_{i_1, i_2, \dots, i_N}^S \end{array} \right\} (i_l \neq i_k) = |n_1, n_2, \dots, n_i, \dots\rangle. \quad (440)$$

The sum of the occupation numbers necessarily N :

$$\sum_{i \in \mathbb{N}} n_i = N. \quad (441)$$

If the one particle wavefunctions are the eigenfunctions of the one-particle Hamiltonian,

$$H_1 \varphi_i = \varepsilon_i \varphi_i, \quad (442)$$

the $|n_1, n_2, \dots, n_i, \dots\rangle$ state is eigenfunction of the non-interacting N particle Hamiltonian,

$$H_N(1, \dots, N) = H_1(1) + H_1(2) \dots + H_1(N) \quad (443)$$

with the energy

$$E_N = \sum_{i \in \mathbb{N}} \varepsilon_i n_i. \quad (444)$$

This follows from:

$$\begin{aligned} & (H_1(1) + H_1(2) \dots + H_1(N)) [\varphi_{i_1}(1) \otimes \dots \otimes \varphi_{i_N}(N)] = \\ & = H_1(1) \varphi_{i_1}(1) \otimes \dots \otimes \varphi_{i_N}(N) \\ & + \varphi_{i_1}(1) \otimes H_1(2) \varphi_{i_1}(1) \otimes \dots \otimes \varphi_{i_N}(N) + \dots \\ & + \varphi_{i_1}(1) \otimes \dots \otimes H_1(N) \varphi_{i_N}(N) \\ & = (\varepsilon_{i_1} + \varepsilon_{i_2} + \dots + \varepsilon_{i_N}) [\varphi_{i_1}(1) \otimes \dots \otimes \varphi_{i_N}(N)] \end{aligned}$$

B Variation principle

We can get the eigenvectors of a hermitian Hamiltonian from the minimalization of the energy functional:

$$E[\psi] = \langle \psi | H \psi \rangle , \quad (445)$$

under the normalisation condition

$$\langle \psi | \psi \rangle = 1 . \quad (446)$$

In order to do that we take under consideration the normalisation condition with a Lagrange multiplier and we introduce the following functional:

$$F[\psi] = \langle \psi | H \psi \rangle - \varepsilon \langle \psi | \psi \rangle , \quad (447)$$

where ε is the Lagrange multiplier. Let's calculate the functional at $|\psi\rangle + |\delta\psi\rangle$ up to first order in $\delta\psi$:

$$\begin{aligned} F[\psi + \delta\psi] &= \langle \psi | H \psi \rangle + \langle \delta\psi | H \psi \rangle + \langle \psi | H \delta\psi \rangle - \varepsilon \langle \psi | \psi \rangle - \varepsilon \langle \delta\psi | \psi \rangle - \varepsilon \langle \psi | \delta\psi \rangle + \mathcal{O}(\delta\phi^2) \\ &= F[\psi] + \langle \delta\psi | (H - \varepsilon) \psi \rangle + \langle \psi | (H - \varepsilon) \delta\psi \rangle + \mathcal{O}(\delta\phi^2) \\ &= F[\psi] + \langle \delta\psi | (H - \varepsilon) \psi \rangle + \langle (H - \varepsilon) \psi | \delta\psi \rangle + \mathcal{O}(\delta\phi^2) , \end{aligned} \quad (448)$$

from that, by neglecting the terms second order in $\delta\psi$ we get the variation of $F[\psi]$:

$$\begin{aligned} \delta F[\psi, \delta\psi] &= F[\psi + \delta\psi] - F[\psi] \\ &= \langle \delta\psi | (H - \varepsilon) \psi \rangle + \langle (H - \varepsilon) \psi | \delta\psi \rangle = 2\text{Re} \langle \delta\psi | (H - \varepsilon) \psi \rangle . \end{aligned} \quad (449)$$

Now consider the variation for $|\psi\rangle + |\imath\delta\psi\rangle$:

$$\begin{aligned} \delta F[\psi, \imath\delta\psi] &= \langle \imath\delta\psi | (H - \varepsilon) \psi \rangle + \langle (H - \varepsilon) \psi | \imath\delta\psi \rangle \\ &= -\imath (\langle \delta\psi | (H - \varepsilon) \psi \rangle - \langle (H - \varepsilon) \psi | \delta\psi \rangle) = 2\text{Im} \langle \delta\psi | (H - \varepsilon) \psi \rangle . \end{aligned} \quad (450)$$

Let $|\psi\rangle$ be such a vector that for a small change in it the change in $F[\psi]$ is zero, so $F[\psi]$ is stationary for the change in $|\psi\rangle$:

$$\delta F[\psi] = 0 , \quad (451)$$

and from that follows:

$$\langle \delta\psi | (H - \varepsilon) \psi \rangle = 0 \iff (H - \varepsilon) |\psi\rangle = 0 , \quad (452)$$

Remark: We can arrive to the result above directly if we calculate the variation of the $F[\psi]$ functional with respect to $\langle \psi | + \langle \delta\psi |$, while we fix $|\psi\rangle$.

C Hartree–Fock approximation

The Hamiltonian of an atom with atomic number Z and N electrons:

$$H = \sum_{i=1}^N H_0(\vec{r}_i) + \frac{1}{2} \sum_{\substack{i,j=1 \\ (i \neq j)}}^N V(\vec{r}_i, \vec{r}_j) \quad (453)$$

where H_0 is the one-electron Hamiltonian:

$$H_0(\vec{r}_i) = -\frac{\hbar^2}{2m} \Delta_i - \frac{kZe^2}{r_i} \quad (454)$$

and the electron-electron interaction is:

$$V(\vec{r}_i, \vec{r}_j) = \frac{ke^2}{|\vec{r}_i - \vec{r}_j|} . \quad (455)$$

This Hamiltonian contains only the energy of the electron system and for the core we assumed it is in rest.

We are looking for the wavefunction of the N electron system as a Slater determinant:

$$\psi(1, 2, \dots, N) = \frac{1}{\sqrt{N!}} \sum_{P(1, \dots, N)} (-1)^P P(1, \dots, N) \varphi_{i_1}(1) \varphi_{i_2}(2) \dots \varphi_{i_N}(N) \quad (456)$$

$$= A \varphi_{i_1}(1) \varphi_{i_2}(2) \dots \varphi_{i_N}(N) , \quad (457)$$

where

$$A = \frac{1}{\sqrt{N!}} \sum_{P(1, \dots, N)} (-1)^P P(1, \dots, N) \quad (458)$$

is the antisymmetrizing operator, and the φ_i one electron wavefunctions are form an orthonormal set:

$$\langle \varphi_i | \varphi_j \rangle = \delta_{ij} . \quad (459)$$

The functional describing the energy of the system by including the normalisation condition is:

$$F[\{\varphi_i\}] = \langle \psi | H \psi \rangle - \sum_{i,j} \varepsilon_{ij} \langle \varphi_i | \varphi_j \rangle , \quad (460)$$

where $\varepsilon_{ij} = \varepsilon_{ji}$, what provides the real valuednes off the energy functional.

The expectation value of the Hamiltonian:

$$\langle \psi | H \psi \rangle = \langle A \varphi_{i_1}(1) \varphi_{i_2}(2) \dots \varphi_{i_N}(N) | H A \varphi_{i_1}(1) \varphi_{i_2}(2) \dots \varphi_{i_N}(N) \rangle \quad (461)$$

$$= \langle \varphi_{i_1}(1) \varphi_{i_2}(2) \dots \varphi_{i_N}(N) | A H A \varphi_{i_1}(1) \varphi_{i_2}(2) \dots \varphi_{i_N}(N) \rangle \quad (462)$$

because A is hermition.

See for $N = 2$

$$\begin{aligned} & \frac{1}{\sqrt{2}} \langle \varphi_3(1) \varphi_4(2) | \varphi_1(1) \varphi_2(2) - \varphi_1(2) \varphi_2(1) \rangle \\ &= \frac{1}{\sqrt{2}} \langle \varphi_3(1) \varphi_4(2) | \varphi_1(1) \varphi_2(2) \rangle - \frac{1}{\sqrt{2}} \langle \varphi_3(1) \varphi_4(2) | \varphi_1(2) \varphi_2(1) \rangle \\ &= \frac{1}{\sqrt{2}} \langle \varphi_3(1) \varphi_4(2) | \varphi_1(1) \varphi_2(2) \rangle - \frac{1}{\sqrt{2}} \langle \varphi_3(2) \varphi_4(1) | \varphi_1(1) \varphi_2(2) \rangle \\ &= \frac{1}{\sqrt{2}} \langle \varphi_3(1) \varphi_4(2) - \varphi_3(2) \varphi_4(1) | \varphi_1(1) \varphi_2(2) \rangle . \end{aligned}$$

from the second to the third row we used the interchange of the variables $(1) \leftrightarrow (2)$, what we can do because we integrate both of them over the whole space in the expectation value.

The expectation value of $\sum_i H_0(i)$:

$$\begin{aligned} [H_0(1) + H_0(2)] A\varphi_1(1)\varphi_2(2) &= \frac{1}{\sqrt{2}} ([H_0(1)\varphi_1(1)]\varphi_2(2) - \varphi_1(2)[H_0(1)\varphi_2(1)]) \\ &\quad + \frac{1}{\sqrt{2}} (\varphi_1(1)[H_0(2)\varphi_2(2)] - [H_0(2)\varphi_1(2)]\varphi_2(1)) \end{aligned}$$

$$\begin{aligned} \frac{1}{\sqrt{2}} A [H_0(1)\varphi_1(1)]\varphi_2(2) &= \frac{1}{2} ([H_0(1)\varphi_1(1)]\varphi_2(2) - [H_0(2)\varphi_1(2)]\varphi_2(1)) \\ -\frac{1}{\sqrt{2}} A \varphi_1(2)[H_0(1)\varphi_2(1)] &= \frac{1}{2} (-\varphi_1(2)[H_0(1)\varphi_2(1)] + \varphi_1(1)[H_0(2)\varphi_2(2)]) \\ \frac{1}{\sqrt{2}} A \varphi_1(1)[H_0(2)\varphi_2(2)] &= \frac{1}{2} (\varphi_1(1)[H_0(2)\varphi_2(2)] - \varphi_1(2)[H_0(1)\varphi_2(1)]) \\ -\frac{1}{\sqrt{2}} A [H_0(2)\varphi_1(2)]\varphi_2(1) &= \frac{1}{2} (-[H_0(2)\varphi_1(2)]\varphi_2(1) + [H_0(1)\varphi_1(1)]\varphi_2(2)) \end{aligned}$$

$$\begin{aligned} A [H_0(1) + H_0(2)] A\varphi_1(1)\varphi_2(2) &= [H_0(1)\varphi_1(1)]\varphi_2(2) - [H_0(2)\varphi_1(2)]\varphi_2(1) \\ &\quad + \varphi_1(1)[H_0(2)\varphi_2(2)] - \varphi_1(2)[H_0(1)\varphi_2(1)] \end{aligned}$$

$$\langle \varphi_1(1)\varphi_2(2) | A [H_0(1) + H_0(2)] A\varphi_1(1)\varphi_2(2) \rangle = \langle \varphi_1(1) | H_0(1)\varphi_1(1) \rangle + \langle \varphi_2(2) | H_0(2)\varphi_2(2) \rangle$$

Generalisation for arbitrary N :

$$\langle A\varphi_{i_1}(1)\varphi_{i_2}(2)\dots\varphi_{i_N}(N) | \sum_{i=1}^N H_0(i) A |\varphi_{i_1}(1)\varphi_{i_2}(2)\dots\varphi_{i_N}(N) \rangle = \sum_{k=1}^N \langle \varphi_{i_k}(1) | H_0(1)\varphi_{i_k}(1) \rangle \quad (463)$$

The expectation value of $\frac{1}{2} \sum_{i \neq j} V(i, j)$

$$V(1, 2) A\varphi_1(1)\varphi_2(2) = \frac{1}{\sqrt{2}} (V(1, 2)\varphi_1(1)\varphi_2(2) - V(2, 1)\varphi_1(2)\varphi_2(1))$$

$$\begin{aligned} AV(1, 2) A\varphi_1(1)\varphi_2(2) &= \frac{1}{2} [V(1, 2)\varphi_1(1)\varphi_2(2) - V(2, 1)\varphi_1(2)\varphi_2(1) \\ &\quad - V(2, 1)\varphi_1(2)\varphi_2(1) + V(1, 2)\varphi_1(1)\varphi_2(2)] \\ &= V(1, 2)\varphi_1(1)\varphi_2(2) - V(2, 1)\varphi_1(2)\varphi_2(1) \end{aligned}$$

$$\begin{aligned} \langle \varphi_1(1)\varphi_2(2) | AV(1, 2) A\varphi_1(1)\varphi_2(2) \rangle &= \langle \varphi_1(1)\varphi_2(2) | V(1, 2)\varphi_1(1)\varphi_2(2) \rangle \\ &\quad - \langle \varphi_1(1)\varphi_2(2) | V(2, 1)\varphi_1(2)\varphi_2(1) \rangle \end{aligned}$$

Generalisation for arbitrary N :

$$\begin{aligned} &\langle A\varphi_{i_1}(1)\varphi_{i_2}(2)\dots\varphi_{i_N}(N) | \frac{1}{2} \sum_{\substack{i,j=1 \\ (i \neq j)}}^N V(i, j) A |\varphi_{i_1}(1)\varphi_{i_2}(2)\dots\varphi_{i_N}(N) \rangle \\ &= \frac{1}{2} \sum_{k,l=1}^N \langle \varphi_{i_k}(1)\varphi_{i_l}(2) | V(1, 2)\varphi_{i_k}(1)\varphi_{i_l}(2) \rangle - \frac{1}{2} \sum_{k,l=1}^N \langle \varphi_{i_k}(1)\varphi_{i_l}(2) | V(1, 2)\varphi_{i_k}(2)\varphi_{i_l}(1) \rangle \end{aligned} \quad (464)$$

Finally if we bring everything together, the expectation value of the Hamiltonian is:

$$\begin{aligned} \langle \psi | H \psi \rangle = & \sum_{i=1}^N \langle \varphi_i(1) | H_0(1) \varphi_i(1) \rangle + \frac{1}{2} \sum_{i,j=1}^N \langle \varphi_i(1) \varphi_j(2) | V(1,2) \varphi_i(1) \varphi_j(2) \rangle \\ & - \frac{1}{2} \sum_{i,j=1}^N \langle \varphi_i(1) \varphi_j(2) | V(1,2) \varphi_j(2) \varphi_i(1) \rangle, \end{aligned} \quad (465)$$

where for simplicity we noted the one electron wavefunctions with $i = 1, \dots, N$, what can not be confused with the electron index, because there is only one and two electron terms in the expression. Note that, in the second and third term of the above equation the $i = j$ terms are eliminate each other leading to the following form of the $F[\{\varphi_i\}]$ functional:

$$\begin{aligned} F[\{\varphi_i\}] = & \sum_{i=1}^N \langle \varphi_i(1) | H_0(1) \varphi_i(1) \rangle + \frac{1}{2} \sum_{\substack{i,j=1 \\ (i \neq j)}}^N \langle \varphi_i(1) \varphi_j(2) | V(1,2) \varphi_i(1) \varphi_j(2) \rangle \\ & - \frac{1}{2} \sum_{\substack{i,j=1 \\ (i \neq j)}}^N \langle \varphi_i(1) \varphi_j(2) | V(1,2) \varphi_j(2) \varphi_i(1) \rangle - \sum_{i,j} \varepsilon_{ij} \langle \varphi_i | \varphi_j \rangle. \end{aligned} \quad (466)$$

Let's calculate the variation of this expression respect to $\langle \varphi_k |$

$$\begin{aligned} \delta_{(k)} F[\{\varphi_i\}] = & \langle \delta \varphi_k | H_0 \varphi_k \rangle + \sum_{\substack{i=1 \\ (i \neq k)}}^N \langle \delta \varphi_k(1) \varphi_i(2) | V(1,2) \varphi_k(1) \varphi_i(2) \rangle \\ & - \sum_{\substack{i=1 \\ (i \neq k)}}^N \langle \delta \varphi_k(1) \varphi_i(2) | V(1,2) \varphi_k(2) \varphi_i(1) \rangle - \sum_{i=1}^N \varepsilon_{ki} \langle \delta \varphi_k | \varphi_i \rangle, \end{aligned} \quad (467)$$

what can be written as:

$$\delta_{(k)} F[\{\varphi_i\}] = \left\langle \delta \varphi_k \left| \frac{\delta F[\{\varphi_i\}]}{\delta \langle \varphi_k |} \right. \right\rangle, \quad (468)$$

where $\frac{\delta F[\{\varphi_i\}]}{\delta \langle \varphi_k |}$ is the functional derivative of $F[\{\varphi_i\}]$:

$$\frac{\delta F[\{\varphi_i\}]}{\delta \langle \varphi_k |} = H_0 |\varphi_k\rangle + \sum_{\substack{i=1 \\ (i \neq k)}}^N \langle \varphi_i(2) | V(1,2) \varphi_i(2) \rangle \varphi_k - \sum_{\substack{i=1 \\ (i \neq k)}}^N \langle \varphi_i(2) | V(1,2) \varphi_k(2) \rangle \varphi_i - \sum_{i=1}^N \varepsilon_{ki} |\varphi_i\rangle. \quad (469)$$

In the spirit of the variation principle we require that the functional derivative of $F[\{\varphi_i\}]$ vanish. Obviously the Slater determinant is invariant under a unitary transformation. Choose the transformation in such a way that, it diagonalize the symmetry ε_{ki} matrix. If we note the eigenvalues with ε_k and we act on the φ_i states with the matrix of the unitary transformation we arrive at the *canonical Hartree-Fock equations*:

$$H_0 \varphi_k + \sum_{\substack{i=1 \\ (i \neq k)}}^N \langle \varphi_i(2) | V(1,2) \varphi_i(2) \rangle \varphi_k - \sum_{\substack{i=1 \\ (i \neq k)}}^N \langle \varphi_i(2) | V(1,2) \varphi_k(2) \rangle \varphi_i = \varepsilon_k \varphi_k. \quad (470)$$

If we consider the one electron wavefunctions as $\varphi_i(1) = \varphi_i(\vec{r}) \chi_{m_{s_i}}$ and we utilize that $H_0(1)$ and $V(1, 2)$ don't contain any spin operator (don't depend on the spin):

$$\langle \varphi_i(2) | V(1, 2) \varphi_i(2) \rangle = \int d^3 r_2 \varphi_i(\vec{r}_2)^* \frac{ke^2}{|\vec{r}_1 - \vec{r}_2|} \varphi_i(\vec{r}_2) \quad (471)$$

and

$$\langle \varphi_i(2) | V(1, 2) \varphi_k(2) \rangle = \delta_{m_{s_i} m_{s_k}} \int d^3 r' \varphi_i(\vec{r}_2)^* \frac{ke^2}{|\vec{r}_1 - \vec{r}_2|} \varphi_k(\vec{r}_2) . \quad (472)$$

(We note that, if $m_{s_i} \neq m_{s_j}$, then $\varphi_i(\vec{r}) = \varphi_j(\vec{r})$ is allowed.)

If we introduce the so called *Hartree potential*:

$$V^H(\vec{r}) = \sum_{\substack{i=1 \\ (i \neq k)}}^N \int d^3 r' \varphi_i(\vec{r}')^* \frac{ke^2}{|\vec{r} - \vec{r}'|} \varphi_i(\vec{r}') \quad (473)$$

and the non local exchange potential:

$$V^x(\vec{r}, \vec{r}') = - \sum_{\substack{i=1 \\ (i \neq k)}}^N \delta_{m_{s_i} m_{s_k}} \varphi_i(\vec{r}')^* \frac{ke^2}{|\vec{r} - \vec{r}'|} \varphi_k(\vec{r}) ,$$

then the Hartree–Fock equations in coordinate space can be written as:

$$(H_0(\vec{r}) + V^H(\vec{r})) \varphi_k(\vec{r}) + \int d^3 r' V^x(\vec{r}, \vec{r}') \varphi_k(\vec{r}') = \varepsilon_k \varphi_k(\vec{r}) \quad (k = 1, 2, \dots, N) , \quad (474)$$

what can be solved by selfconsistent iterations.

We have a look at the meaning of the ε_k Lagrange multipliers. If we multiply the Hartree–Fock equations with $\varphi_k(\vec{r})^*$ and we integrate it over \vec{r} , then we get:

$$\begin{aligned} \varepsilon_k = \int d^3 r \varphi_k(\vec{r})^* H_0(\vec{r}) \varphi_k(\vec{r}) + \int d^3 r \varphi_k(\vec{r})^* V^H(\vec{r}) \varphi_k(\vec{r}) \\ + \int d^3 r \int d^3 r' \varphi_k(\vec{r})^* V_k^x(\vec{r}, \vec{r}') \varphi_k(\vec{r}') , \end{aligned} \quad (475)$$

or

$$\begin{aligned} \varepsilon_k = \int d^3 r \varphi_k(\vec{r})^* H_0(\vec{r}) \varphi_k(\vec{r}) + \sum_{i(\neq k)} \int d^3 r \int d^3 r' \varphi_k(\vec{r})^* \varphi_i(\vec{r}')^* \frac{ke^2}{|\vec{r} - \vec{r}'|} \varphi_k(\vec{r}) \varphi_i(\vec{r}') \\ - \sum_{i(\neq k)} \int d^3 r \int d^3 r' \varphi_k(\vec{r})^* \varphi_i(\vec{r}') \frac{ke^2}{|\vec{r} - \vec{r}'|} \varphi_k(\vec{r}') \varphi_i(\vec{r}) , \end{aligned} \quad (476)$$

what is the sum of such terms from $E = \langle \psi | H \psi \rangle$, what contains the φ_k one electron state. Thus if we remove from the N electron system the electron from the φ_k one electron state and we don't change the other one electron states, then the energy of the system decreases with ε_k , so the ionization energy is $-\varepsilon_k$.

By summing up the one electron energies we end up with the following relation:

$$\sum_{k=1}^N \varepsilon_k = \langle \psi | H \psi \rangle + E_H + E_x \quad (477)$$

where the electrostatic (Hartree) energy coming from the charge density is:

$$\begin{aligned}
E_H &= \frac{1}{2} \sum_k \int d^3r \varphi_k(\vec{r})^* V^H(\vec{r}) \varphi_k(\vec{r}) \\
&= \frac{1}{2} \sum_{\substack{i,j \\ (i \neq j)}} \int \int d^3r' d^3r \varphi_i(\vec{r})^* \varphi_j(\vec{r}')^* \frac{ke^2}{|\vec{r} - \vec{r}'|} \varphi_i(\vec{r}) \varphi_j(\vec{r}') ,
\end{aligned} \tag{478}$$

and the exchange energy is:

$$\begin{aligned}
E_x &= \frac{1}{2} \sum_k \int d^3r \int d^3r' \varphi_k(\vec{r})^* V_k^x(\vec{r}, \vec{r}') \varphi_k(\vec{r}') \\
&= -\frac{1}{2} \sum_{\substack{i,j \\ (i \neq j)}} \int d^3r \int d^3r' \varphi_i(\vec{r})^* \varphi_j(\vec{r}')^* \frac{ke^2}{|\vec{r} - \vec{r}'|} \varphi_i(\vec{r}') \varphi_j(\vec{r}) .
\end{aligned} \tag{479}$$

The energy of the interaction electron system can be calculate if we substract from the sum of the one electron energies the interaction and exchange energies calculated from the selfconsistent solutions (double-counting contributions). This result shows high similarity with the mean field approximation used at the spin models, so we can call the Hartree–Fock approximation as the mean field approximation of the interacting electron system.

D Adiabatic time evolution

We are going to consider Hamiltonians depend on time via the $R(t)$ function what is an element of a multidimensional parameter space:

$$H(t) = H(R(t)) \quad (480)$$

The parametric eigenstates and eigenenergies:

$$H(R) \varphi_m(R) = E_m(R) \varphi_m(R) \quad (481)$$

$$\langle \varphi_n(R) | \varphi_m(R) \rangle = \delta_{nm} \quad (482)$$

The parametric time dependence of the eigenstates:

$$\varphi_n(t) \equiv \varphi_n(R(t)) , \quad (483)$$

$$\dot{\varphi}_n(t) = \dot{R}(t) \nabla_R \varphi_n(R) , \quad (484)$$

where we used the chain rule. From the time derivative of Eq.(482) we get:

$$\langle \varphi_n(t) | \dot{\varphi}_m(t) \rangle + \langle \dot{\varphi}_n(t) | \varphi_m(t) \rangle = \langle \varphi_n(t) | \dot{\varphi}_m(t) \rangle^* + \langle \varphi_m(t) | \dot{\varphi}_n(t) \rangle^* = 0 , \quad (485)$$

if $n = m$

$$\text{Re} \langle \varphi_n(t) | \dot{\varphi}_n(t) \rangle = 0 \quad (486)$$

what means the $\langle \varphi_n(R) | \nabla_R \varphi_n(R) \rangle$ quantity is imaginary.

The time dependence of the wave function:

$$i\hbar \partial_t \psi(t) = H(t) \psi(t) . \quad (487)$$

If we expand the wavefunction on the parametric solutions:

$$\psi(t) = \sum_m c_m(t) \varphi_m(t) \quad (488)$$

we get the following Schrödinger equation:

$$i\hbar \sum_m (\dot{c}_m(t) \varphi_m(t) + c_m(t) \dot{\varphi}_m(t)) = \sum_m E_m(t) c_m(t) \varphi_m(t) . \quad (489)$$

After multiplying from the left with $\phi_n(t)$ we get:

$$\dot{c}_n(t) + \frac{i}{\hbar} E_n(t) c_n(t) + \sum_m c_m(t) \langle \varphi_n(t) | \dot{\varphi}_m(t) \rangle = 0 \quad (490)$$

with the following initial condition:

$$\psi(t_0) = \varphi_k(t_0) \implies c_n(t_0) = \delta_{nk} , \quad (491)$$

what means we start from the k th eigenstate.

Adiabatic solution:

There are no transition between eigenstates, or in other words during the time evolution the system stays in a given eigenstate. In thermodynamics we call something adiabatic when we evolve the system through equilibrium states, this is the quantum analog of this. So we are going to investigate the time evolution of the eigenstates,

$$c_n^{ad}(t) = \delta_{nk} c_k(t), \quad c_k(t_0) = 1 \quad (492)$$

The time dependence of the expansion coefficients is

$$\dot{c}_k(t) + \left(\frac{i}{\hbar} E_k(t) + \langle \varphi_k(t) | \dot{\varphi}_k(t) \rangle \right) c_k(t) = 0, \quad (493)$$

what is equal with the following differential equation

$$\frac{d}{dt} \ln c_k(t) = -\frac{i}{\hbar} E_k(t) - \langle \varphi_k(t) | \dot{\varphi}_k(t) \rangle, \quad (494)$$

with the solution:

$$c_k(t) = e^{-id_k(t)} e^{i\gamma_k(t)} \quad (495)$$

where $d_k(t)$ is the *dynamic phase*:

$$d_k(t) = \frac{1}{\hbar} \int_{t_0}^t E_k(t') dt' \quad (496)$$

and $\gamma_k(t)$ is the *geometric phase*:

$$\gamma_k(t) = i \int_{t_0}^t \langle \varphi_k(t') | \dot{\varphi}_k(t') \rangle dt'. \quad (497)$$

and the adiabatic solution in terms of the phases above:

$$\underline{\psi^{ad}(t)} = e^{-id_k(t)} e^{i\gamma_k(t)} \varphi_k(t), \quad (498)$$

so the instantaneous wavefunction differs only in a phase factor from the initial one, called as the *quantum adiabatic theorem*.

The condition for the adiabatic approximation ($n \neq k$):

$$\langle \varphi_k(t) | H(t) | \varphi_n(t) \rangle = E_n(t) \langle \varphi_k(t) | \varphi_n(t) \rangle = 0 \quad (499)$$

$$\begin{aligned} \frac{d}{dt} \langle \varphi_k(t) | H(t) | \varphi_n(t) \rangle &= \langle \dot{\varphi}_k(t) | H(t) | \varphi_n(t) \rangle + \langle \varphi_k(t) | \dot{H}(t) | \varphi_n(t) \rangle + \langle \varphi_k(t) | H(t) | \dot{\varphi}_n(t) \rangle \\ &= E_n(t) \langle \dot{\varphi}_k(t) | \varphi_n(t) \rangle + E_k(t) \langle \varphi_k(t) | \dot{\varphi}_n(t) \rangle + \langle \varphi_k(t) | \dot{H}(t) | \varphi_n(t) \rangle \\ &= (E_k(t) - E_n(t)) \langle \varphi_k(t) | \dot{\varphi}_n(t) \rangle + \langle \varphi_k(t) | \dot{H}(t) | \varphi_n(t) \rangle \end{aligned} \quad (500)$$

what gives the condition:

$$\langle \varphi_k(t) | \dot{\varphi}_n(t) \rangle = \frac{\langle \varphi_k(t) | \dot{H}(t) | \varphi_n(t) \rangle}{E_n(t) - E_k(t)} \rightarrow 0. \quad (501)$$

This quantity has frequency dimension, what have to be negligible respect to the characteristic frequency of the $k \rightarrow n$ transition:

$$\left| \frac{\langle \varphi_k(t) | \dot{H}(t) | \varphi_n(t) \rangle}{E_n(t) - E_k(t)} \right| \ll |\omega_{kn}(t)| = \frac{1}{\hbar} |E_n(t) - E_k(t)| \quad (502)$$

i.e.

$$\hbar \left| \langle \varphi_k(t) | \dot{H}(t) | \varphi_n(t) \rangle \right| \ll (E_n(t) - E_k(t))^2 \quad (503)$$

Let's take a look at the geometric phase! From Eq.(486) it is obvious that $\gamma_k(t) \in R$. Furthermore

$$\langle \varphi_k(t) | \dot{\varphi}_k(t) \rangle \equiv \dot{R}(t) \langle \varphi_k(R(t)) | \nabla_R \varphi_k(R(t)) \rangle \quad (504)$$

what implies:

$$\gamma_k(t) = \imath \int_{t_0}^t \langle \varphi_k(t') | \dot{\varphi}_k(t') \rangle dt' = \int_{t_0}^t \langle \varphi_k(R(t')) | \nabla_R \varphi_k(R(t')) \rangle \dot{R}(t') dt' \quad (505)$$

$$= \imath \int_{R(t_0)}^{R(t)} \langle \varphi_k(R') | \nabla_{R'} \varphi_k(R') \rangle dR', \quad (506)$$

so the geometric phase can be expressed with the line integral of the *Berry vector potential*:

$$A_k(R) = \imath \langle \varphi_k(R) | \nabla_R \varphi_k(R) \rangle \quad (507)$$

$$\underline{\gamma_k(t) = \int_{R(t_0)}^{R(t)} A_k(R') dR'}. \quad (508)$$

D.1 Gauge transformation

Let $\alpha(R)$ be a real function on the parameter space and we introduce the

$$\tilde{\varphi}_k(R) = e^{\imath\alpha(R)} \varphi_k(R) \quad (509)$$

gauge transformed basis functions, what are still the eigenfunctions of the $H(R)$ Hamiltonian. The transformation of $A_k(R)$ is:

$$\tilde{A}_k(R) = \imath \langle \tilde{\varphi}_k(R) | \nabla_R \tilde{\varphi}_k(R) \rangle = A_k(R) - \nabla_R \alpha(R), \quad (510)$$

this give the analogy with the vector potential. The transformation of the geometric phase:

$$\tilde{\gamma}_k(t) = \int_{R(t_0)}^{R(t)} \tilde{A}_k(R') dR' = \gamma_k(t) - \alpha(R(t)) + \alpha(R(t_0)), \quad (511)$$

and the tranformation of the adiabatic wave function form (498) is:

$$\begin{aligned} \tilde{\psi}^{ad}(t) &= e^{-\imath d_k(t)} e^{\imath \tilde{\gamma}_k(t)} \tilde{\varphi}_k(t) = e^{-\imath d_k(t)} e^{\imath \gamma_k(t)} e^{-\imath \alpha(R(t))} e^{\imath \alpha(R(t_0))} \tilde{\varphi}_k(t) \\ &= e^{-\imath d_k(t)} e^{\imath \gamma_k(t)} \varphi_k(t) = \psi^{ad}(t), \end{aligned} \quad (512)$$

so the adiabatic wave function is invariant under the gauge transformation of the basis functions.

We may think that, with

$$\alpha(R(t)) = \gamma_k(t) \quad (513)$$

the geometric phase can be transformed out:

$$\tilde{\gamma}_k(t) \equiv 0 \quad (514)$$

↓

$$\tilde{\psi}^{ad}(t) = e^{-\imath d_k(t)} \tilde{\varphi}_k(t), \quad (515)$$

so we don't have to introduce it because it can be gauged out (*implication of Vladimir Fock*).

D.2 Cyclic motion

There is an obvious contradiction if we deal with parametric motion in the parameter phase with period T :

$$R(t_0 + T) = R(t_0) . \quad (516)$$

In this case because the $\tilde{\varphi}_k(R)$ basis functions are single valued:

$$e^{i\alpha(R(t_0+T))} = e^{i\alpha(R(t_0))} , \quad (517)$$

what implies:

$$\alpha(R(t_0 + T)) = \alpha(R(t_0)) + 2\pi k \quad (k \in Z) \quad (518)$$

and for the gauge transformation in (513):

$$\tilde{\gamma}_k(t_0 + T) = \gamma_k(t_0 + T) - \alpha(R(t_0 + T)) + \alpha(R(t_0)) = \gamma_k(t_0 + T) + 2\pi k . \quad (519)$$

The gauge transformed adiabatic wavefunction:

$$\begin{aligned} \tilde{\psi}^{ad}(t_0 + T) &= e^{-id_k(t_0+T)} e^{i\tilde{\gamma}_k(t_0+T)} \tilde{\varphi}_k(t_0 + T) = e^{-id_k(t_0+T)} e^{i\gamma_k(t_0+T)} \tilde{\varphi}_k(t_0 + T) \\ &= e^{-id_k(t_0+T)} e^{i\gamma_k(t_0+T)} \tilde{\varphi}_k(t_0) = e^{-id_k(t_0+T)} e^{i\gamma_k(t_0+T)} \tilde{\psi}^{ad}(t_0) , \end{aligned} \quad (520)$$

the gauge transformation doesn't eliminate the geometric phase. So on a closed curve C in the parameter phase the wave function always pick up a geometric phase next to the dynamic phase:

$$\gamma_k(C) = \oint_C A_k(R) dR + 2\pi k , \quad (521)$$

what we call as the *Berry phase*.

For simplicity in the following we consider a *tree dimensional* parameter space. Due to Stoke's theorem we can write the Berry phase as

$$\gamma_k(C) = \int_S \vec{B}_k(\vec{R}) d^2S + 2\pi k \quad (522)$$

where the surface integral goes for the surface bounded by the closed curve C , and the

$$\vec{B}_k(\vec{R}) = \nabla_{\vec{R}} \times \vec{A}_k(\vec{R}) \quad (523)$$

quantity used to called as *Berry curvature*. Obviously $\vec{B}_k(R)$ is gauge invariant:

$$\tilde{\vec{B}}_k(\vec{R}) = \nabla_{\vec{R}} \times \tilde{\vec{A}}_k(\vec{R}) = \nabla_{\vec{R}} \times \vec{A}_k(\vec{R}) - \underbrace{\nabla_{\vec{R}} \times \nabla_{\vec{R}} \alpha(\vec{R})}_{=0} = \vec{B}_k(\vec{R}) . \quad (524)$$

Furthermore:

$$\vec{B}_k(\vec{R}) = i \nabla_{\vec{R}} \times \left\langle \varphi_k(\vec{R}) \left| \nabla_{\vec{R}} \varphi_k(\vec{R}) \right\rangle = i \left\langle \nabla_{\vec{R}} \varphi_k(\vec{R}) \left| \times \nabla_{\vec{R}} \varphi_k(\vec{R}) \right\rangle \quad (525)$$

or in index notation:

$$B_k^\alpha(\vec{R}) = i \varepsilon_{\alpha\beta\gamma} \left\langle \partial_\beta \varphi_k(\vec{R}) \left| \partial_\gamma \varphi_k(\vec{R}) \right\rangle = \varepsilon_{\alpha\beta\gamma} F_k^{\beta\gamma}(\vec{R}) , \quad (526)$$

where

$$F_k^{\beta\gamma}(\vec{R}) = -\text{Im} \left\langle \partial_\beta \varphi_k(\vec{R}) \left| \partial_\gamma \varphi_k(\vec{R}) \right. \right\rangle \quad (527)$$

is the *Berry curvature*, what has the following alternative form:

$$F_k^{\beta\gamma}(\vec{R}) = -\text{Im} \sum_{n(\neq k)} \left\langle \partial_\beta \varphi_k(\vec{R}) \left| \varphi_n(\vec{R}) \right. \right\rangle \left\langle \varphi_n(\vec{R}) \left| \partial_\gamma \varphi_k(\vec{R}) \right. \right\rangle \quad (528)$$

$$= -\text{Im} \sum_{n(\neq k)} \frac{\left\langle \varphi_k(\vec{R}) \left| \partial_\beta H(\vec{R}) \right| \varphi_n(\vec{R}) \right\rangle \left\langle \varphi_n(\vec{R}) \left| \partial_\gamma H(\vec{R}) \right| \varphi_k(\vec{R}) \right\rangle}{\left(E_n(\vec{R}) - E_k(\vec{R}) \right)^2}, \quad (529)$$

where in the first row we inserted a complete set and for the second row we used the same idea as in Eq.(500). This way we get a useful formula for the calculation of the Berry curvature:

$$\vec{B}_k(\vec{R}) = -\text{Im} \sum_{n(\neq k)} \frac{\left\langle \varphi_k(\vec{R}) \left| \nabla_{\vec{R}} H(\vec{R}) \right| \varphi_n(\vec{R}) \right\rangle \times \left\langle \varphi_n(\vec{R}) \left| \nabla_{\vec{R}} H(\vec{R}) \right| \varphi_k(\vec{R}) \right\rangle}{\left(E_n(\vec{R}) - E_k(\vec{R}) \right)^2}. \quad (530)$$

D.3 Dealing with degeneracies

Starting from the formula above in Eq.(530) we can evaluate the Berry phase in the vicinity of a twofold degeneracy. Let

$$E_m(\vec{R}^*) = E_k(\vec{R}^*) = E(\vec{R}^*) \quad (531)$$

and choose \vec{R} from the neighborhood of \vec{R}^* , where

$$\left| E_n(\vec{R}) - E_k(\vec{R}) \right| \gg \left| E_m(\vec{R}) - E_k(\vec{R}) \right| \quad (n \neq m, k), \quad (532)$$

namely in this region of the parameterspace the other eigenvalues of the Hamiltonian are far. In this case we can use the following approximation:

$$\vec{B}_k(\vec{R}) \simeq -\text{Im} \frac{\left\langle \varphi_k(\vec{R}) \left| \nabla_{\vec{R}} H(\vec{R}) \right| \varphi_m(\vec{R}) \right\rangle \times \left\langle \varphi_m(\vec{R}) \left| \nabla_{\vec{R}} H(\vec{R}) \right| \varphi_k(\vec{R}) \right\rangle}{\left(E_m(\vec{R}) - E_k(\vec{R}) \right)^2} \quad (533)$$

where we have only one term, because all the others are giving a negligible contribution due to the condition above.

With the usage of the $\vec{R} \rightarrow \vec{R} - \vec{R}^*$ translation on the parameter space:

$$E_m(\vec{0}) = E_k(\vec{0}) = E(\vec{0}) \quad (534)$$

the matrix of the Hamiltonian can be chosen on the two dimensional $\left\{ \left| \varphi_k(\vec{0}) \right\rangle, \left| \varphi_m(\vec{0}) \right\rangle \right\}$ subspace as:

$$H(\vec{R}) = \vec{\sigma} \cdot \mathbf{C} \vec{R}, \quad (535)$$

where \mathbf{C} is a 3×3 real matrix. Let's change our basis as $\vec{R}' = 2\mathbf{C}\vec{R}$, this way we get:

$$H(\vec{R}') = \frac{1}{2} \vec{\sigma} \vec{R}', \quad (536)$$

what has eigenvalues

$$E_{\pm}(\vec{R}') = \pm \frac{R'}{2}. \quad (537)$$

The coordinate system can be choosed as $\vec{R}' = (0, 0, R')$, pointing to the z direction. This way we get the following simple eigenvectors:

$$|\varphi_+(\vec{R}')\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |\varphi_-(\vec{R}')\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \quad (538)$$

Taking the derivative of the Hamiltonian: $\nabla_{\vec{R}'} H(\vec{R}') = \frac{1}{2}\sigma$ and then putting things together:

$$\langle \varphi_-(\vec{R}') | \nabla_{\vec{R}'} H(\vec{R}') | \varphi_+(\vec{R}') \rangle = \frac{1}{2} \langle \varphi_-(\vec{R}') | \vec{\sigma} | \varphi_+(\vec{R}') \rangle = \frac{1}{2} (1, i, 0) \quad (539)$$

$$\langle \varphi_+(\vec{R}') | \nabla_{\vec{R}'} H(\vec{R}') | \varphi_-(\vec{R}') \rangle = \frac{1}{2} \langle \varphi_+(\vec{R}') | \vec{\sigma} | \varphi_-(\vec{R}') \rangle = \frac{1}{2} (1, -i, 0) \quad (540)$$

and

$$\vec{B}_+(\vec{R}') = -\frac{1}{4R'^2} \text{Im} (1, -i, 0) \times (1, i, 0) = -\frac{1}{2R'^2} (0, 0, 1) = -\frac{\vec{e}_z}{2R'^2}. \quad (541)$$

Then we rotate back the coordinate system in order to get the final result:

$$\vec{B}_+(\vec{R}') = -\frac{\vec{R}'}{2R'^3} = -\vec{B}_-(\vec{R}'), \quad (542)$$

what is equal to the field strength of a magnetic monopole with $-\frac{1}{2}$ charge on the parameter space.

The Berry phase for a cyclic motion around a degeneracy point on a closed curve C :

$$\gamma_+(C) = -\int_S \frac{\vec{R}'}{2R'^3} d^2 S' = -\int_S \frac{\vec{R}'}{2R'^3} \frac{\vec{R}'}{R'} R'^2 d\Omega = -\frac{1}{2} \Omega(C), \quad (543)$$

where $C = \partial S$ and $\Omega(C)$ is the solid angle corresponding to the C curve from the degeneracy point \vec{R}^* .

D.4 A single spin in magnetic field

Let the Hamiltonian be

$$H(\vec{R}(t)) = \frac{g\mu_B}{\hbar} \vec{S} \vec{R}(t) \quad (544)$$

where $\vec{R}(t)$ is the time dependent magnetic induction, g is the giromagnetic factor, μ_B is the Bohr magneton and $\vec{S} = (S_x, S_y, S_z)$ is a spin operator with angular momentum s . The energy eigenvalues are

$$E_m(\vec{R}) = g\mu_B m R, \quad (545)$$

where $R = |\vec{R}|$, $m \in \{-s, -s+1, \dots, s-1, s\}$. The Berry curvature corresponding to the m th eigenstate is:

$$\vec{B}_m(\vec{R}) = -\frac{1}{\hbar^2} \text{Im} \sum_{n(\neq m)} \frac{\langle m | \vec{S} | n \rangle \times \langle n | \vec{S} | m \rangle}{R^2 (n-m)^2}. \quad (546)$$

We get the eigenstates from the $\mathcal{O} \in \mathcal{O}(3)$ orthogonal transformation, by rotating \vec{R} to the z direction:

$$\vec{S} \vec{R} = (\mathcal{O} \vec{S})(\mathcal{O} \vec{R}) = (\mathcal{O} \vec{S})(0, 0, R), \quad (547)$$

where the rotation can be expressed on the spin space as:

$$\mathcal{O}\vec{S} = U^{-1}\vec{S}U, \quad (548)$$

where $U \in SU(2)$. The Hamiltonian transformed into the new coordinate system is:

$$H(\vec{R}) = U^{-1}H'(\vec{R})U, \quad (549)$$

with

$$H'(\vec{R}) = \frac{g\mu_B}{\hbar}S_z R. \quad (550)$$

For the eigenstates $|m'\rangle$ holds,

$$H'(\vec{R})|m'\rangle = E_m(R)|m'\rangle \quad (551)$$

$$\vec{S}^2|m'\rangle = \hbar^2 s(s+1)|m'\rangle \quad (552)$$

$$S_z|m'\rangle = \hbar m'|m'\rangle \quad (553)$$

$$S_{\pm}|m'\rangle = \hbar\sqrt{s(s+1) - m'(m' \pm 1)}|m' \pm 1\rangle. \quad (554)$$

From that we get the eigenstates of the original Hamiltonian:

$$UH(\vec{R})U^{-1}|m'\rangle = E_m(R)|m'\rangle \quad (555)$$

by multipling from the left with U^{-1} we get:

$$|m\rangle = U^{-1}|m'\rangle. \quad (556)$$

This way

$$\vec{B}_m(\vec{R}) = -\frac{1}{\hbar^2} \text{Im} \sum_{n(\neq m)} \frac{\langle m|\vec{S}|n\rangle \times \langle n|\vec{S}|m\rangle}{R^2(n-m)^2} \quad (557)$$

$$= -\frac{1}{\hbar^2} \text{Im} \sum_{n(\neq m)} \frac{\langle m'|U\vec{S}U^{-1}|n'\rangle \times \langle n'|U\vec{S}U^{-1}|m'\rangle}{R^2(n-m)^2} \quad (558)$$

$$= -\frac{1}{\hbar^2} \text{Im} \sum_{n(\neq m)} \frac{\langle m'|O^{-1}\vec{S}|n'\rangle \times \langle n'|O^{-1}\vec{S}|m'\rangle}{R^2(n-m)^2} = O^{-1}\vec{B}'_m(R), \quad (559)$$

where

$$\vec{B}'_m(R) = -\frac{1}{\hbar^2} \text{Im} \sum_{n'(\neq m')} \frac{\langle m'|\vec{S}|n'\rangle \times \langle n'|\vec{S}|m'\rangle}{R^2(n-m)^2}. \quad (560)$$

We have only offdiagonal matrix elements so the matrix elements of S_z doesn't appear in the expression, implying that

$$\vec{B}'_m(R) = (0, 0, B_m'^z(R)), \quad (561)$$

where

$$\begin{aligned} B_m'^z(R) &= -\frac{1}{\hbar^2 R^2} \text{Im} \{ \langle m'|S_x|m'+1\rangle \langle m'+1|S_y|m'\rangle - \langle m'|S_y|m'+1\rangle \langle m'+1|S_x|m'\rangle \\ &\quad + \langle m'|S_x|m'-1\rangle \langle m'-1|S_y|m'\rangle - \langle m'|S_y|m'-1\rangle \langle m'-1|S_x|m'\rangle \} \end{aligned} \quad (562)$$

$$= -\frac{1}{R^2} \text{Im} \frac{1}{4i} \{ 2s(s+1) - 2m'(m'+1) - 2s(s+1) + 2m'(m'-1) \} \quad (563)$$

$$= -\frac{m'}{R^2} \quad (564)$$

Finally if we rotate back with \mathcal{O}^{-1} , then we get the Berry curvature:

$$\vec{B}_m(\vec{R}) = -m \frac{\vec{R}}{R^3}, \quad (565)$$

and the Berry phase

$$\gamma_m(C) = \oint \vec{B}_m(\vec{R}) d^2S = -m \Omega(C), \quad (566)$$

where $\Omega(C)$ is defined as before in the case of degeneracies.

E Classical electrodynamics

E.1 Maxwell equations

The Lorentz force acting on a charged particle in electromagnetic fields:

$$\vec{F} = q \left(\vec{E} + \vec{v} \times \vec{B} \right) , \quad (567)$$

where \vec{E} is the electric field and \vec{B} is the magnetic field (B-field).

Electrodynamics in presence of matter

$$\rho_{\text{tot}} = \rho_{\text{f}} + \rho_{\text{b}} , \quad \rho_{\text{b}} = -\vec{\nabla} \cdot \vec{P} , \quad (568)$$

$$\vec{j}_{\text{tot}} = \vec{j}_{\text{f}} + \vec{j}_{\text{b}} , \quad \vec{j}_{\text{b}} = \vec{\nabla} \times \vec{M} + \partial_t \vec{P} , \quad (569)$$

where ρ_{tot} , ρ_{f} , and ρ_{b} stand for the total, free and bound electric charge densities, while \vec{j}_{tot} , \vec{j}_{f} , and \vec{j}_{b} denote the total, free and bound electric current densities, respectively. In addition, \vec{P} is the electric polarization density and \vec{M} is the magnetisation density. The electric displacement field \vec{D} is defined as

$$\vec{D} = \varepsilon_0 \vec{E} + \vec{P} , \quad (570)$$

where ε_0 is the vacuum permittivity. The relationship between the magnetic H-field \vec{H} , B-field \vec{B} and the magnetisation density \vec{M} reads as,

$$\vec{H} = \frac{\vec{B}}{\mu_0} - \vec{M} . \quad (571)$$

Maxwell equations:

$$\vec{\nabla} \cdot \vec{E} = \frac{\rho_{\text{tot}}}{\varepsilon_0} = \frac{1}{\varepsilon_0} \left(\rho_{\text{f}} - \vec{\nabla} \cdot \vec{P} \right) \rightarrow \vec{\nabla} \cdot \vec{D} = \rho_{\text{f}} , \quad (572)$$

$$\vec{\nabla} \times \vec{E} = -\partial_t \vec{B} , \quad (573)$$

$$\vec{\nabla} \cdot \vec{B} = 0 , \quad (574)$$

$$\vec{\nabla} \times \vec{B} = \mu_0 \vec{j}_{\text{tot}} = \mu_0 \left(\vec{j}_{\text{f}} + \vec{\nabla} \times \vec{M} + \partial_t \vec{P} + \varepsilon_0 \partial_t \vec{E} \right) \rightarrow \vec{\nabla} \times \vec{H} = \vec{j}_{\text{f}} + \partial_t \vec{D} . \quad (575)$$

In *vacuum* $\vec{P} = 0$ and $\vec{M} = 0$, thus, $\vec{D} = \varepsilon_0 \vec{E}$ and $\vec{H} = \frac{\vec{B}}{\mu_0}$. The Maxwell equations are then given as

$$\vec{\nabla} \cdot \vec{E} = \frac{\rho}{\varepsilon_0} , \quad (576)$$

$$\vec{\nabla} \times \vec{E} = -\partial_t \vec{B} , \quad (577)$$

$$\vec{\nabla} \cdot \vec{B} = 0 , \quad (578)$$

$$\vec{\nabla} \times \vec{B} = \mu_0 \left(\vec{j} + \varepsilon_0 \partial_t \vec{E} \right) . \quad (579)$$

Based on the second and the third Maxwell equations, we can define a scalar and a vector potential, $\phi(\vec{r}, t)$ and $\vec{A}(\vec{r}, t)$, respectively such that

$$\vec{B} = \vec{\nabla} \times \vec{A} , \quad (580)$$

$$\vec{E} = -\vec{\nabla}\phi - \partial_t\vec{A}. \quad (581)$$

The gauge transformation of the potentials for the $\Lambda(\vec{r}, t)$ gauge field:

$$\left. \begin{array}{l} \vec{A}' = \vec{A} + \vec{\nabla}\Lambda \\ \phi' = \phi - \partial_t\Lambda \end{array} \right\} \implies \begin{array}{l} \vec{E}' = \vec{E} \\ \vec{B}' = \vec{B} \end{array}. \quad (582)$$

E.2 Lagrangian formalism

We define the Lagrange function in presence of electric and magnetic fields as

$$L(\vec{r}, \dot{\vec{r}}) = -mc^2\sqrt{1 - \frac{\dot{\vec{r}}^2}{c^2}} + q\vec{A}(\vec{r}, t) \cdot \dot{\vec{r}} - q\phi(\vec{r}, t). \quad (583)$$

The conjugated *canonical momentum* is then given by

$$\begin{aligned} \vec{p} &= \frac{\partial L(\vec{r}, \dot{\vec{r}})}{\partial \dot{\vec{r}}} = -\frac{mc^2 \left(-2\frac{\dot{\vec{r}}}{c^2}\right)}{2\sqrt{1 - \frac{\dot{\vec{r}}^2}{c^2}}} + q\vec{A}(\vec{r}, t) = \\ &= \frac{m\dot{\vec{r}}}{\sqrt{1 - \frac{\dot{\vec{r}}^2}{c^2}}} + q\vec{A}(\vec{r}, t) = \vec{K} + q\vec{A}(\vec{r}, t), \end{aligned} \quad (584)$$

where \vec{K} is the so called *kinetic momentum*:

$$\vec{K} = \frac{m\dot{\vec{r}}}{\sqrt{1 - \frac{\dot{\vec{r}}^2}{c^2}}} = \vec{p} - q\vec{A}. \quad (585)$$

Euler-Lagrange equation of motion:

$$\frac{\partial L(\vec{r}, \dot{\vec{r}})}{\partial \vec{r}} - \frac{d}{dt} \frac{\partial L(\vec{r}, \dot{\vec{r}})}{\partial \dot{\vec{r}}} = 0 \quad (586)$$

↓

$$\frac{d\vec{p}}{dt} = \frac{\partial L(\vec{r}, \dot{\vec{r}})}{\partial \vec{r}} = q(\vec{\nabla} \circ \vec{A})\dot{\vec{r}} - q\vec{\nabla}\phi, \quad (587)$$

where

$$(\vec{\nabla} \circ \vec{A})_{ij} = \partial_i A_j. \quad (588)$$

Using the vector identity,

$$(\vec{a} \circ \vec{b})\vec{c} = \vec{c} \times (\vec{a} \times \vec{b}) + (\vec{c}\vec{a})\vec{b}, \quad (589)$$

we can proceed as

$$(\vec{\nabla} \circ \vec{A})\dot{\vec{r}} = \dot{\vec{r}} \times (\vec{\nabla} \times \vec{A}) + (\dot{\vec{r}} \cdot \vec{\nabla})\vec{A} = \dot{\vec{r}} \times \vec{B} + (\dot{\vec{r}} \cdot \vec{\nabla})\vec{A}, \quad (590)$$

yielding

$$\frac{d\vec{p}}{dt} = q(\dot{\vec{r}} \cdot \vec{\nabla})\vec{A} - q\vec{\nabla}\phi + q(\dot{\vec{r}} \times \vec{B}). \quad (591)$$

The substantial derivative of the vector potential is defined as

$$\frac{d\vec{A}}{dt} = \frac{\partial\vec{A}}{\partial t} + (\dot{\vec{r}}\vec{\nabla})\vec{A}, \quad (592)$$

by which we obtain

$$\frac{d\vec{p}}{dt} = q\frac{d\vec{A}}{dt} - q\frac{\partial\vec{A}}{\partial t} - q\vec{\nabla}\phi + q(\dot{\vec{r}}\times\vec{B}). \quad (593)$$

Now we can express the time derivative of the kinetic momentum,

$$\frac{d\vec{K}}{dt} = -q\frac{\partial\vec{A}}{\partial t} - q\vec{\nabla}\phi + q(\dot{\vec{r}}\times\vec{B}) = q\vec{E} + q(\dot{\vec{r}}\times\vec{B}), \quad (594)$$

which is identical with the Lorentz force as required.

E.3 Hamiltonian formalism

The Hamilton function is related to the Lagrange function as

$$\begin{aligned} H &= \dot{\vec{r}}\vec{p} - L(\vec{r}, \dot{\vec{r}}) \\ &= \dot{\vec{r}}\vec{K} + q\vec{A}\dot{\vec{r}} + mc^2\sqrt{1 - \frac{\dot{\vec{r}}^2}{c^2}} - q\vec{A}\dot{\vec{r}} + q\phi \\ &= \frac{m\dot{\vec{r}}^2}{\sqrt{1 - \frac{\dot{\vec{r}}^2}{c^2}}} + mc^2\sqrt{1 - \frac{\dot{\vec{r}}^2}{c^2}} + q\phi = \frac{mc^2}{\sqrt{1 - \frac{\dot{\vec{r}}^2}{c^2}}} + q\phi. \end{aligned} \quad (595)$$

From the relationships,

$$\frac{m^2c^4}{1 - \frac{\dot{\vec{r}}^2}{c^2}} = m^2c^2 \left(c^2 + \frac{\dot{\vec{r}}^2}{1 - \frac{\dot{\vec{r}}^2}{c^2}} \right) = \quad (596)$$

$$= m^2c^4 + c^2\vec{K}^2 = m^2c^4 + c^2(\vec{p} - q\vec{A})^2, \quad (597)$$

we obtain the well-known expression for the Hamilton function,

$$H(\vec{r}, \vec{p}) = \sqrt{(mc^2)^2 + c^2(\vec{p} - q\vec{A})^2} + q\phi. \quad (598)$$

In the non-relativistic limit,

$$\frac{(\vec{p} - q\vec{A})^2}{mc^2} \ll 1, \quad (599)$$

therefore,

$$H(\vec{r}, \vec{p}) \simeq mc^2 + \frac{(\vec{p} - q\vec{A})^2}{2m} + q\phi, \quad (600)$$

so within a *non-relativistic* framework,

$$H(\vec{r}, \vec{p}) = \frac{(\vec{p} - q\vec{A})^2}{2m} + q\phi. \quad (601)$$

The equations of motion:

$$\frac{d\vec{r}}{dt} = \vec{v} = \frac{\partial H(\vec{r}, \vec{p})}{\partial \vec{p}} = \frac{\vec{p} - q\vec{A}}{m} = \frac{\vec{K}}{m} \quad (602)$$

and

$$\begin{aligned} \frac{d\vec{p}}{dt} &= -\frac{\partial H(\vec{r}, \vec{p})}{\partial \vec{r}} = q(\vec{\nabla} \circ \vec{A}) \frac{\vec{p} - q\vec{A}}{m} - q\vec{\nabla}\phi \\ &= q(\vec{\nabla} \circ \vec{A})\dot{\vec{r}} - q\vec{\nabla}\phi = q(\dot{\vec{r}} \times \vec{B}) + q(\dot{\vec{r}}\vec{\nabla})\vec{A} - q\vec{\nabla}\phi \\ &= q(\dot{\vec{r}} \times \vec{B}) + q\frac{d\vec{A}}{dt} - q\frac{\partial \vec{A}}{\partial t} - q\vec{\nabla}\phi. \end{aligned} \quad (603)$$

From this we again get the Lorentz force as the substantial derivative of kinetic momentum,

$$\begin{aligned} \frac{d\vec{K}}{dt} &= m\frac{d^2\vec{r}}{dt^2} = q(-\vec{\nabla}\phi - \frac{\partial \vec{A}}{\partial t}) + q(\dot{\vec{r}} \times \vec{B}) \\ &= q\vec{E} + q(\dot{\vec{r}} \times \vec{B}). \end{aligned} \quad (604)$$