

Quantum Mechanics 2

Lecture notes

(Relativistic Quantum Mechanics not included)

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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 act on 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 the other Hilbert space unchanged. Accordingly, the action of the operator $\vec{J}_1$ on a vector $|j_1, m_1\rangle \otimes |j_2, m_2\rangle \in \mathcal{H}_1 \otimes \mathcal{H}_2$ can be written as (from now on 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 the relationships,

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

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

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

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 coefficients $C(j_1 m_1, j_2 m_2 | j, m)$, denoted often by $\langle j_1 m_1, j_2 m_2 | j, m \rangle$, 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 group 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 quantum numbers m 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:

The state $|j_1, j_1\rangle |j_2, j_2\rangle$ is clearly eigenstate of J_z with the eigenvalue $\hbar(j_1 + j_2)$:

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

The operator J^2 can be rewritten as,

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

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, $\mathcal{H}_i$. Q.E.D.

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: Let's calculate 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, the equality

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

only holds if one of j_1 and j_2 is zero. In these cases, we have found all of the eigenstates of J^2 and J_z that satisfy (15). For $j_1j_2 \neq 0$ we can find further eigenstates corresponding to the quantum numbers $j < j_{\max} = j_1 + j_2$. First 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,

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

implies, up to a multiplicative factor of ± 1 , the solutions

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

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

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 the construction of 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) all j 's are integer (or $2j + 1$ is odd):

The sum of the odd numbers up to $2j_{\max} + 1$ equals

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

from which we obtain

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

(2) all j 's are half-integer (or $2j + 1$ is even):

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

$$= j_{\max} + 1 + (j_{\max} + 1)^2 = (j_{\max} + 1)(j_{\max} + 2) , \quad (40)$$

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

$$\begin{aligned} \sum_{j=j_{\min}}^{j_{\max}} (2j+1) &= (j_{\max} + \frac{1}{2})(j_{\max} + \frac{3}{2}) - (j_{\min} - \frac{1}{2})(j_{\min} + \frac{1}{2}) \\ &= j_{\max}^2 + 2j_{\max} + 1 - j_{\min}^2 = (j_1 + j_2 + 1)^2 - j_{\min}^2, \end{aligned} \quad (41)$$

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

$$j_{\min}^2 = (j_1 + j_2 + 1)^2 - (2j_1 + 1)(2j_2 + 1) = (j_1 + j_2)^2 - 4j_1j_2 = (j_1 - j_2)^2 \quad (42)$$

or

$$j_{\min} = |j_1 - j_2|. \quad (43)$$

The possible quantum numbers j are then as follows,

$$j \in [|j_1 - j_2|, |j_1 - j_2| + 1, \dots, j_1 + j_2 - 1, j_1 + j_2], \quad (44)$$

or

$$C(j_1m_1, j_2m_2|jm) = 0 \text{ if } j < |j_1 - j_2| \text{ or } j > j_1 + j_2, \quad (45)$$

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:

$$\langle jm | j'm' \rangle = \delta_{jj'} \delta_{mm'}. \quad (46)$$

Expanding the above scalar product using (15),

$$\langle jm | j'm' \rangle = \sum_{m_1m_2} \sum_{m'_1m'_2} C(j_1m_1; j_2m_2|jm) C(j'_1m'_1; j'_2m'_2|j'm') \underbrace{\langle j_1m_1 | j'_1m'_1 \rangle}_{\delta_{j_1j'_1} \delta_{m_1m'_1}} \underbrace{\langle j_2m_2 | j'_2m'_2 \rangle}_{\delta_{j_2j'_2} \delta_{m_2m'_2}} \quad (47)$$

$\Downarrow$

$$\sum_{m_1m_2} C(j_1m_1; j_2m_2|jm) C(j_1m_1; j_2m_2|j'm') = \delta_{jj'} \delta_{mm'}. \quad (48)$$

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 $\{|j_1m_1\rangle |j_2m_2\rangle : -j_1 \leq m_1 \leq j_1, -j_2 \leq m_2 \leq j_2\}$:

$$\begin{aligned} \sum_{j=|j_1-j_2|}^{j_1+j_2} \sum_{m=-j}^j |jm\rangle \langle jm| &= \sum_{m_1m_2} |j_1m_1\rangle |j_2m_2\rangle \otimes \langle j_1m_1| \langle j_2m_2| \\ &\equiv \sum_{m_1m_2} |j_1m_1\rangle \langle j_1m_1| \otimes |j_2m_2\rangle \langle j_2m_2|. \end{aligned} \quad (49)$$

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, 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 $m_s = \pm\frac{1}{2}$,

$$\begin{aligned} \phi_{n,\ell,m,m_s}(i) &= \phi_{n,\ell,m}(\vec{r}_i) \left| \frac{1}{2}, m_s \right\rangle_i , \\ H_1(i) \phi_{n,\ell,m,m_s}(i) &= E_n \phi_{n,\ell,m,m_s}(i) \end{aligned} \quad (57)$$

while the eigenenergies depend just on n ,

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

2.1 Ground state

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

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

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

$$\psi_{1s,1s}(1, 2) = \phi_{1s}(\vec{r}_1) \phi_{1s}(\vec{r}_2) |0, 0\rangle , \quad (60)$$

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

$$|0, 0\rangle = \frac{1}{\sqrt{2}} \left(\left| \frac{1}{2}, +\frac{1}{2} \right\rangle_1 \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_2 - \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_1 \left| \frac{1}{2}, +\frac{1}{2} \right\rangle_2 \right) \quad (61)$$

is the antisymmetric two-spin singlet state ($S = 0, m_S = 0$). This is the ground state of the non-interacting two-electron Hamiltonian, $H^0(1, 2)$, which we consider the Hamiltonian of the unperturbed system,

$$H^0(1, 2)\psi_{1s,1s}(1, 2) = E_{1s,1s}^{(0)} \psi_{1s,1s}(1, 2) \quad (62)$$

$$E_{1s,1s}^{(0)} = -8 \text{ Ryd} . \quad (63)$$

The first-order perturbation correction of the ground state is given by the non-degenerate perturbation theory as

$$\Delta E_{1s,1s}^{(1)} = \langle \psi_{1s,1s}(1, 2) | V(1, 2) | \psi_{1s,1s}(1, 2) \rangle \quad (64)$$

$$= \underbrace{\langle 00 | 00 \rangle}_{=1} k e^2 \int \int \frac{\phi_{1s}^*(\vec{r}_1) \phi_{1s}^*(\vec{r}_2) \phi_{1s}(\vec{r}_1) \phi_{1s}(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d^3 r_1 d^3 r_2 \quad (65)$$

$$= k e^2 \int \int \frac{\varrho_{1s}(\vec{r}_1) \varrho_{1s}(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d^3 r_1 d^3 r_2 = C_{1s,1s} > 0 , \quad (66)$$

where $\varrho_{1s}(\vec{r}) = \phi_{1s}^*(\vec{r}) \phi_{1s}(\vec{r}) = |\phi_{1s}(\vec{r})|^2$ and $C_{1s,1s}$ is the Coulomb interaction energy of the classical charge distribution, $e\varrho_{1s}(\vec{r})$. The result of the calculation is,

$$C_{1s,1s} = \frac{5}{4} \frac{Z m (k e^2)^2}{\hbar^2} = 2.5 \text{ Ryd} , \quad (67)$$

thus, the first-order ground-state energy of the He atom equals

$$E_{1s,1s}^{(1)} = E_{1s,1s}^{(0)} + \Delta E_{1s,1s}^{(1)} = -5.5 \text{ Ryd} . \quad (68)$$

Actually, this is a surprisingly good approximation of the exact ground state energy, -5.807 Ryd .

2.2 Excited states

The first excited states of the unperturbed Hamiltonian can be generated from the $1s$ and $2s, 2p$ one-electron states. Let's consider first the eight-dimensional tensor product space of the $1s$ and $2s$ states. By using the two-spin eigenstates,

$$|00\rangle = \frac{1}{\sqrt{2}} \left(\left| \frac{1}{2}, +\frac{1}{2} \right\rangle_1 \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_2 - \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_1 \left| \frac{1}{2}, +\frac{1}{2} \right\rangle_2 \right) \quad \text{singlet} \quad (69)$$

$$\left. \begin{aligned} |1-1\rangle &= \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_1 \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_2 \\ |10\rangle &= \frac{1}{\sqrt{2}} \left(\left| \frac{1}{2}, +\frac{1}{2} \right\rangle_1 \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_2 + \left| \frac{1}{2}, -\frac{1}{2} \right\rangle_1 \left| \frac{1}{2}, +\frac{1}{2} \right\rangle_2 \right) \\ |11\rangle &= \left| \frac{1}{2}, +\frac{1}{2} \right\rangle_1 \left| \frac{1}{2}, +\frac{1}{2} \right\rangle_2 \end{aligned} \right\} \quad \text{triplet} \quad (70)$$

and the symmetric and antisymmetric combinations of the spatial parts of the hydrogen-like wavefunctions,

$$\phi_{1s,2s}^+(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}} (\phi_{1s}(\vec{r}_1) \phi_{2s}(\vec{r}_2) + \phi_{2s}(\vec{r}_1) \phi_{1s}(\vec{r}_2)) \quad (71)$$

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

four antisymmetric two-electron states can be constructed as follows,

$$\psi_{1s,2s}^1(1,2) = \phi_{1s,2s}^+(\vec{r}_1, \vec{r}_2) |00\rangle \quad (73)$$

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

$$\psi_{1s,2s}^3(1,2) = \phi_{1s,2s}^-(\vec{r}_1, \vec{r}_2) |10\rangle \quad (75)$$

$$\psi_{1s,2s}^4(1,2) = \phi_{1s,2s}^-(\vec{r}_1, \vec{r}_2) |11\rangle . \quad (76)$$

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

$$H^0(1,2)\psi_{1s,2s}^\alpha(1,2) = E_{1s,2s} \psi_{1s,2s}^\alpha(1,2) \quad (\alpha = 1, 2, 3, 4) \quad (77)$$

$$E_{1s,2s} = -4 \left(1 + \frac{1}{4}\right) \text{ Ryd} = -5 \text{ Ryd} . \quad (78)$$

To obtain the correction of the energy due to the electron-electron interaction we have to apply degenerate first-order perturbation theory. Since the Coulomb interaction is independent of the spin and $\psi_{1s,2s}^\alpha(1,2)$ contain orthonormal two-spin states, the matrix of the Coulomb interaction is diagonal on the basis $\{\psi_{1s,2s}^\alpha\}$. The first-order energy corrections are then obtained as the diagonal elements of the matrix of perturbation,

$$\Delta E_{1s,2s}^{(1),1} = \langle \psi_{1s,2s}^1(1,2) | V(1,2) | \psi_{1s,2s}^1(1,2) \rangle \quad (79)$$

$$= \int \int \phi_{1s,2s}^+(\vec{r}_1, \vec{r}_2)^* \frac{ke^2}{|\vec{r}_1 - \vec{r}_2|} \phi_{1s,2s}^+(\vec{r}_1, \vec{r}_2) d^3r_1 d^3r_2 , \quad (80)$$

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

$$\Delta E_{1s,2s}^{(1),\alpha} = \langle \psi_{1s,2s}^\alpha(1,2) | V(1,2) | \psi_{1s,2s}^\alpha(1,2) \rangle \quad (81)$$

$$= \int \int \phi_{1s,2s}^-(\vec{r}_1, \vec{r}_2)^* \frac{ke^2}{|\vec{r}_1 - \vec{r}_2|} \phi_{1s,2s}^-(\vec{r}_1, \vec{r}_2) d^3r_1 d^3r_2 . \quad (82)$$

We can see that the triplet states remain degenerate but the degeneracy between the triplet and singlet states is lifted. Let's evaluate the energy corrections:

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

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

The first two terms on the right-hand side of the above equation are clearly identical and equal to the classical Coulomb interaction energy between the charge distributions, $e\rho_{1s}(\vec{r}_1)$ and $e\rho_{2s}(\vec{r}_2)$:

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

The remaining two terms that are also identical have no classical analogue. Since they contain two different wavefunctions with the same (coordinate) argument, we call these terms the *exchange integral*,

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

which gives the energy splitting between the singlet and triplet states formed from the tensor product of $1s$ and $2s$ one-electron states:

$$\Delta E_{1s,2s}^{(1),\text{singlet}} = C_{1s,2s} + K_{1s,2s}, \quad (87)$$

$$\Delta E_{1s,2s}^{(1),\text{triplet}} = C_{1s,2s} - K_{1s,2s}. \quad (88)$$

For a complete description first excited states of the Helium atom we have to consider also the Slater determinants formed by the $1s$ and $2p^3$ one-electron states, because they are eigenfunctions of the unperturbed Hamiltonian with the same energy, $E = -5$ Ryd. The corresponding two-electron states can be constructed as above,

$$\psi_{1s,2p_m}^1(1,2) = \phi_{1s,2p_m}^+(\vec{r}_1, \vec{r}_2) |00\rangle \quad (89)$$

$$\psi_{1s,2p_m}^2(1,2) = \phi_{1s,2p_m}^-(\vec{r}_1, \vec{r}_2) |1-1\rangle \quad (90)$$

$$\psi_{1s,2p_m}^3(1,2) = \phi_{1s,2p_m}^-(\vec{r}_1, \vec{r}_2) |10\rangle \quad (91)$$

$$\psi_{1s,2p_m}^4(1,2) = \phi_{1s,2p_m}^-(\vec{r}_1, \vec{r}_2) |11\rangle, \quad (92)$$

where $m \in \{-1, 0, 1\}$ refer to the hydrogen-like one-electron eigenfunctions $\phi_{2,1,m}(\vec{r})$. Therefore, 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 angular momentum operator, $\vec{L} = \vec{L}_1 + \vec{L}_2$, commutes with the Hamiltonian $H(1,2)$, thus, we can look for the common eigenstates of the operators $H(1,2)$, L_z and L^2 . Furthermore, based on the addition of angular momenta, it is obvious that the states (73)-(76) are eigenfunctions of L_z and L^2 with $L = 0$ and $M = 0$, while the states (89)-(92) correspond to angular momentum eigenstates with $L = 1$ and $M = m$. Obviously, the matrix of $V(1,2)$ is again diagonal and the degeneracies are lifted as above,

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

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

where $C_{1s,2p}$ is the Coulomb integral and $K_{1s,2p}$ is the exchange integral defined in (85) and (86), respectively, by simply replacing ϕ_{2s} by ϕ_{2p_m} . 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 Figure 1.

For the eigenstates of the He atom, in Figure 1 we used 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 $L = 0, 1, \dots$ we use the conventional notation $S, P, \dots$, respectively. Due to the addition rules of angular momenta, for the singlet states $S = 0$ ($2S + 1 = 1$), the total angular momentum quantum number J is unambiguously defined as $J = L$. 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 , i.e. the $L = 1$ and $S = 1$ states correspond to $J = 0, 1, 2$, so this level is $1 + 3 + 5 = 9$ times

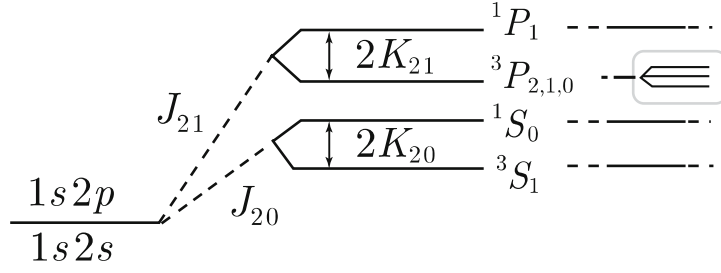


Figure 1: The energy levels of the low-energy excited states in the He atom. The notations are as follows: $J_{20} \equiv C_{1s,2s}$, $J_{21} \equiv C_{1s,2p}$, $K_{20} \equiv K_{1s,2s}$, $K_{21} \equiv K_{1s,2p}$.

degenerate. We will see later that this level splits according to the three different values of J due to spin-orbit coupling as indicated in Figure 1.

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 isotropic Heisenberg model with the so-called exchange interaction 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,

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

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

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

If the particle is described by a wave packet, localized both in coordinate and momentum space, then we should consider the superposition of plane waves.

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

The scattering process can be described by solving 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 the $V(\vec{r})$ the potential energy stands for the interaction between the scattered particle and the target (target potential). If the target potential is time independent, the energy of the particle is a conserved (*elastic scattering*), so we can change to the time independent Schrödinger equation:

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

$\Downarrow$

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

Without loss of generality it is worth to take the 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, our goal is to express the scattered wave for large $r = |\vec{r}| \rightarrow \infty$, which is 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

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

$\Downarrow$

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

and obtain the following equation for the scattered wave,

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

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

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

Multiplying with $V(\vec{r}') \psi(\vec{r}')$ and integrating over $\vec{r}'$, we obtain

$$\begin{aligned} & \left(-\frac{\hbar^2 \Delta}{2m} - E\right) \int G_0(\vec{r}, \vec{r}'; E) V(\vec{r}') \psi(\vec{r}') d^3 r' = \\ & = - \int \delta(\vec{r} - \vec{r}') V(\vec{r}') \psi(\vec{r}') d^3 r' = -V(\vec{r}) \psi(\vec{r}). \end{aligned} \quad (113)$$

Comparing with equation (111) we conclude that the scattered wavefunction satisfies the equality

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

thus, the solution of (106) can be written as

$$\psi(\vec{r}) = \psi_0(\vec{r}) + \int G_0(\vec{r}, \vec{r}'; E) V(\vec{r}') \psi(\vec{r}') d^3 r', \quad (115)$$

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 in such a way that it includes the boundary conditions for the solution by a suitable choice of the Green's function $G_0(\vec{r}, \vec{r}'; E)$. In our case, we expect spherical outgoing waves (e^{ikr}/r) far away from the target (see later).

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

$$(H_0 - zI) G_0(z) = -I \quad (116)$$

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,

$$\langle \vec{r} | (H_0 - zI) G_0(z) | \vec{r}' \rangle = -\langle \vec{r} | \vec{r}' \rangle = -\delta(\vec{r} - \vec{r}') \quad (117)$$

$\Downarrow$

$$\int d^3 r'' \langle \vec{r} | (H_0 - zI) | \vec{r}'' \rangle \langle \vec{r}'' | G_0(z) | \vec{r}' \rangle = (H_0(\vec{r}) - z) G_0(\vec{r}, \vec{r}'; z) = -\delta(\vec{r} - \vec{r}'), \quad (118)$$

where we used that H_0 is diagonal in coordinate representation,

$$\langle \vec{r} | H_0 | \vec{r}' \rangle = H_0(\vec{r}, \vec{r}') = H_0(\vec{r}) \delta(\vec{r} - \vec{r}'). \quad (119)$$

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 ,

$$H_0 = \sum_n \varepsilon_n |n\rangle \langle n|, \quad (120)$$

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 the generalized eigenvalues. From Eq. (116) it follows,

$$\langle n | (zI - H_0) G_0(z) | m \rangle = (z - \varepsilon_n) \langle n | G_0(z) | m \rangle = \delta_{nm} \quad (121)$$

from which we get

$$\langle n | G_0(z) | m \rangle = \delta_{nm} \frac{1}{z - \varepsilon_n}, \quad (122)$$

and the spectral resolution of the resolvent,

$$G_0(z) = \sum_n \frac{|n\rangle \langle n|}{z - \varepsilon_n}. \quad (123)$$

Since ε_n can take only real values, in order to avoid zero values in the denominator, for real values of $z = E$ 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

$$G_0^\pm(E) = \sum_n \frac{|n\rangle \langle n|}{E - \varepsilon_n \pm i0}. \quad (124)$$

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 (i.e. out of the spectrum of H_0).

The Green's function can be written as

$$G_0^\pm(\vec{r}', \vec{r}; z) = \sum_n \frac{\langle \vec{r}' | n \rangle \langle n | \vec{r} \rangle}{z - \varepsilon_n \pm i0} = \sum_n \frac{\varphi_n(\vec{r}') \varphi_n(\vec{r})^*}{z - \varepsilon_n \pm i0}, \quad (125)$$

where $\varphi_n(\vec{r})$ denote the eigenfunctions of H_0 . Taking into account that the properly normalized generalized eigenfunctions of H_0 are $\varphi_{\vec{p}}(\vec{r}) = \frac{1}{h^{3/2}} e^{\frac{i}{h} \vec{p} \vec{r}}$ 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:

$$G_0(\vec{r}', \vec{r}; z) = \frac{1}{h^3} \int \frac{e^{\frac{i}{h} \vec{p}(\vec{r}' - \vec{r})}}{\frac{\hbar^2 k^2}{2m} - \frac{p^2}{2m}} d^3 p = \frac{2m}{h^3} \int \frac{e^{\frac{i}{h} \vec{p}(\vec{r}' - \vec{r})}}{\hbar^2 k^2 - p^2} d^3 p \quad (126)$$

$$= \frac{4\pi m}{h^3} \int_0^\infty \frac{p^2 dp}{\hbar^2 k^2 - p^2} \int_{-1}^1 dx e^{\frac{i}{h} p |\vec{r}' - \vec{r}| x} \quad (127)$$

$$= \frac{2m}{h^2 |\vec{r}' - \vec{r}|} \frac{1}{i} \int_0^\infty dp p \frac{e^{\frac{i}{h} p |\vec{r}' - \vec{r}|} - e^{-\frac{i}{h} p |\vec{r}' - \vec{r}|}}{\hbar^2 k^2 - p^2} \quad (128)$$

$$= \frac{2m}{i h^2 |\vec{r}' - \vec{r}|} \int_{-\infty}^\infty dp \frac{p e^{\frac{i}{h} p |\vec{r}' - \vec{r}|}}{\hbar^2 k^2 - p^2}. \quad (129)$$

The integral can be calculated by using the residue theorem by closing the contour in the upper complex semiplane. For $\text{Re } z > 0$ and $\text{Im } z > 0 \rightarrow \text{Re } z > 0, \text{Im } k > 0$ we get

$$G_0(\vec{r}', \vec{r}; z) = -\frac{4\pi m}{h^2 |\vec{r}' - \vec{r}|} \text{Res}\left(\frac{p e^{\frac{i}{h} p |\vec{r}' - \vec{r}|}}{(p - \hbar k)(p + \hbar k)}, \hbar k\right) = -\frac{2m}{h^2} \frac{e^{ik|\vec{r}' - \vec{r}|}}{4\pi |\vec{r}' - \vec{r}|}, \quad (130)$$

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

$$G_0(\vec{r}', \vec{r}; z) = -\frac{4\pi m}{h^2 |\vec{r}' - \vec{r}|} \text{Res}\left(\frac{p e^{\frac{i}{h} p |\vec{r}' - \vec{r}|}}{(p - \hbar k)(p + \hbar k)}, -\hbar k\right) = -\frac{2m}{h^2} \frac{e^{-ik|\vec{r}' - \vec{r}|}}{4\pi |\vec{r}' - \vec{r}|}, \quad (131)$$

$\Downarrow$

$$E > 0 : G_0^\pm(\vec{r}', \vec{r}; E) = -\frac{2m}{\hbar^2} \frac{e^{\pm ik|\vec{r}-\vec{r}'|}}{4\pi|\vec{r}-\vec{r}'|}. \quad (132)$$

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 note that for $E < 0$, $E \pm i0 = (\pm ik)^2$ with $k = \sqrt{-E}$, therefore,

$$G_0^\pm(\vec{r}', \vec{r}; E) = -\frac{2m}{\hbar^2} \frac{e^{-k|\vec{r}-\vec{r}'|}}{4\pi|\vec{r}-\vec{r}'|}, \quad (133)$$

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

$$|\psi\rangle = |\psi_0\rangle + G_0^+ V |\psi\rangle, \quad (134)$$

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

$$|\psi^{(0)}\rangle = |\psi_0\rangle \quad (135)$$

$$|\psi^{(1)}\rangle = |\psi_0\rangle + G_0^+ V |\psi_0\rangle = |\psi_0\rangle + G_0^+ V |\psi_0\rangle \quad (136)$$

$$|\psi^{(2)}\rangle = |\psi_0\rangle + G_0^+ V |\psi^{(1)}\rangle = |\psi_0\rangle + G_0^+ V |\psi_0\rangle + (G_0^+ V)^2 |\psi_0\rangle \quad (137)$$

$$|\psi^{(3)}\rangle = |\psi_0\rangle + G_0^+ V |\psi^{(2)}\rangle = |\psi_0\rangle + G_0^+ V |\psi_0\rangle + (G_0^+ V)^2 |\psi_0\rangle + (G_0^+ V)^3 |\psi_0\rangle \quad (138)$$

and so on

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

$$|\psi\rangle = |\psi_0\rangle + G_0^+ \sum_{n=0}^{\infty} (VG_0^+)^n V |\psi_0\rangle. \quad (139)$$

If $\|VG_0^+\| < 1$, that is the scattering potential is weak, we can use the sum of the Neumann-series,

$$\sum_{n=0}^{\infty} (VG_0^+)^n = (I - VG_0^+)^{-1} \quad (140)$$

and the solution of the Lippmann–Schwinger equation can be written as

$$|\psi\rangle = |\psi_0\rangle + G_0^+ (I - VG_0^+)^{-1} V |\psi\rangle_0. \quad (141)$$

We recognize that

$$\begin{aligned} G_0^+ (I - VG_0^+)^{-1} &= \left((G_0^+)^{-1} - V \right)^{-1} = (E + i0 - H_0 - V)^{-1} \\ &= (E + i0 - H)^{-1} = G^+(E) \end{aligned} \quad (142)$$

is the resolvent operator of the scattering target. This gives the complete solution of the Lippmann–Schwinger equation,

$$|\psi\rangle = |\psi_0\rangle + G^+ V |\psi_0\rangle \quad (143)$$

or in coordinate representation,

$$\psi(\vec{r}) = \psi_0(\vec{r}) + \int G^+(\vec{r}, \vec{r}'; E) V(\vec{r}') \psi_0(\vec{r}') d^3r'. \quad (144)$$

3.2 Scattering amplitudes and cross sections

Putting the origin of the coordinate system into the compact domain of the target potential $V(\vec{r}')$ and considering the position $\vec{r}$ of the detector far from the target, we get the asymptotic form of the scattered wave by determining the Green's function in the limit of $r \gg r'$. It is easy to see that the lowest decay in r is provided by the first term of the Born series, which is called the *Born approximation*:

$$\psi(\vec{r}) \simeq \psi^{(1)}(\vec{r}) = \psi_0(\vec{r}) + \int G_0^\pm(\vec{r}, \vec{r}'; E) V(\vec{r}') \psi_0(\vec{r}') d^3r'. \quad (145)$$

In the denominator of $e^{\pm ik|\vec{r}-\vec{r}'|}/|\vec{r}-\vec{r}'|$, we can take the approximation $|\vec{r}-\vec{r}'| \simeq r$, because with further terms in the expansion of $1/|\vec{r}-\vec{r}'|$ lead to contributions to $\psi(\vec{r})$ proportional with $1/r^2$ or $1/r^3$ etc. decaying 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* $\vec{e}_r = \frac{\vec{r}}{r}$,

$$k|\vec{r}-\vec{r}'| = kr \sqrt{\left(\frac{\vec{r}}{r} - \frac{\vec{r}'}{r}\right)^2} = kr \sqrt{1 - \frac{2\vec{r}\vec{r}'}{r^2} + \frac{r'^2}{r^2}} \xrightarrow{r \gg r'} kr \left(1 - \frac{\vec{r}\vec{r}'}{r^2}\right) \quad (146)$$

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

$$G_0^\pm(\vec{r}', \vec{r}; E) \rightarrow -\frac{2m}{\hbar^2} \frac{e^{\pm ikr}}{4\pi r} e^{\mp i\vec{k}'\vec{r}'} = -\frac{m}{2\pi\hbar^2} \frac{e^{\pm ikr}}{r} e^{\mp i\vec{k}'\vec{r}'} , \quad (147)$$

where

$$\vec{k}' = k\vec{e}_r = k\frac{\vec{r}}{r} \quad (148)$$

denotes the wavevector for the particle propagating towards the detector.

Considering the time dependent phase factor $e^{-i\frac{E}{\hbar}t}$, the function e^{ikr}/r describes a spherical wave propagating outwards (away the target), while e^{-ikr}/r stands for a spherical wave propagating inwards (to the target). For the solution of the scattering problem we therefore use the Green's function $G_0^+(\vec{r}, \vec{r}'; E)$ and obtain for the scattered wave in the asymptotic limit,

$$\psi_{sc}(\vec{r}) \simeq -\frac{e^{ikr}}{r} \frac{m}{2\pi\hbar^2} \int e^{-i\vec{k}'\vec{r}'} V(\vec{r}') e^{i\vec{k}\vec{r}'} d^3r'. \quad (149)$$

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

$$\psi(\vec{r}) \simeq A \left(e^{i\vec{k}\vec{r}} + f(\vec{q}) \frac{e^{ikr}}{r} \right) , \quad (150)$$

where we introduced the so called *scattering amplitude*

$$f(\vec{q}) = -\frac{m}{2\pi\hbar^2} \int V(\vec{r}') e^{-i\vec{q}\vec{r}'} d^3r' , \quad (151)$$

with $\vec{q}$ defined as the change of the wavevector of the scattered particle,

$$\vec{q} = \vec{k}' - \vec{k} = k\frac{\vec{r}}{r} - \vec{k} = k(\vec{e}_r - \vec{e}_k) . \quad (152)$$

Without loss of generality, let's choose the z axis parallel to the direction of the incoming wave, $\vec{e}_k = \vec{e}_z$. Parametrizing the direction of the detector by spherical coordinates, $\vec{e}_r = (\sin \vartheta \cos \varphi, \sin \vartheta \sin \varphi, \cos \vartheta)$, it is easy to see that the length of $\vec{q}$ depends only on ϑ ,

$$\vec{q}^2 = 2k^2 (1 - \vec{e}_z \vec{e}_r) = 2k^2 (1 - \cos \vartheta) = 4k^2 \sin^2 \frac{\vartheta}{2} \rightarrow q = 2k \sin \frac{\vartheta}{2}. \quad (153)$$

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

$$\begin{aligned} f(q) &= -\frac{m}{\hbar^2} \int_0^\infty r'^2 dr' V(r') \int_{-1}^1 dx e^{-iqr'x} \\ &= -\frac{2m}{q\hbar^2} \int_0^\infty r' dr' V(r') \sin(qr'), \end{aligned} \quad (154)$$

where we choose the z' axis along the direction of the $\vec{q}$ vector. This also implies that the asymptotic wavefunction depends only on the coordinates r and ϑ ,

$$\psi(\vec{r}) \simeq A \left(e^{ikz} + f(q) \frac{e^{ikr}}{r} \right) = A \left(e^{ikr \cos \vartheta} + f(\vartheta) \frac{e^{ikr}}{r} \right). \quad (155)$$

As indicated in context of equation (139), the condition for the Born approximation is that the scattering potential has to be enough weak. The expression (154) is inversely proportional with q , i.e. with the square root of the energy, which suggests that the scattering amplitude is going to be sufficiently small for *high energies* making the *Born approximation applicable*. The Born approximation works for potentials that can be Fourier-transformed implying that the potential has to have sufficiently fast spatial decay. An example is the Yukawa potential, $V(r) \sim e^{-\kappa r}/r$, while in case of the limit of zero screening length, $\kappa \rightarrow 0$, we get correct results for the Coulomb potential (Rutherford scattering).

The output of the scattering experiments is the *differential scattering cross section*, i.e. the number of particles measured by the detector at a given direction per unit solid angle, $dN(\vartheta, \varphi)/d\Omega$, divided by the number of the incoming particles per unit area N_0 ,

$$\sigma(\vartheta, \varphi) = \frac{dN(\vartheta, \varphi)}{N_0 d\Omega}. \quad (156)$$

In case of stationary states, the probability current density which is identical with the particle flux (number of particles travelling through a unit area per unit time) is constant in time. This means that instead of counting (integrating) the number of particles observed by the detector for a long time, the instantaneous particle flux can be used for the calculation of the differential cross sections.

The probability current density of the incoming wave is

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

The radial current density of the scattered wave is,

$$\begin{aligned} \vec{j}_{sc}(\vec{r}) \vec{e}_r &= \frac{\hbar}{i2m} (\psi_{sc}^*(\vec{r}) \partial_r \psi_{sc}(\vec{r}) - \psi_{sc}(\vec{r}) \partial_r \psi_{sc}^*(\vec{r})) \\ &= \text{Re} \left(\frac{\hbar}{im} \psi_{sc}^*(\vec{r}) \partial_r \psi_{sc}(\vec{r}) \right). \end{aligned} \quad (157)$$

Making the following approximation,

$$\begin{aligned} \partial_r \psi_{sc}(\vec{r}) &= Af(\vartheta, \varphi) \partial_r \frac{e^{ikr}}{r} = -Af(\vartheta, \varphi) \frac{e^{ikr}}{r^2} + ikAf(\vartheta, \varphi) \frac{e^{ikr}}{r} \\ &\xrightarrow{r \rightarrow \infty} ikAf(\vartheta, \varphi) \frac{e^{ikr}}{r}, \end{aligned} \quad (158)$$

the radial current density can be expressed as

$$\vec{j}_{sc}(\vec{r})\vec{e}_r \simeq |A|^2 \frac{\hbar k}{m} \frac{|f(\vartheta, \varphi)|^2}{r^2} = j_0 \frac{|f(\vartheta, \varphi)|^2}{r^2}. \quad (159)$$

The number of the scattered particles flowing through the area of the detector $d\vec{A} = r^2 d\vec{\Omega}$ (where $\vec{e}_r d\vec{A} = 0$) per unit time is,

$$dN(\vartheta, \varphi) = (\vec{j}_{sc}\vec{e}_r) r^2 d\Omega = j_0 |f(\vartheta, \varphi)|^2 d\Omega. \quad (160)$$

The differential cross section is then simply given by the square of magnitude of the scattering amplitude,

$$\sigma(\vartheta, \varphi) = \frac{dN(\vartheta, \varphi)}{j_0 d\Omega} = |f(\vartheta, \varphi)|^2. \quad (161)$$

In the Born approximation the differential cross section can be calculated as

$$\sigma(\vartheta, \varphi) = \frac{m^2}{4\pi^2 \hbar^4} \left| \int V(\vec{r}) e^{-i\vec{q}\vec{r}} d^3r \right|^2. \quad (162)$$

The total cross section is defined as

$$\sigma = \int d\Omega \sigma(\Omega). \quad (163)$$

Note 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

$$V(\vec{r}) = \sum_i V_0(\vec{r} - \vec{R}_i). \quad (164)$$

In this case the following expression enters the scattering amplitude in Born approximation,

$$\int V(\vec{r}') e^{i\vec{q}\vec{r}'} d^3r' = \left(\int V_0(\vec{r}) e^{-i\vec{q}\vec{r}} d^3r \right) \sum_i e^{i\vec{q}\vec{R}_i}. \quad (165)$$

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

$$\sigma(\vec{q}) = \sigma_0(\vec{q}) S(\vec{q}), \quad (166)$$

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

$$\sigma_0(\vec{q}) = \frac{m^2}{4\pi^2 \hbar^4} \left| \int V_0(\vec{r}) e^{-i\vec{q}\vec{r}} d^3r \right|^2, \quad (167)$$

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

$$S(\vec{q}) = \sum_{i,j} e^{i\vec{q}(\vec{R}_j - \vec{R}_i)}. \quad (168)$$

3.3 The method of partial waves

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

$$\psi_{\ell m}(E, \vec{r}) = P_{\ell}(E, r) Y_{\ell}^m(\vartheta, \varphi) \quad (169)$$

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

$$\left(-\frac{\hbar^2}{2m} \frac{1}{r} \frac{d^2}{dr^2} r + \frac{\hbar^2}{2m} \frac{\ell(\ell+1)}{r^2} + V(r) - E \right) P_{\ell}(E, r) = 0, \quad (170)$$

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

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

$$\left(\frac{1}{r} \frac{d^2}{dr^2} r - \frac{\ell(\ell+1)}{r^2} + k^2 \right) P_{\ell}(r) = 0. \quad (171)$$

The *regular solutions*, being finite at the origin, are defined by

$$P_{\ell}^{\text{reg}}(r) = j_{\ell}(kr), \quad (172)$$

where $j_{\ell}(x)$ are the so-called spherical Bessel functions.

Let us derive the differential equation of the spherical Bessel functions! Introducing the variable $x = kr$, equation (171) transforms to

$$\left(\frac{1}{x} \frac{d^2}{dx^2} x - \frac{\ell(\ell+1)}{x^2} + 1 \right) j_{\ell}(x) = 0 \quad (173)$$

$\Downarrow$

$$\left(x \frac{d^2}{dx^2} x + (x^2 - \ell(\ell+1)) \right) j_{\ell}(x) = 0. \quad (174)$$

Since

$$x \frac{d^2}{dx^2} x = x \frac{d}{dx} \left(x \frac{d}{dx} + 1 \right) = x^2 \frac{d}{dx} + 2x \frac{d}{dx} \quad (175)$$

$\Downarrow$

$$x^2 \frac{d^2}{dx^2} j_{\ell}(x) + 2x \frac{d}{dx} j_{\ell}(x) + (x^2 - \ell(\ell+1)) j_{\ell}(x) = 0. \quad (176)$$

The spherical Bessel functions satisfy the boundary conditions,

$$j_{\ell}(x) \xrightarrow{x \rightarrow 0} \frac{x^{\ell}}{(2\ell+1)!!} \quad j_{\ell}(x) \xrightarrow{x \rightarrow \infty} \frac{1}{x} \sin\left(x - \ell \frac{\pi}{2}\right). \quad (177)$$

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

$$P_{\ell}^{\text{irreg}}(r) = r n_{\ell}(kr), \quad (178)$$

where the so-called spherical Neumann functions $n_{\ell}(x)$ also satisfy Eq. (176) with the boundary conditions,

$$n_{\ell}(x) \xrightarrow{x \rightarrow 0} -\frac{(2\ell-1)!!}{x^{\ell+1}} \quad n_{\ell}(x) \xrightarrow{x \rightarrow \infty} -\frac{1}{x} \cos\left(x - \ell \frac{\pi}{2}\right). \quad (179)$$

Let us note that the so-called Wronski determinant of the spherical Bessel and Neumann functions can easily be derived from the differential equation (174) and the asymptotic expressions of these functions,

$$j'_\ell(x) n_\ell(x) - n'_\ell(x) j_\ell(x) = -\frac{1}{x^2} \quad (180)$$

for any $x \in \mathbb{R} \setminus \{0\}$.

We have seen in the previous section that in case of a *spherically symmetric potential* the asymptotic limit of the wavefunction has cylindrical symmetry, i.e. it doesn't depend on the azimuthal angle φ . The cylindrical symmetry of the scattering wavefunction persists, however, independent of the Born approximation and the asymptotic limit. Obviously, the zeroth order solution of the Born series has cylindrical symmetry,

$$\psi^{(0)}(\vec{r}) = \psi_0(\vec{r}) = A e^{ikz} = A e^{ikr \cos \vartheta}. \quad (181)$$

Using successive approximation (Born series) it is easy to show that cylindrical symmetry of $\psi^{(n-1)}(\vec{r})$ comes down to $\psi^{(n)}(\vec{r})$ ($n = 1, 2, \dots$),

$$\psi^{(n)}(\vec{r}) = \psi_0(\vec{r}) + \int G_0^+(|\vec{r} - \vec{r}'|; E) V(\vec{r}') \psi^{(n-1)}(\vec{r}') d^3 r'. \quad (182)$$

Since

$$|\vec{r} - \vec{r}'|^2 = r^2 + r'^2 - 2\vec{r}\vec{r}' = r^2 + r'^2 - 2rr'[\sin \vartheta \sin \vartheta' \cos(\varphi' - \varphi) + \cos \vartheta \cos \vartheta'], \quad (183)$$

the Green's function depends on the azimuthal angles through the function $\cos(\varphi' - \varphi)$,

$$G_0^+(|\vec{r} - \vec{r}'|; E) = G_0^+(r, r', \vartheta, \vartheta', \cos(\varphi' - \varphi); E). \quad (184)$$

Then the integral in equation (182) can be written as

$$\begin{aligned} \int G_0^+(|\vec{r} - \vec{r}'|; E) V(\vec{r}') \psi^{(n-1)}(\vec{r}') d^3 r' = \\ \int_0^\infty r'^2 dr' \int_0^\pi \sin \vartheta d\vartheta \left[\int_0^{2\pi} d\varphi' G_0^+(r, r', \vartheta, \vartheta', \cos(\varphi' - \varphi); E) \right] V(r') \psi^{(n-1)}(r', \vartheta'), \end{aligned} \quad (185)$$

while the integral over φ' ,

$$\begin{aligned} \int_0^{2\pi} d\varphi' G_0^+(r, r', \vartheta, \vartheta', \cos(\varphi - \varphi'); E) &= \int_{-\varphi}^{2\pi - \varphi} d\varphi' G_0^+(r, r', \vartheta, \vartheta', \cos \varphi'; E) \\ &= \int_0^{2\pi} d\varphi' G_0^+(r, r', \vartheta, \vartheta', \cos \varphi'; E) \end{aligned} \quad (186)$$

is independent of φ and so is the n^{th} approximation of the scattering wavefunction, $\psi^{(n)}(\vec{r}) = \psi^{(n)}(r, \vartheta)$. This implies

$$\psi(\vec{r}) = \lim_{n \rightarrow \infty} \psi^{(n)}(\vec{r}) = \psi(r, \vartheta). \quad (187)$$

Out of the range of the target potential we consider a general solution of the free-space Schrödinger equation,

$$\psi(\vec{r}) = \sum_{\ell=0}^{\infty} [a_\ell j_\ell(kr) - b_\ell n_\ell(kr)] Y_\ell^0(\vartheta) \quad (188)$$

$$\underset{r \rightarrow \infty}{\simeq} \sum_{\ell=0}^{\infty} \frac{1}{kr} \left[a_\ell \sin\left(kr - \ell \frac{\pi}{2}\right) + b_\ell \cos\left(kr - \ell \frac{\pi}{2}\right) \right] Y_\ell^0(\vartheta), \quad (189)$$

where we omitted the contributions containing $Y_\ell^m(\vartheta, \varphi)$ with $m \neq 0$, since they break cylindrical symmetry. Since the radial Schrödinger equation (171) contains no complex number or complex function, the radial wavefunctions can be chosen as real valued functions up to a complex phase. This means that the coefficients a_ℓ and b_ℓ have the same complex phase,

$$\frac{a_\ell}{b_\ell} \in \mathbb{R},$$

thus $\exists c_\ell \in \mathbb{C} \quad |c_\ell|^2 = |a_\ell|^2 + |b_\ell|^2$ 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,

$$\psi(\vec{r}) = \sum_{\ell=0}^{\infty} \frac{c_\ell}{kr} \left[\cos \delta_\ell \sin \left(kr - \ell \frac{\pi}{2} \right) + \sin \delta_\ell \cos \left(kr - \ell \frac{\pi}{2} \right) \right] Y_\ell^0(\vartheta) \quad (190)$$

$$= \sum_{\ell=0}^{\infty} \frac{c_\ell}{kr} \sin \left(kr - \ell \frac{\pi}{2} + \delta_\ell \right) Y_\ell^0(\vartheta) \quad (191)$$

$$= \sum_{\ell=0}^{\infty} \frac{c_\ell}{kr} \frac{e^{i(kr - \ell \frac{\pi}{2} + \delta_\ell)} - e^{-i(kr - \ell \frac{\pi}{2} + \delta_\ell)}}{2i} Y_\ell^0(\vartheta) \quad (192)$$

$$= \sum_{\ell=0}^{\infty} \left(\frac{c_\ell e^{i\delta_\ell} e^{-i\ell \frac{\pi}{2}}}{2ki} \frac{e^{ikr}}{r} - \frac{c_\ell e^{-i\delta_\ell} e^{i\ell \frac{\pi}{2}}}{2ki} \frac{e^{-ikr}}{r} \right) Y_\ell^0(\vartheta). \quad (193)$$

This means that the partial radial wave functions related to $Y_\ell^0(\vartheta)$ are *a sum of an outgoing and an incoming spherical wave*.

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

$$e^{ikz} = e^{ikr \cos \vartheta} = \sum_{\ell=0}^{\infty} \sqrt{4\pi(2\ell+1)} i^\ell j_\ell(kr) Y_\ell^0(\vartheta). \quad (194)$$

Let us also expand the scattering amplitude $f(\vartheta)$ with respect to the spherical harmonics $Y_\ell^0(\vartheta)$,

$$f(\vartheta) = \sum_{\ell=0}^{\infty} F_\ell Y_\ell^0(\vartheta),$$

where $F_\ell \in \mathbb{C}$. Recalling the asymptotic form of the wavefunction (150),

$$\begin{aligned} \psi(\vec{r}) &= A e^{ikz} + A f(\vartheta) \frac{e^{ikr}}{r} \\ &= \sum_{\ell=0}^{\infty} \left(\frac{A}{kr} \sqrt{4\pi(2\ell+1)} i^\ell \sin\left(kr - \ell\frac{\pi}{2}\right) + A F_\ell \frac{e^{ikr}}{r} \right) Y_\ell^0(\vartheta) \end{aligned} \quad (195)$$

$$= \sum_{\ell=0}^{\infty} \left(\frac{A}{kr} \sqrt{4\pi(2\ell+1)} i^\ell \frac{e^{i(kr-\ell\frac{\pi}{2})} - e^{-i(kr-\ell\frac{\pi}{2})}}{2i} + A F_\ell \frac{e^{ikr}}{r} \right) Y_\ell^0(\vartheta) \quad (196)$$

$$= \sum_{\ell=0}^{\infty} \left\{ \left(A F_\ell + \frac{A}{2k i} \sqrt{4\pi(2\ell+1)} \right) \frac{e^{ikr}}{r} - \frac{A(-1)^\ell}{2k i} \sqrt{4\pi(2\ell+1)} \frac{e^{-ikr}}{r} \right\} Y_\ell^0(\vartheta), \quad (197)$$

i.e. the partial radial wavefunctions are again the superposition of an incoming and an outgoing spherical wave.

The equality of the functions (193) and (197) implies that the coefficients of both the incoming and outgoing spherical waves must be identical. Matching the coefficients of the incoming waves means

$$\frac{A(-1)^\ell}{2k i} \sqrt{4\pi(2\ell+1)} = \frac{c_\ell e^{-i\delta_\ell} i^\ell}{2k i} \quad (198)$$

$\Downarrow$

$$c_\ell = A e^{i\delta_\ell} i^\ell \sqrt{4\pi(2\ell+1)}. \quad (199)$$

From the matching of the coefficients of the outgoing spherical wave,

$$\begin{aligned} A F_\ell + \frac{A}{2k i} \sqrt{4\pi(2\ell+1)} &= \frac{c_\ell e^{i\delta_\ell} i^{-\ell}}{2k i} \\ &= \frac{A e^{2i\delta_\ell}}{2k i} \sqrt{4\pi(2\ell+1)}, \end{aligned} \quad (200)$$

we derive,

$$F_\ell = \frac{e^{2i\delta_\ell} - 1}{2k i} \sqrt{4\pi(2\ell+1)} = \frac{\sqrt{4\pi(2\ell+1)}}{k} e^{i\delta_\ell} \sin \delta_\ell, \quad (201)$$

and the partial wave expansion of the scattering amplitudes,

$$f(\vartheta) = \sum_{\ell=0}^{\infty} \frac{\sqrt{4\pi(2\ell+1)}}{k} e^{i\delta_\ell} \sin \delta_\ell Y_\ell^0(\vartheta). \quad (202)$$

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

$$\begin{aligned} \sigma_{\text{tot}} &= \int d\Omega \sigma(\vartheta) = \int d\Omega |f(\vartheta)|^2 \\ &= \frac{4\pi}{k^2} \sum_{\ell, \ell'=0}^{\infty} \sqrt{(2\ell+1)(2\ell'+1)} e^{i\delta_\ell} e^{-i\delta_{\ell'}} \sin \delta_\ell \sin \delta_{\ell'} \underbrace{\int d\Omega Y_\ell^0(\vartheta)^* Y_{\ell'}^0(\vartheta)}_{\delta_{\ell\ell'}} \\ &= \frac{4\pi}{k^2} \sum_{\ell=0}^{\infty} (2\ell+1) \sin^2 \delta_\ell, \end{aligned} \quad (203)$$

where we used that the spherical harmonics are orthonormal.

The above expression of the total cross section is in principle exact, but the evaluation of the infinite sum of 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

$$L^2 = \hbar^2 \ell (\ell + 1) . \quad (204)$$

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 $a \gtrsim R$, so the partial waves with

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

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 (203). *So the method of partial waves can be best 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 $\ell = 0$ phaseshift 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 maxima, $\sigma_\ell = \frac{4\pi(2\ell+1)}{k^2}$. 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. (202) and (203) there is a direct connection between the scattering amplitude and the total cross section. Namely

$$\text{Im } f(\vartheta) = \sum_{\ell=0}^{\infty} \frac{\sqrt{4\pi(2\ell+1)}}{k} \sin^2 \delta_\ell Y_\ell^0(\vartheta) \quad (205)$$

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

$$\text{Im } f(\vartheta=0) = \frac{1}{k} \sum_{\ell=0}^{\infty} (2\ell+1) \sin^2 \delta_\ell , \quad (206)$$

implying that

$$\sigma_{\text{tot}} = \frac{4\pi}{k} \text{Im } f(\vartheta=0) . \quad (207)$$

This means, that the imaginary part of the forward scattering is proportional to the total cross section, which is termed as the *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 (sum of the incoming plane wave and the scattered wave) 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 (207).

Proof:

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

$$\psi(\vec{r}) = \psi_0(\vec{r}) + \psi_{sc}(\vec{r}) . \quad (208)$$

The probability current density can then be expressed as

$$\begin{aligned} \vec{j} &= \frac{\hbar}{2mi} \left(\psi^* \vec{\nabla} \psi - \psi \vec{\nabla} \psi^* \right) \\ &= \frac{\hbar}{2mi} \left[(\psi_0^* + \psi_{sc}^*) \vec{\nabla} (\psi_0 + \psi_{sc}) - (\psi_0 + \psi_{sc}) \vec{\nabla} (\psi_0^* + \psi_{sc}^*) \right] \end{aligned} \quad (209)$$

$$\begin{aligned} &\Downarrow \\ \vec{j} &= \vec{j}_0 + \vec{j}_{sc} + \vec{j}_{int} , \end{aligned} \quad (210)$$

with the current density of the incoming wave,

$$\vec{j}_0 = \frac{\hbar}{2mi} \left(\psi_0^* \vec{\nabla} \psi_0 - \psi_0 \vec{\nabla} \psi_0^* \right) , \quad (211)$$

the current density of the scattered wave,

$$\vec{j}_{sc} = \frac{\hbar}{2mi} \left(\psi_{sc}^* \vec{\nabla} \psi_{sc} - \psi_{sc} \vec{\nabla} \psi_{sc}^* \right) , \quad (212)$$

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

$$\vec{j}_{int} = \frac{\hbar}{2mi} \left[\psi_0^* \vec{\nabla} \psi_{sc} + \psi_{sc}^* \vec{\nabla} \psi_0 - \psi_0 \vec{\nabla} \psi_{sc}^* - \psi_{sc} \vec{\nabla} \psi_0^* \right] . \quad (213)$$

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

$$\vec{j}_{int} \vec{e}_r = \frac{\hbar}{2mi} \left[\psi_0^* \partial_r \psi_{sc} + \psi_{sc}^* \partial_r \psi_0 - \psi_0 \partial_r \psi_{sc}^* - \psi_{sc} \partial_r \psi_0^* \right] , \quad (214)$$

can be formulated by the below approximations,

$$\psi_0(\vec{r}) = e^{ikr \cos \vartheta} \rightarrow \partial_r \psi_0(\vec{r}) = ik \cos \vartheta e^{ikr \cos \vartheta} \quad (215)$$

$$\psi_{sc}(\vec{r}) = f(\vartheta, \varphi) \frac{e^{ikr}}{r} \rightarrow \partial_r \psi_{sc}(\vec{r}) = ik f(\vartheta, \varphi) \frac{e^{ikr}}{r} + o\left(\frac{1}{r^2}\right) , \quad (216)$$

yielding

$$\begin{aligned} \vec{j}_{int} \vec{e}_r &\simeq \frac{\hbar k}{2mr} \left[e^{ikr(1-\cos \vartheta)} f(\vartheta, \varphi) + e^{-ikr(1-\cos \vartheta)} \cos \vartheta f^*(\vartheta, \varphi) \right. \\ &\quad \left. + e^{-ikr(1-\cos \vartheta)} f^*(\vartheta, \varphi) + e^{ikr(1-\cos \vartheta)} \cos \vartheta f(\vartheta, \varphi) \right] \end{aligned} \quad (217)$$

$$\simeq \frac{\hbar k}{2mr} \left[e^{ikr(1-\cos \vartheta)} (1 + \cos \vartheta) f(\vartheta, \varphi) + e^{-ikr(1-\cos \vartheta)} (1 + \cos \vartheta) f^*(\vartheta, \varphi) \right] \quad (218)$$

$$= \frac{\hbar k}{mr} \operatorname{Re} \left(e^{ikr(1-\cos \vartheta)} (1 + \cos \vartheta) f(\vartheta, \varphi) \right) . \quad (219)$$

If $\vartheta \neq 0$, then $1 - \cos \vartheta \neq 0$, so because of $kr \gg 1$ the function $e^{ikr(1-\cos \vartheta)}$ 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:

$$\lim_{\vartheta \rightarrow 0} \vec{j}_{\text{int}} \vec{e}_r \simeq \frac{2\hbar k}{mr} \text{Re} \left(e^{ikr\vartheta^2/2} f(\vartheta = 0) \right) \quad (220)$$

and the corresponding flux is,

$$\begin{aligned} \int d\Omega \vec{j}_{\text{int}} \vec{e}_r &\simeq \frac{2\hbar k}{mr} \text{Re} \left(f(0) \int_0^{2\pi} d\varphi \int_0^{\delta\vartheta} d\vartheta \sin \vartheta e^{ikr\vartheta^2/2} \right) \\ &\simeq \frac{4\pi\hbar k}{mr} \text{Re} \left(f(0) \int_0^{\delta\vartheta} d\vartheta \vartheta e^{ikr\vartheta^2/2} \right) \\ &\stackrel{x=\vartheta^2/2}{=} \frac{4\pi\hbar k}{mr} \text{Re} \left(f(0) \int_0^{\delta x} dx e^{ikr x} \right) \\ &= \frac{4\pi\hbar k}{mr} \text{Re} \left(\frac{f(0)}{ikr} (e^{ikr\delta x} - 1) \right) \end{aligned} \quad (221)$$

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,

$$\lim_{\alpha \rightarrow +0} G_0(\vec{r}', \vec{r}, E + i\alpha) = -\frac{2m}{\hbar^2} \lim_{\beta \rightarrow +0} \frac{e^{i(k+i\beta)|\vec{r}'-\vec{r}|}}{4\pi|\vec{r}'-\vec{r}|}, \quad (222)$$

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

$$e^{i(k+i\beta)r\delta x} = e^{ikr\delta x} e^{-\beta r\delta x} \xrightarrow{r \rightarrow \infty} 0, \quad (223)$$

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

$$\int d\Omega \vec{j}_{\text{int}} \vec{e}_r \simeq \frac{4\pi\hbar k}{mr} \text{Re} \left(-\frac{f(0)}{ikr} \right) \simeq -\frac{4\pi}{r^2} \frac{\hbar}{m} \text{Im} f(0). \quad (224)$$

The probability current of the incoming wave vanishes,

$$\int d\Omega \vec{j}_0 \vec{e}_r = \frac{\hbar k}{m} \int d\Omega \vec{e}_r = 0, \quad (225)$$

while the probability current of the outgoing wave is given by

$$r^2 \int d\Omega \vec{j}_s \vec{e}_r = \frac{\hbar k}{m} \sigma_{\text{tot}}. \quad (226)$$

The total probability current of the stationary wavefunction is zero,

$$r^2 \int d\Omega \vec{j} \vec{e}_r = \frac{\hbar k}{m} \sigma_{\text{tot}} - 4\pi \frac{\hbar}{m} \text{Im} f(0) = 0, \quad (227)$$

leading to the optical theorem,

$$\sigma_{\text{tot}} = \frac{4\pi}{k} \text{Im} f(0). \quad (228)$$

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

$$\partial_t H^S(t) = 0, \quad (229)$$

where the superscript S refers to the Schrödinger picture. This picture is defined by the time dependent Schrödinger equation valid for the physical states,

$$i\hbar \partial_t \psi^S(t) = H^S \psi^S(t), \quad (230)$$

where the initial condition for the wavefunction is fixed,

$$\psi^S(t_0) = \varphi. \quad (231)$$

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

$$\psi^S(t) = U(t, t_0) \psi^S(t_0), \quad (232)$$

with the obvious boundary condition,

$$U(t_0, t_0) = I. \quad (233)$$

Substituting the right-hand side of Eq. (232) into the Schrödinger equation (230), we get

$$i\hbar \frac{d}{dt} U(t, t_0) = H^S U(t, t_0), \quad (234)$$

or after integration,

$$U(t, t_0) = I - \frac{i}{\hbar} \int_{t_0}^t H^S U(t', t_0) dt'. \quad (235)$$

This equation can be solved by successive approximation,

$$U^{(k+1)}(t, t_0) = I - \frac{i}{\hbar} \int_{t_0}^t H^S U^{(k)}(t', t_0) dt', \quad (236)$$

$\Downarrow$

$$U^{(0)}(t, t_0) = I \quad (237)$$

$$U^{(1)}(t, t_0) = I - \frac{i}{\hbar} \int_{t_0}^t H^S dt' = I - \frac{i}{\hbar} H^S (t - t_0) \quad (238)$$

$$U^{(2)}(t, t_0) = I - \frac{i}{\hbar} H^S (t - t_0) + \left(-\frac{i}{\hbar}\right)^2 \frac{(H^S)^2 (t - t_0)^2}{2} \quad (239)$$

$$U^{(3)}(t, t_0) = I - \frac{i}{\hbar} H^S (t - t_0) + \left(-\frac{i}{\hbar}\right)^2 \frac{(H^S)^2 (t - t_0)^2}{2} + \left(-\frac{i}{\hbar}\right)^3 \frac{(H^S)^3 (t - t_0)^3}{3!} \quad (240)$$

$$\Downarrow$$

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

We can realize that this is the Taylor expansion of the exponential function, so the complete solution of equation (234) can be written as

$$U(t, t_0) = e^{-\frac{i}{\hbar} H^S(t-t_0)} , \quad (241)$$

Statement: The time evolution operator is unitary.

Proof:

$$i\hbar \frac{d}{dt} U^\dagger(t, t_0) = -U^\dagger(t, t_0) H^S \quad (242)$$

$\Downarrow$

$$\frac{d}{dt} [U^\dagger(t, t_0) U(t, t_0)] = \frac{1}{i\hbar} (-U^\dagger(t, t_0) H U(t, t_0) + U^\dagger(t, t_0) H U(t, t_0)) = 0 . \quad (243)$$

Since

$$U^\dagger(t_0, t_0) U(t_0, t_0) = I \quad (244)$$

$\Downarrow$

$$U^\dagger(t, t_0) U(t, t_0) = I \Rightarrow U^\dagger(t, t_0) = U(t, t_0)^{-1} . \quad (245)$$

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

$$U(t, t_0)^{-1} = e^{-\frac{i}{\hbar} H^S(t_0-t)} = U(t_0, t) . \quad (246)$$

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

$$a_{ij}^S(t) = \langle \psi_i^S(t) | A^S(t) | \psi_j^S(t) \rangle = \langle \varphi_i | U^\dagger(t, t_0) A^S(t) U(t, t_0) | \varphi_j \rangle . \quad (247)$$

By using equations (234) and (242), the time evolution of this matrix element can be expressed as

$$\begin{aligned} \frac{d}{dt} a_{ij}^S(t) &= \langle \varphi_i | [\partial_t U^\dagger(t, t_0)] A^S(t) U(t, t_0) | \varphi_j \rangle + \langle \varphi_i | U^\dagger(t, t_0) A^S(t) [\partial_t U(t, t_0)] | \varphi_j \rangle \\ &\quad + \langle \varphi_i | U^\dagger(t, t_0) [\partial_t A^S(t)] U(t, t_0) | \varphi_j \rangle \end{aligned} \quad (248)$$

$$\begin{aligned} &= -\frac{1}{i\hbar} \langle \varphi_i | U^\dagger(t, t_0) H^S A^S(t) U(t, t_0) | \varphi_j \rangle + \frac{1}{i\hbar} \langle \varphi_i | U^\dagger(t, t_0) A^S(t) H^S U(t, t_0) | \varphi_j \rangle \\ &\quad + \langle \psi_i^S(t) | \partial_t A^S(t) | \psi_j^S(t) \rangle \end{aligned} \quad (249)$$

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

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,

$$\psi^H(t) = U^\dagger(t, t_0) \psi^S(t) = \psi^S(t_0) = \varphi, \quad (251)$$

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

$$\varphi^S(t) = A^S(t) \psi^S(t) \quad (252)$$

$\Downarrow$

$$\begin{aligned} \varphi^H(t) &= U^\dagger(t, t_0) (A^S(t) \psi^S(t)) \\ &= U^\dagger(t, t_0) (A^S(t) U(t, t_0) U^\dagger(t, t_0) \psi^S(t)) \\ &= U^\dagger(t, t_0) A^S(t) U(t, t_0) \psi^H(t) \\ &= A^H(t) \psi^H(t) \rightarrow A^H(t) = U^\dagger(t, t_0) A^S(t) U(t, t_0). \end{aligned} \quad (253)$$

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

$$\begin{aligned} \frac{d}{dt} A^H(t) &= \frac{1}{i\hbar} (-U^\dagger(t, t_0) H^S A^S(t) U(t, t_0) + U^\dagger(t, t_0) A^S(t) H^S U(t, t_0)) \\ &\quad + U^\dagger(t, t_0) \partial_t A^S(t) U(t, t_0) \end{aligned} \quad (254)$$

$$= \frac{1}{i\hbar} [A^H(t), H^H(t)] + \partial_t A^H(t), \quad (255)$$

where

$$H^H(t) = U^\dagger(t, t_0) H^S U(t, t_0) \quad (256)$$

and

$$\partial_t A^H(t) \equiv U^\dagger(t, t_0) \partial_t A^S(t) U(t, t_0). \quad (257)$$

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:

$$\frac{d}{dt} H^H(t) = \frac{1}{i\hbar} (-U^\dagger(t, t_0) (H^S)^2 U(t, t_0) + U^\dagger(t, t_0) (H^S)^2 U(t, t_0)) = 0 \quad (258)$$

$\Downarrow$

$$H^H(t) = H^S. \quad (259)$$

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

$$a_{ij}^H(t) = \langle \psi_i^H | A^H(t) | \psi_j^H \rangle = \langle \psi_i^S(t) | A^S(t) | \psi_j^S(t) \rangle = a_{ij}^S(t), \quad (260)$$

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

$$\frac{d}{dt} a_{ij}^H(t) = \langle \psi_i^H | \frac{1}{i\hbar} [A^H(t), H^H(t)] + \partial_t A^H(t) | \psi_j^H \rangle. \quad (261)$$

4.3 The Dirac (interaction) picture

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

$$H^S(t) = H_0^S + V^S(t) . \quad (262)$$

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

$$U(t, t_0) = e^{-\frac{i}{\hbar} H_0^S(t-t_0)} \quad (263)$$

$\Downarrow$

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

with the boundary condition,

$$\psi^D(t_0) = \psi^S(t_0) = \varphi . \quad (265)$$

Correspondingly, the operators are defined in the Dirac picture as

$$A^D(t) = U^\dagger(t, t_0) A^S(t) U(t, t_0) . \quad (266)$$

The time evolution of the operators looks formally similar as in the Heisenberg picture,

$$\begin{aligned} \frac{d}{dt} A^D(t) &= -\frac{1}{i\hbar} U^\dagger(t, t_0) H_0^S A^S(t) U(t, t_0) + \frac{1}{i\hbar} U^\dagger(t, t_0) A^S(t) H_0^S U(t, t_0) \\ &\quad + U^\dagger(t, t_0) \partial_t A^S(t) U(t, t_0) \end{aligned} \quad (267)$$

$$= \frac{1}{i\hbar} [A^D(t), H_0^D(t)] + (\partial_t A)^D(t) , \quad (268)$$

where

$$(\partial_t A)^D(t) \equiv U^\dagger(t, t_0) \partial_t A^S(t) U(t, t_0) . \quad (269)$$

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

$$\frac{d}{dt} H_0^D(t) = 0 \Rightarrow H_0^D(t) = H_0^S . \quad (270)$$

Let's derive the equation of motion for the wavefunction within the Dirac picture:

$$i\hbar \partial_t \psi^D(t) = i\hbar \partial_t U^\dagger(t, t_0) \psi^S(t) + i\hbar U^\dagger(t, t_0) \partial_t \psi^S(t) \quad (271)$$

$$= -U^\dagger(t, t_0) H_0^S \psi^S(t) + U^\dagger(t, t_0) (H_0 + V^S(t)) \psi^S(t) \quad (272)$$

$$= U^\dagger(t, t_0) V^S(t) \psi^S(t) \quad (273)$$

$$= V^D(t) \psi^D(t) , \quad (274)$$

where

$$V^D(t) = U^\dagger(t, t_0) V^S(t) U(t, t_0) \quad (275)$$

is the perturbation operator in the Dirac picture.

The time dependence of the matrix elements of observables,

$$a_{ij}(t) = \langle \psi_i^D(t) | A^D(t) | \psi_j^D(t) \rangle \quad (276)$$

$\Downarrow$

$$\frac{d}{dt} a_{ij}(t) = -\frac{1}{i\hbar} \langle \psi_i^D(t) | V^D(t) A^D(t) | \psi_j^D(t) \rangle + \frac{1}{i\hbar} \langle \psi_i^D(t) | A^D(t) V^D(t) | \psi_j^D(t) \rangle \quad (277)$$

$$+ \frac{1}{i\hbar} \langle \psi_i^D(t) | [A^D(t), H_0^D] | \psi_j^D(t) \rangle + \langle \psi_i^D(t) | (\partial_t A)^D(t) | \psi_j^D(t) \rangle \quad (278)$$

$$= \frac{1}{i\hbar} \langle \psi_i^D(t) | [A^D(t), H^D(t)] + (\partial_t A)^D(t) | \psi_j^D(t) \rangle, \quad (279)$$

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:

$$\psi^D(t) = U^D(t, t_0) \psi^D(t_0) = U^D(t, t_0) \varphi, \quad (280)$$

with

$$U^D(t_0, t_0) = I. \quad (281)$$

Using Eq. (274) we get the differential equation for the time evolution operator in the Dirac picture,

$$\frac{d}{dt} U^D(t, t_0) = -\frac{i}{\hbar} V^D(t) U^D(t, t_0), \quad (282)$$

which yields by integration,

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

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

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

$$U^{D(k+1)}(t, t_0) = I - \frac{i}{\hbar} \int_{t_0}^t V^D(t') U^{D(k)}(t', t_0) dt' \quad (k = 0, 1, 2, \dots) \quad (284)$$

$\Downarrow$

$$U^D(t, t_0) = \sum_{k=0}^{\infty} \left(-\frac{i}{\hbar}\right)^k \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \dots \int_{t_0}^{t_{k-1}} dt_k V^D(t_1) V^D(t_2) \dots V^D(t_k) \quad (285)$$

$$= \sum_{k=0}^{\infty} \frac{1}{k!} \left(-\frac{i}{\hbar}\right)^k \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \dots \int_{t_0}^{t_k} dt_k T[V^D(t_1) V^D(t_2) \dots V^D(t_k)] \quad (286)$$

$$:= T \exp \left(-\frac{i}{\hbar} \int_{t_0}^t dt_1 V^D(t_1) \right), \quad (287)$$

where we introduced the time ordered product of the operators:

$$\begin{aligned} T[V^D(t_1) V^D(t_2) \dots V^D(t_k)] &= V^D(t_{i_1}) V^D(t_{i_2}) \dots V^D(t_{i_k}) \\ t_{i_l} &\in \{t_1, t_2, \dots, t_k\} \quad (l = 1, 2, \dots, k) \\ t_{i_1} &> t_{i_2} > t_{i_3} \dots > t_{i_{k-1}} > t_k \end{aligned} \quad (288)$$

Statement: Using the notation,

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

$$\begin{aligned} \int_{t_0}^t dt_1 \int_{t_0}^t dt_2 \dots \int_{t_0}^t dt_k T f(t_1, t_2, \dots, t_k) = \\ k! \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \dots \int_{t_0}^{t_{k-1}} dt_k f(t_1, t_2, \dots, t_k) . \end{aligned} \quad (289)$$

Proof: $k = 2$

$$\begin{aligned} \int_{t_0}^t dt_1 \int_{t_0}^t dt_2 T f(t_1, t_2) &= \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 f(t_1, t_2) + \int_{t_0}^t dt_2 \int_{t_0}^{t_2} dt_1 f(t_2, t_1) \\ &= 2 \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 f(t_1, t_2) , \end{aligned} \quad (290)$$

$k = 3$:

$$\begin{aligned} \int_{t_0}^t dt_1 \int_{t_0}^t dt_2 \int_{t_0}^t dt_3 T f(t_1, t_2, t_3) &= \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \int_{t_0}^{t_2} dt_3 f(t_1, t_2, t_3) && ((\text{TO-31})) \\ &+ \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_3 \int_{t_0}^{t_3} dt_2 f(t_1, t_3, t_2) && ((\text{TO-32})) \\ &+ \int_{t_0}^t dt_2 \int_{t_0}^{t_2} dt_1 \int_{t_0}^{t_1} dt_3 f(t_2, t_1, t_3) && ((\text{TO-33})) \\ &+ \int_{t_0}^t dt_2 \int_{t_0}^{t_2} dt_3 \int_{t_0}^{t_3} dt_1 f(t_2, t_3, t_1) && ((\text{TO-34})) \\ &+ \int_{t_0}^t dt_3 \int_{t_0}^{t_3} dt_1 \int_{t_0}^{t_1} dt_2 f(t_3, t_1, t_2) && ((\text{TO-35})) \\ &+ \int_{t_0}^t dt_3 \int_{t_0}^{t_3} dt_2 \int_{t_0}^{t_2} dt_1 f(t_3, t_2, t_1) && ((\text{TO-36})) \\ &= 6 \int_{t_0}^t dt_1 \int_{t_0}^{t_1} dt_2 \int_{t_0}^{t_2} dt_3 f(t_1, t_2, t_3) , \end{aligned} \quad (291)$$

where in each of the integrals (TO-32), (TO-33), ..., (TO-36) we changed the names of the integration variables to (t_1, t_2, t_3) .

In general: On the left hand side of Eq. (289) we divide the integration domain into $k!$ pieces, 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's obvious that all off them are identical with the integral that appears on the right hand side of Eq. (289).

Connection with time dependent perturbation theory:

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

$$U^{D(1)}(t, t_0) = I - \frac{i}{\hbar} \int_{t_0}^t V^D(t') dt' = I - \frac{i}{\hbar} \int_{t_0}^t e^{\frac{i}{\hbar} H_0^S(t'-t_0)} V^S(t') e^{-\frac{i}{\hbar} H_0^S(t'-t_0)} dt' , \quad (292)$$

and the wave function in the Dirac picture reads as,

$$|\psi^{D(1)}(t)\rangle = |\varphi\rangle - \frac{i}{\hbar} \int_{t_0}^t e^{\frac{i}{\hbar} H_0^S(t'-t_0)} V^S(t') e^{-\frac{i}{\hbar} H_0^S(t'-t_0)} |\varphi\rangle dt' . \quad (293)$$

The wavefunction in the Schrödinger picture is written as,

$$|\psi^{S(1)}(t)\rangle = e^{-\frac{i}{\hbar}H_0^S(t-t_0)}|\psi^{D(1)}(t)\rangle \quad (294)$$

$$= e^{-\frac{i}{\hbar}H_0^S(t-t_0)}|\varphi\rangle - \frac{i}{\hbar}e^{-\frac{i}{\hbar}H_0^S(t-t_0)}\int_{t_0}^t e^{\frac{i}{\hbar}H_0^S(t'-t_0)}V^S(t')e^{-\frac{i}{\hbar}H_0^S(t'-t_0)}|\varphi\rangle dt'. \quad (295)$$

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

$$|\psi(t_0)\rangle = |\varphi\rangle = |k\rangle, \quad (296)$$

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

$$H_0^S = \sum_n \varepsilon_n |n\rangle \langle n|. \quad (297)$$

The wave function can then be evaluated as

$$|\psi^{S(1)}(t)\rangle = e^{-\frac{i}{\hbar}H_0^S(t-t_0)}|k\rangle - \frac{i}{\hbar}\sum_n e^{-\frac{i}{\hbar}H_0^S(t-t_0)}\times \int_{t_0}^t e^{\frac{i}{\hbar}H_0^S(t'-t_0)}|n\rangle \langle n| V^S(t') e^{-\frac{i}{\hbar}H_0^S(t'-t_0)}|k\rangle dt' \quad (298)$$

$$= e^{-\frac{i}{\hbar}\varepsilon_k(t-t_0)}|k\rangle - \frac{i}{\hbar}\sum_n e^{-\frac{i}{\hbar}\varepsilon_n(t-t_0)}|n\rangle \int_{t_0}^t e^{\frac{i}{\hbar}\omega_{nk}(t'-t_0)}V_{nk}^S(t') dt' \quad (299)$$

where

$$\omega_{nk} = \frac{\varepsilon_n - \varepsilon_k}{\hbar} \quad (300)$$

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

$$|\psi^{S(1)}(t)\rangle = \sum_n c_n^{(1)}(t) e^{-\frac{i}{\hbar}\varepsilon_n(t-t_0)}|n\rangle, \quad (301)$$

where

$$c_k^{(1)}(t) = 1 - \frac{i}{\hbar}\int_{t_0}^t V_{kk}^S(t') dt' \simeq 1 \quad (302)$$

and for $n \neq k$

$$c_n^{(1)}(t) = -\frac{i}{\hbar}\int_{t_0}^t e^{i\omega_{nk}(t'-t_0)}V_{nk}^S(t') dt'. \quad (303)$$

The above expressions are identical with the results we obtained in first order of the time dependent perturbation theory in the course Quantum Mechanics 1.

5 Motion in electromagnetic field

According to the theory of special relativity, the Hamiltonian of a particle with rest mass m and electric charge q is given by

$$H(\vec{r}, \vec{p}) = \sqrt{m^2 c^4 + c^2 (\vec{p} - q \vec{A}(\vec{r}))^2} + q\phi(\vec{r}), \quad (304)$$

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

$$\vec{E} = -\vec{\nabla}\phi - \frac{\partial \vec{A}}{\partial t} \text{ and } \vec{B} = \vec{\nabla} \times \vec{A}. \quad (305)$$

Using the approximation,

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

in nonrelativistic limit the following Hamiltonian applies,

$$H(\vec{r}, \vec{p}) = \frac{(\vec{p} - q \vec{A}(\vec{r}))^2}{2m} + V(\vec{r}), \quad (306)$$

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,

$$\vec{K} = \vec{p} - q \vec{A} = \frac{m \dot{\vec{r}}}{\sqrt{1 - \frac{\dot{\vec{r}}^2}{c^2}}} \simeq m \dot{\vec{r}} = m \vec{v}. \quad (307)$$

5.1 Commutation relations of the kinetic momentum operators

We extend quantum mechanics in the presence of electromagnetic field in terms of the Hamiltonian (306) by keeping the commutator relation between the coordinate operators and the canonical momentum operators,

$$[p_i, x_j] = \frac{\hbar}{i} \delta_{ij}. \quad (308)$$

Brief note on canonical quantization

In the Hamiltonian formalism of classical mechanics the Poisson bracket of two dynamical variables, $f(q, p)$ and $g(q, p)$, is defined as

$$\{f, g\} = \sum_i \left(\frac{\partial f}{\partial q_i} \frac{\partial g}{\partial p_i} - \frac{\partial f}{\partial p_i} \frac{\partial g}{\partial q_i} \right)$$

where $\{q_i\}$ and $\{p_i\}$ are the canonical coordinates and momenta. The Poisson brackets of the canonical variables is trivial:

$$\{q_i, q_j\} = 0 \quad \{p_i, p_j\} = 0 \quad \{q_i, p_j\} = \delta_{ij}.$$

From the Hamiltonian equations of motion,

$$\dot{q}_i = \frac{\partial H(q, p)}{\partial p_i} \quad \dot{p}_i = -\frac{\partial H(q, p)}{\partial q_i},$$

the time evolution of a dynamical variable $f(q, p; t)$ can be expressed as

$$\frac{d}{dt}f(q, p; t) = \{f(q, p; t), H(q, p)\} + \partial_t f(q, p; t).$$

Following Dirac (P.A.M. Dirac: Principles of Quantum Mechanics. USA: Oxford University, 1984), we assign operators (marked only here by hat) to the dynamical variables replacing the Poisson bracket by the commutator divided by $i\hbar$,

$$\{f, g\} = c \rightarrow \frac{1}{i\hbar} [\hat{f}, \hat{g}] = \hat{c}.$$

Consequently, the operators of the canonical coordinates and momenta satisfy,

$$[\hat{q}_i, \hat{q}_j] = 0 \quad [\hat{p}_i, \hat{p}_j] = 0 \quad [\hat{p}_i, \hat{q}_j] = \frac{\hbar}{i} \delta_{ij}.$$

Moreover, the time evolution of dynamical quantities is manifested by the time evolution of the operators within the Heisenberg picture,

$$\frac{d}{dt}\hat{O}(t) = \frac{1}{i\hbar} [\hat{O}, \hat{H}] + \partial_t \hat{O}(t).$$

In coordinate representation, the coordinate operators being the multiplication with the coordinates, the operators of the canonical momenta operator are then defined as

$$\vec{p} = \frac{\hbar}{i} \vec{\nabla}, \quad (309)$$

and those of the kinetic momenta as

$$\vec{K} = \frac{\hbar}{i} \vec{\nabla} - q\vec{A}, \quad (310)$$

where qA_i is a multiplication operator. The components of the canonical momentum operator commute with each other, but this is not true for the kinetic momentum operators, in general:

$$\begin{aligned} [K_i, K_j] &= i\hbar q ([\partial_i, A_j] + [A_i, \partial_j]) \\ &= i\hbar q (\partial_i A_j - A_j \partial_i + A_i \partial_j - \partial_j A_i) \\ &= i\hbar q ((\partial_i A_j) - (\partial_j A_i)), \end{aligned} \quad (311)$$

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

$$\varepsilon_{ijk} B_k = \varepsilon_{ijk} \varepsilon_{lmk} (\partial_l A_m) = (\delta_{il} \delta_{jm} - \delta_{im} \delta_{jl}) (\partial_l A_m) = (\partial_i A_j) - (\partial_j A_i), \quad (312)$$

therefore,

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

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

$$\vec{K} \times \vec{K} = i\hbar q \vec{B}. \quad (313)$$

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,

$$[K_i, x_j] = [p_i, x_j] = \frac{\hbar}{i} \delta_{ij}. \quad (314)$$

5.2 The Hamilton operator

As what follows, we investigate the coordinate representation of the Hamiltonian (306). To this end, we expand the square of the kinetic momentum operator,

$$\left(\frac{\hbar}{i}\vec{\nabla} - q\vec{A}\right)^2 = -\hbar^2\Delta + q^2A^2 - \frac{\hbar q}{i}\left(\vec{\nabla}\vec{A} + \vec{A}\vec{\nabla}\right). \quad (315)$$

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

$$\partial_i A_i \psi + A_i \partial_i \psi = (\partial_i A_i) \psi + 2A_i (\partial_i \psi), \quad (316)$$

or written compactly,

$$\vec{\nabla}\vec{A} + \vec{A}\vec{\nabla} = \text{div}\vec{A} + 2\vec{A}\vec{\nabla}, \quad (317)$$

yields the Hamilton operator

$$H = -\frac{\hbar^2}{2m}\Delta + V + \frac{q^2}{2m}A^2 + \frac{i\hbar q}{2m}\text{div}\vec{A} + \frac{i\hbar q}{m}\vec{A}\vec{\nabla}. \quad (318)$$

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

$$H = \underbrace{-\frac{\hbar^2}{2m}\Delta + V}_{H_0} + \frac{i\hbar q}{m}\vec{A}\vec{\nabla} + \frac{q^2}{2m}A^2. \quad (319)$$

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, i.e. $\vec{B}$ is constant in both space and time, the vector potential can be chosen using the so-called *symmetric gauge*,

$$\vec{A}(\vec{r}) = \frac{1}{2}\vec{B} \times \vec{r}. \quad (320)$$

This is a Coulomb gauge,

$$\text{div}\vec{A} = \partial_i A_i = \frac{1}{2}\varepsilon_{ijk} B_j \partial_i x_k = \frac{1}{2}\varepsilon_{ijk} \delta_{ik} B_j = \frac{1}{2}\varepsilon_{kjk} B_j = 0, \quad (321)$$

and, the curl of $\vec{A}$ yields indeed $\vec{B}$:

$$\begin{aligned} (\vec{\nabla} \times \vec{A})_i &= \frac{1}{2}\varepsilon_{ijk}\varepsilon_{klm} B_l \partial_j x_m \\ &= \frac{1}{2}B_l (\delta_{il}\delta_{jm} - \delta_{im}\delta_{jl}) \delta_{jm} \\ &= \frac{1}{2}B_l (\delta_{il}\delta_{jj} - \delta_{il}) \\ &= \frac{1}{2}(3B_i - B_i) = B_i. \end{aligned} \quad (322)$$

When the magnetic field points along the z direction, $\vec{B} = (0, 0, B)$, the vector potential is given by $\vec{A} = \frac{1}{2}(-By, Bx, 0)$. 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. (319) can then be expressed as

$$\begin{aligned}\frac{i\hbar q}{m}\vec{A}\vec{\nabla}\psi &= \frac{i\hbar q}{2m}(\vec{B} \times \vec{r})(\vec{\nabla}\psi) = \frac{i\hbar q}{2m}(\vec{r} \times (\vec{\nabla}\psi))\vec{B} \\ &= \frac{i\hbar q}{2m}(\vec{r} \times \vec{\nabla})\vec{B}\psi,\end{aligned}\quad (323)$$

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

$$\frac{i\hbar q}{m}\vec{A}\vec{\nabla} = -\frac{q}{2m}(\vec{r} \times \vec{p})\vec{B} = -\frac{q}{2m}\vec{L}\vec{B} = -\vec{M}_L\vec{B}, \quad (324)$$

where $\vec{M}_L$ is the operator of the magnetic moment related to the angular momentum $\vec{L}$, which for electrons, $q = -e$, is defined as

$$\vec{M}_L = \frac{q}{2m}\vec{L} = -\mu_B\frac{\vec{L}}{\hbar}, \quad (325)$$

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,

$$H_{\text{para}} = -(\vec{M}_L + 2\vec{M}_S)\vec{B} = \frac{\mu_B}{\hbar}(\vec{L} + 2\vec{S})\vec{B}. \quad (326)$$

The Zeemann effect: Due to the paramagnetic term the energy levels of the hydrogen atom in a homogeneous magnetic field along the z direction split as

$$E_{n\ell m_\ell m_s} = E_n^{(0)} + \mu_B(m_\ell + 2m_s)B, \quad (327)$$

where $E_n^{(0)} = -\frac{m(ke^2)^2}{2\hbar^2}\frac{1}{n^2}$ are the energy eigenvalues in the absence of magnetic field. 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 four 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. (319) is the so called *Langevin diamagnetic term*. Using the symmetric gauge again,

$$\frac{q^2}{2m}A^2 = \frac{q^2}{8m}(\vec{B} \times \vec{r})^2 = \frac{q^2}{8m}(r^2B^2 - (\vec{r}\vec{B})^2) = \frac{q^2B^2}{8m}(x^2 + y^2), \quad (328)$$

where for the final expression we assumed that the magnetic field is parallel to the z axis. Let's perform a simple estimation for the diamagnetic energy in first order perturbation theory relative to the paramagnetic energy:

$$\frac{\delta E_{\text{dia}}}{\delta E_{\text{para}}} = \frac{e^2B^2}{8m} \left(\frac{eB}{2m}\right)^{-1} \frac{|\langle x^2 + y^2 \rangle|}{|\langle L_z + 2S_z \rangle|} \simeq \frac{ea_0^2}{4\hbar}B,$$

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

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

Thus, we can see that in atoms the diamagnetic energy correction is usually negligible as compared to the paramagnetic correction. 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 energy term appears because the permanent magnetic moment of the atom $\vec{\mu} = -\frac{\mu_B}{\hbar} \langle \vec{L} + 2\vec{S} \rangle$ interacts with the external magnetic field. On the contrary, the Langevin diamagnetism is related to an induced magnetic moment defined as,

$$\vec{\mu}_{\text{dia}} = -\frac{\partial E_{\text{dia}}}{\partial \vec{B}} = -\frac{e^2}{8m} \frac{\partial \langle (\vec{B} \times \vec{r})^2 \rangle}{\partial \vec{B}} \\ = -\frac{e^2}{4m} \left(\langle r^2 \rangle \vec{B} - \langle \vec{r}(\vec{r} \cdot \vec{B}) \rangle \right)_{\vec{B} \parallel \vec{e}_z} = -\frac{e^2 B}{4m} \langle x^2 + y^2 \rangle \vec{e}_z , \quad (329)$$

being proportional to the external magnetic field and pointing into 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

$$\underline{\chi}_{\text{dia}} = -\frac{e^2}{4m} \left(\langle r^2 \rangle \underline{I} - \langle \vec{r} \circ \vec{r} \rangle \right) , \quad (330)$$

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

$$\vec{\mu}_{\text{dia}} = \underline{\chi}_{\text{dia}} \vec{B} \quad (331)$$

and

$$\delta E_{\text{dia}} = -\frac{1}{2} \vec{B} \underline{\chi}_{\text{dia}} \vec{B} = \frac{e^2}{8m} \langle (\vec{B} \times \vec{r})^2 \rangle . \quad (332)$$

5.4 Continuity equation

Similarly as we discussed earlier, also 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,

$$i\hbar \partial_t \psi = -\frac{\hbar^2}{2m} \Delta \psi + \frac{q^2}{2m} \vec{A}^2 \psi + \frac{i\hbar q}{2m} (\text{div } \vec{A} + 2 \vec{A} \cdot \vec{\nabla}) \psi \\ + V \psi + \mu_B \vec{B} \cdot \vec{\sigma} \psi , \quad (333)$$

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

$$\psi = \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} . \quad (334)$$

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

$$i\hbar \partial_t \psi_r = -\frac{\hbar^2}{2m} \Delta \psi_r + \frac{q^2}{2m} \vec{A}^2 \psi_r + \frac{i\hbar q}{2m} (\text{div } \vec{A} + 2 \vec{A} \cdot \vec{\nabla}) \psi_r \\ + V \psi_r + \mu_B B_i \sigma_i^{rs} \psi_s \quad (r, s \in \{1, 2\}) , \quad (335)$$

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

$$\begin{aligned} -i\hbar\partial_t^*\psi_r &= -\frac{\hbar^2}{2m}\Delta\psi_r^* + \frac{q^2}{2m}\vec{A}^2\psi_r - \frac{i\hbar q}{2m}\left(\text{div}\vec{A} + 2\vec{A}\vec{\nabla}\right)\psi_r^* \\ &\quad + V\psi_r^* + \mu_B B_i \psi_s^* \sigma_i^{sr} \quad (r, s \in \{1, 2\}) , \end{aligned} \quad (336)$$

which can compactly be written as,

$$\begin{aligned} -i\hbar\partial_t\psi^\dagger &= -\frac{\hbar^2}{2m}\Delta\psi^\dagger + \frac{q^2}{2m}\vec{A}^2\psi^\dagger - \frac{i\hbar q}{2m}\left(\text{div}\vec{A} + 2\vec{A}\vec{\nabla}\right)\psi^\dagger \\ &\quad + V\psi^\dagger + \mu_B \psi^\dagger \vec{B}\vec{\sigma} , \end{aligned} \quad (337)$$

where

$$\psi^\dagger = \begin{pmatrix} \psi_1^* & \psi_2^* \end{pmatrix} . \quad (338)$$

From Eqs. (333) and (337) we get,

$$\begin{aligned} i\hbar\left(\psi^\dagger(\partial_t\psi) + (\partial_t\psi^\dagger)\psi\right) &= -\frac{\hbar^2}{2m}\left(\psi^\dagger\Delta\psi - (\Delta\psi^\dagger)\psi\right) \\ &\quad + \frac{i\hbar q}{m}\left((\vec{\nabla}\vec{A})\psi^\dagger\psi + \vec{A}\psi^\dagger(\vec{\nabla}\psi) + \vec{A}(\vec{\nabla}\psi^\dagger)\psi\right) , \end{aligned} \quad (339)$$

where the inner rounded brackets explicitly mark on which functions the $\vec{\nabla}$ operator acts. Remarkably, the Pauli paramagnetic part of equation (333) containing the Pauli matrices doesn't contribute to the right-hand side of the above equation. After manipulating both sides of the equation above:

$$\psi^\dagger\partial_t\psi + (\partial_t\psi^\dagger)\psi = \partial_t(\psi^\dagger\psi) \quad (340)$$

$$\psi^\dagger\Delta\psi - (\Delta\psi^\dagger)\psi = \vec{\nabla}\left(\psi^\dagger\vec{\nabla}\psi - (\vec{\nabla}\psi^\dagger)\psi\right) , \quad (341)$$

and

$$(\vec{\nabla}\vec{A})\psi^\dagger\psi + \vec{A}\psi^\dagger(\vec{\nabla}\psi) + \vec{A}(\vec{\nabla}\psi^\dagger)\psi = \vec{\nabla}(\vec{A}\psi^\dagger\psi) , \quad (342)$$

we arrive at the following continuity equation,

$$\partial_t\rho + \vec{\nabla}\vec{j} = 0 \quad , \quad (343)$$

where

$$\rho = \psi^\dagger\psi \quad (344)$$

and

$$\vec{j} = \frac{\hbar}{2mi}\left(\psi^\dagger(\vec{\nabla}\psi - (\vec{\nabla}\psi^\dagger)\psi)\right) - \frac{q}{m}\vec{A}\psi^\dagger\psi . \quad (345)$$

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

$$\vec{j} = \frac{1}{m}\text{Re}(\psi^\dagger\vec{K}\psi) = \frac{1}{m}\text{Re}(\psi^\dagger(\vec{p} - \frac{q}{c}\vec{A})\psi) \quad (346)$$

$$= \frac{\hbar}{2mi}\left\{\psi^\dagger(\vec{\nabla}\psi) - (\vec{\nabla}\psi^\dagger)\psi\right\} - \frac{q}{m}\vec{A}\psi^\dagger\psi . \quad (347)$$

We note that the continuity equation remains valid if we add a divergenceless term to the probability current density. The spin-magnetisation probability current density,

$$\vec{j}_M = -\frac{1}{e}\text{curl}(\psi^\dagger \vec{M}_S \psi) = \frac{1}{m}\text{curl}(\psi^\dagger \vec{S} \psi) = \frac{\hbar}{2m}\text{curl}(\psi^\dagger \vec{\sigma} \psi), \quad (348)$$

can be obtained from the nonrelativistic limit of the Dirac equation (see in Relativistic Quantum Mechanics), but it doesn't enter the continuity equation derived in this section.

5.5 Gauge transformation of the wavefunction

The electric field $\vec{E}$ and the magnetic field $\vec{B}$ can be obtained from the scalar potential ϕ and vector potential $\vec{A}$ as

$$\vec{E} = -\vec{\nabla}\phi - \frac{\partial \vec{A}}{\partial t} \text{ and } \vec{B} = \vec{\nabla} \times \vec{A}. \quad (349)$$

The potentials are not uniquely defined, since the gauge transformation,

$$\vec{A}'(\vec{r}, t) = \vec{A}(\vec{r}, t) + \vec{\nabla}\Lambda(\vec{r}, t) \quad \phi'(\vec{r}, t) = \phi(\vec{r}, t) - \partial_t \Lambda(\vec{r}, t), \quad (350)$$

leaves the fields unchanged,

$$\vec{E} = -\vec{\nabla}\phi' - \frac{\partial \vec{A}'}{\partial t} \text{ and } \vec{B} = \vec{\nabla} \times \vec{A}'. \quad (351)$$

The time dependent Schrödinger equation,

$$i\hbar\partial_t\psi(\vec{r}, t) = \left[\frac{1}{2m} \left(\frac{\hbar}{i}\vec{\nabla} - q\vec{A}(\vec{r}, t) \right)^2 + q\phi(\vec{r}, t) \right] \psi(\vec{r}, t), \quad (352)$$

contains the potentials which are not physical observables. Therefore, it is mandatory to look for the solutions $\psi'(\vec{r}, t)$ when substituting the gauge transformed potentials into equation (352),

$$\begin{aligned} i\hbar\partial_t\psi'(\vec{r}, t) &= \left[\frac{1}{2m} \left(\frac{\hbar}{i}\vec{\nabla} - q\vec{A}'(\vec{r}, t) \right)^2 + q\phi'(\vec{r}, t) \right] \psi'(\vec{r}, t) \\ &= \left[\frac{1}{2m} \left(\frac{\hbar}{i}\vec{\nabla} - q\vec{A}(\vec{r}, t) - q\vec{\nabla}\Lambda(\vec{r}, t) \right)^2 + q\phi(\vec{r}, t) - q\partial_t\Lambda(\vec{r}, t) \right] \psi'(\vec{r}, t). \end{aligned} \quad (353)$$

Statement: The solution of equation (353) is

$$\psi'(\vec{r}, t) = e^{\frac{iq}{\hbar}\Lambda(\vec{r}, t)} \psi(\vec{r}, t). \quad (354)$$

Proof: First we substitute the expression (354) into the left-hand side of equation (353):

$$i\hbar\partial_t\psi' = i\hbar\partial_t \left(e^{\frac{iq}{\hbar}\Lambda} \psi \right) = e^{\frac{iq}{\hbar}\Lambda} (i\hbar\partial_t\psi - q(\partial_t\Lambda)\psi), \quad (355)$$

then we multiply the equation by $e^{-\frac{iq}{\hbar}\Lambda}$ and add $q(\partial_t\Lambda)\psi$ to both sides, which yields

$$i\hbar\partial_t\psi = \frac{1}{2m} e^{-\frac{iq}{\hbar}\Lambda} \left(\frac{\hbar}{i}\vec{\nabla} - q\vec{A} - q\vec{\nabla}\Lambda \right)^2 e^{\frac{iq}{\hbar}\Lambda} \psi + q\phi\psi. \quad (356)$$

Let's investigate the following expression:

$$\begin{aligned}
e^{-\frac{iq}{\hbar}\Lambda} \left(\frac{\hbar}{i} \vec{\nabla} - q\vec{A} - q\vec{\nabla}\Lambda \right) e^{\frac{iq}{\hbar}\Lambda} \psi &= e^{-\frac{iq}{\hbar}\Lambda} \left(\frac{\hbar}{i} \vec{\nabla} \right) e^{\frac{iq}{\hbar}\Lambda} \psi - q\vec{A}\psi - q(\vec{\nabla}\Lambda)\psi \\
&= \left(\frac{\hbar}{i} \vec{\nabla} + q(\vec{\nabla}\Lambda) \right) \psi - q\vec{A}\psi - q(\vec{\nabla}\Lambda)\psi \\
&= \left(\frac{\hbar}{i} \vec{\nabla} - q\vec{A} \right) \psi,
\end{aligned} \tag{357}$$

which means the following operator identity,

$$e^{-\frac{iq}{\hbar}\Lambda} \left(\frac{\hbar}{i} \vec{\nabla} - q\vec{A} - q\vec{\nabla}\Lambda \right) e^{\frac{iq}{\hbar}\Lambda} = \frac{\hbar}{i} \vec{\nabla} - q\vec{A}. \tag{358}$$

The square of this identity can be expressed as

$$\begin{aligned}
e^{-\frac{iq}{\hbar}\Lambda} \left(\frac{\hbar}{i} \vec{\nabla} - q\vec{A} - q\vec{\nabla}\Lambda \right) e^{\frac{iq}{\hbar}\Lambda} e^{-\frac{iq}{\hbar}\Lambda} \left(\frac{\hbar}{i} \vec{\nabla} - q\vec{A} - q\vec{\nabla}\Lambda \right) e^{\frac{iq}{\hbar}\Lambda} \\
= e^{-\frac{iq}{\hbar}\Lambda} \left(\frac{\hbar}{i} \vec{\nabla} - q\vec{A} - q\vec{\nabla}\Lambda \right)^2 e^{\frac{iq}{\hbar}\Lambda} = \left(\frac{\hbar}{i} \vec{\nabla} - q\vec{A} \right)^2.
\end{aligned} \tag{359}$$

The above expression can be used in equation (356), which then trivially transforms to the Schrödinger equation (352).

5.6 The Aharanov–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

$$\int_{\vec{r}_0}^{\vec{r}} \vec{A}'(\vec{s}) d\vec{s} = \int_{\vec{r}_0}^{\vec{r}} \vec{A}(\vec{s}) d\vec{s} + \Lambda(\vec{r}) - \Lambda(\vec{r}_0). \tag{360}$$

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

$$\Lambda(\vec{r}) = - \int_{\vec{r}_0}^{\vec{r}} \vec{A}(\vec{s}) d\vec{s}, \tag{361}$$

where, by choosing a suitable additive constant for $\Lambda(\vec{r})$, we fixed $\Lambda(\vec{r}_0) = 0$. Since the vector potential is curl free, the above line integral is independent of the path chosen. More precisely, this condition is fulfilled only when the domain where $\vec{B} = 0$ (denoted by Ω_0) is simply connected. Namely, if there is a compact region Ω_B with $\vec{B} \neq 0$ enclosed by Ω_0 then $\Lambda(\vec{r})$ for $\vec{r} \in \Omega_0$ is determined only up to multiples of the magnetic flux in Ω_B :

$$\oint_C \vec{A}(\vec{s}) d\vec{s} = \int_A \text{curl } \vec{A}(\vec{r}) d\vec{a} = \int_A \vec{B}(\vec{r}) d\vec{a} = \Phi_B, \tag{362}$$

where C is a closed loop in Ω_0 that encircles Ω_B , A is a smooth oriented surface with the boundary C and we used Stokes' theorem.

In classical electrodynamics only the fields are measurable, while the potentials are introduced as a mathematical concept. Aharanov and Bohm (1959) predicted first that in quantum

theory the electromagnetic potentials might be real physical quantities and that this could be shown in electron interference experiments [Y. Aharonov and D. Bohm: Significance of electromagnetic potentials in the quantum theory. Physical Review 115, 485, 1959]. More specifically, the question is raised whether the magnetic field in domain Ω_B enclosed by the zero-field region Ω_0 does have any effect on the motion of charged particles moving in Ω_0 . According to the gauge function (361) the magnetic field can have a nonlocal effect through the vectorpotential. The gauge function appears, however, as a phase in the wavefunction, so it is a nontrivial question whether this effect can be detected experimentally.

To illustrate the Aharonov-Bohm effect consider a double-slit electron interference experiment, where a perpendicular magnetic field generated by an infinitely long coil (solenoid) is placed between the two slits. Let $\vec{r}_0$ be the position of the source and $\vec{r}$ is a point of the screen. In general, the Schrödinger equation can only be solved numerically in order to get a single-valued wavefunction, from which the probability density at the screen can be determined. Instead, we construct the intensity pattern at the screen from the superposition of two wavefunctions, 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 out. Let us denote the wavefunctions by ψ_A and ψ_0 in cases of $\vec{A}(\vec{r}) \neq 0$ and $\vec{A}(\vec{r}) = 0$ ($\vec{r} \in \Omega_0$), respectively. They are related to each other by

$$\psi_0(\vec{r}, t) = \psi_A(\vec{r}, t) e^{\frac{iq}{\hbar} \Lambda(\vec{r})} = \psi_A(\vec{r}, t) \exp\left(-\frac{iq}{\hbar} \int_{\vec{r}_0}^{\vec{r}} \vec{A}(\vec{s}) d\vec{s}\right), \quad (363)$$

or

$$\psi_A(\vec{r}, t) = \psi_0(\vec{r}, t) \exp\left(\frac{iq}{\hbar} \int_{\vec{r}_0}^{\vec{r}} \vec{A}(\vec{s}) d\vec{s}\right). \quad (364)$$

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

We use the above result for the cases when either slit 1,

$$\psi_{1A}(\vec{r}, t) = \psi_{10}(\vec{r}, t) \exp\left(\frac{iq}{\hbar} \int_1 \vec{A}(\vec{s}) d\vec{s}\right) \quad (365)$$

or slit 2 is opened,

$$\psi_{2A}(\vec{r}, t) = \psi_{20}(\vec{r}, t) \exp\left(\frac{iq}{\hbar} \int_2 \vec{A}(\vec{s}) d\vec{s}\right), \quad (366)$$

where the paths labelled by 1 or 2 conducts through either slit 1 or slit 2, respectively. The intensity observed on the screen is proportional to the square of the magnitude of the superimposed wavefunctions,

$$\begin{aligned} I &\sim |\psi_{1A}(\vec{r}, t) + \psi_{2A}(\vec{r}, t)|^2 \\ &= \left| \psi_{10}(\vec{r}, t) \exp\left(\frac{iq}{\hbar} \int_2 \vec{A}(\vec{s}) d\vec{s}\right) + \psi_{20}(\vec{r}, t) \exp\left(\frac{iq}{\hbar} \int_1 \vec{A}(\vec{s}) d\vec{s}\right) \right|^2 \\ &= \left| \psi_{10}(\vec{r}, t) \exp\left(\frac{iq}{\hbar} \left[\int_2 \vec{A}(\vec{s}) d\vec{s} - \int_1 \vec{A}(\vec{s}) d\vec{s} \right] \right) + \psi_{20}(\vec{r}, t) \right|^2 \\ &= \left| \psi_{10}(\vec{r}, t) \exp\left(\frac{iq}{\hbar} \oint \vec{A}(\vec{s}) d\vec{s}\right) + \psi_{20}(\vec{r}, t) \right|^2 \\ &= \left| \psi_{10}(\vec{r}, t) \exp\left(\frac{iq}{\hbar} \Phi_B\right) + \psi_{20}(\vec{r}, t) \right|^2 \\ &= |\psi_{10}(\vec{r}, t)|^2 + |\psi_{20}(\vec{r}, t)|^2 + 2 \operatorname{Re}(\psi_{10}(\vec{r}, t) \psi_{20}(\vec{r}, t) e^{\frac{iq}{\hbar} \Phi_B}). \end{aligned} \quad (367)$$

Clearly, the interference term in the intensity contains the magnetic flux of the coil. In order to give a simple quantitative estimate for the positions of the interference fringes, let us assume plane waves for the wavefunctions,

$$\begin{aligned} I &\sim \left| \exp \left(ik\ell_1 + \frac{iq}{\hbar} \Phi_B \right) + \exp(ik\ell_2) \right|^2 \\ &= \left| 1 + \exp \left(i \left[k\ell_1 - k\ell_2 + \frac{q}{\hbar} \Phi_B \right] \right) \right|^2 \\ &= 2 + 2 \cos \left(k\ell_1 - k\ell_2 + \frac{q}{\hbar} \Phi_B \right) , \end{aligned} \quad (368)$$

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

$$k(\ell_1 - \ell_2) - \frac{e}{\hbar} \Phi_B = 2\pi n \longrightarrow \ell_1 - \ell_2 = \lambda \left(n + \frac{\Phi_B}{\Phi_0} \right) = \lambda \left(n + \frac{\Phi_B}{h/e} \right) , \quad (369)$$

where $n \in \mathbb{Z}$, $k = \frac{2\pi}{\lambda}$ and $\lambda = \frac{h}{mv}$ is the de Broglie wavelength and $\Phi_0 = h/e = 4.135 \cdot 10^{-11} \text{ Tcm}^2$ is the flux quantum. This implies that the positions of the intensity maxima (minima) can be tuned by the magnetic flux. The shift of the positions is a periodic function of Φ_B and the period is Φ_0 . These theoretical findings were confirmed by several experiments. It is important to emphasize that the Aharonov-Bohm effect proves that the vectorpotential has physical reality in quantum theory, but the physical observables depend always on gauge invariant quantities as the magnetic flux in case of the interference experiment.

As mentioned, the above explanation of the Aharonov-Bohm effect serves for illustration. 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. (Other experiments also use geometric setups where Ω_0 is multiply 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 (364) can not be used. Sir Michael V. Berry [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 and the asymptotic form of this wavefunction provides a good explanation of the change of the intensity pattern due to the change of the magnetic field.

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 given as

$$A_\phi = \frac{\Phi_B}{2\pi r} , \quad A_r = A_z = 0 . \quad (370)$$

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

$$H = \frac{1}{2m} \left(\frac{\hbar}{i} \frac{1}{a} \frac{\partial}{\partial \phi} - qA_\phi \right)^2 = -\frac{\hbar^2}{2ma^2} \left(\frac{\partial}{\partial \phi} - \frac{iq}{\hbar} \Phi_B \right)^2 \quad (371)$$

$$= -\frac{\hbar^2}{2ma^2} \left(\frac{\partial}{\partial \phi} - i \frac{\Phi_B}{\Phi_0} \right)^2 . \quad (372)$$

The solution of the eigenvalue problem of H is provided by

$$E = \frac{\hbar^2 C^2}{2ma^2} , \quad (373)$$

and

$$\psi(E; \varphi) = \frac{1}{\sqrt{2\pi}} \exp \left(i \left[C + \frac{\Phi_B}{\Phi_0} \right] \varphi \right), \quad (374)$$

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

$$C + \frac{\Phi_B}{\Phi_0} = n \in \mathbb{Z}. \quad (375)$$

The eigenenergies are then

$$E_n = \frac{\hbar^2}{2ma^2} \left(n - \frac{\Phi_B}{\Phi_0} \right)^2, \quad (376)$$

with the eigenfunctions,

$$\psi_n(\varphi) = \frac{1}{\sqrt{2\pi}} e^{in\varphi}. \quad (377)$$

5.7 Flux quantization in type-I superconductors

Due to the Meissner–Ochsenfeld effect, the magnetic field is excluded from a type-I superconductor (perfect diamagnet). Let's consider a superconducting ring placed into a magnetic field perpendicular 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 flux of the magnetic field enclosed by the superconducting ring is quantized*.

In order to understand the phenomenon we have to use the specific properties of type-I superconductors. Since in the superconductor the magnetic field is zero, the Maxwell equation,

$$\nabla \times \vec{B} = \mu_0 \left(\vec{j} + \varepsilon_0 \frac{\partial \vec{E}}{\partial t} \right), \quad (378)$$

implies that for stationary fields the current density $\vec{j}$ is also zero in the superconductor. In fact, a current flows only near the surface of the superconductor within the London penetration depth. In the superconducting phase the charge density is homogeneous, so the wavefunction of the Cooper pairs can be written as

$$\psi(\vec{r}) = \sqrt{\varrho} e^{i\vartheta(\vec{r})}, \quad (379)$$

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

$$\vec{j}(\vec{r}) = \frac{\hbar q}{m} \left(\vec{\nabla} \vartheta(\vec{r}) - \frac{q}{\hbar} \vec{A}(\vec{r}) \right) \varrho. \quad (380)$$

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

$$\vec{\nabla} \vartheta(\vec{r}) = \frac{q}{\hbar} \vec{A}(\vec{r}). \quad (381)$$

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 ,

$$e^{i\vartheta(\vec{r})} = e^{i\vartheta(\vec{r}) + \Delta\vartheta} \rightarrow \Delta\vartheta = 2\pi n, \quad (382)$$

where

$$\Delta\vartheta = \oint \vec{\nabla} \vartheta(\vec{s}) d\vec{s} = \frac{q}{\hbar} \oint \vec{A}(\vec{s}) d\vec{s} = \frac{q}{\hbar} \Phi_B, \quad (383)$$

therefore,

$$\Phi_B = \frac{h}{q} n . \quad (384)$$

Since the charge of the Cooper pairs is $q = -2e$, the magnetic flux enclosed by the type-I superconductor ring is a multiple 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 performs a uniform circular motion in the plane perpendicular to the magnetic field with the cyclotron frequency

$$\omega_c = \frac{qB}{m} . \quad (385)$$

Choosing a magnetic field parallel to the z axis, $\vec{B} = (0, 0, B)$, Newton's second law of motion reads as

$$m \frac{d\vec{v}(t)}{dt} = q \vec{v} \times \vec{B} \rightarrow (\dot{v}_x, \dot{v}_y, 0) = \omega_c (v_y, -v_x, 0) . \quad (386)$$

By fixing the position of the particle for $t = 0$ at $(R, 0, 0)$, the solution is given by

$$\vec{r}(t) = R(\cos \omega_c t, -\sin \omega_c t, 0) , \quad (387)$$

$$\vec{v}(t) = \frac{d\vec{r}(t)}{dt} = R\omega_c (-\sin \omega_c t, -\cos \omega_c t, 0) , \quad (388)$$

$$\vec{a}(t) = \frac{d\vec{v}(t)}{dt} = R\omega_c^2 (-\cos \omega_c t, \sin \omega_c t, 0) , \quad (389)$$

where we supposed $B, q > 0$. The energy of the particle is

$$E = \frac{1}{2} m R^2 \omega_c^2 .$$

Using symmetric gauge for the vector potential,

$$\vec{A}(t) = \left(-\frac{1}{2} B y, \frac{1}{2} B x, 0 \right) \quad (390)$$

$$= \frac{BR}{2} (\sin \omega_c t, \cos \omega_c t, 0) , \quad (391)$$

the canonical momentum can be expressed as

$$\vec{p}(t) = m\vec{v}(t) + q\vec{A}(t) = \frac{1}{2} m R \omega_c (-\sin \omega_c t, -\cos \omega_c t, 0) . \quad (392)$$

Employing the *Bohr-Sommerfeld quantization principle* ,

$$\oint \vec{p} d\vec{\ell} = \int_0^{\frac{2\pi}{\omega_c}} \vec{p}(t) \vec{v}(t) dt = \pi m R^2 \omega_c = n h \Rightarrow \frac{1}{2} m R^2 \omega_c = n \hbar \Rightarrow E_n = n \hbar \omega_c . \quad (393)$$

It is tempting that by solving the Schrödinger equation the planar motion of the charged particle also leads to quantized energy levels. In symmetric gauge the kinetic momentum is given by

$$\vec{K} = (K_x, K_y, K_z) = \left(p_x - \frac{eB}{2} y, p_y + \frac{eB}{2} x, p_z \right) \quad (394)$$

$$= \left(p_x - \frac{m\omega_c}{2} y, p_y + \frac{m\omega_c}{2} x, p_z \right) . \quad (395)$$

(Note that for electrons $q = -e$!), It is easy to prove that the commutator of K_x and K_y is

$$[K_x, K_y] = -i\hbar eB = \frac{\hbar}{i}m\omega_c, \quad (396)$$

as we learned already. The eigenfunctions of the Hamiltonian,

$$H = \frac{1}{2m} (K_x^2 + K_y^2) + \frac{p_z^2}{2m}, \quad (397)$$

can be written as

$$\psi(\vec{r}) = \varphi_k(x, y) e^{ikz}, \quad (398)$$

where k is an arbitrary wavenumber and $\varphi_k(x, y)$ satisfies the equation,

$$\frac{1}{2m} (K_x^2 + K_y^2) \varphi_k(x, y) = \left(E - \frac{\hbar^2 k^2}{2m} \right) \varphi_k(x, y). \quad (399)$$

Now we can introduce the operators,

$$X = \frac{K_y}{eB} = \frac{K_y}{m\omega_c} \quad \text{and} \quad P = K_x. \quad (400)$$

From Eq. (396) the following commutation relation follows,

$$[P, X] = \frac{\hbar}{i}, \quad (401)$$

and the eigenvalue equation (399) transforms to

$$\left(\frac{P^2}{2m} + \frac{1}{2}m\omega_c^2 X^2 \right) \varphi_k(x, y) = \left(E - \frac{\hbar^2 k^2}{2m} \right) \varphi_k(x, y). \quad (402)$$

This is analogous with the Schrödinger equation of a linear harmonic oscillator. We can then introduce the ladder operators,

$$a = \sqrt{\frac{m\omega_c}{2\hbar}} \left(X + \frac{i}{m\omega_c} P \right) \quad (403)$$

$$= \frac{1}{\sqrt{2}\ell_B} \frac{1}{m\omega_c} (K_x + iK_y) \quad (404)$$

and

$$a^+ = \sqrt{\frac{m\omega_c}{2\hbar}} \left(X - \frac{i}{m\omega_c} P \right) \quad (405)$$

$$= \frac{1}{\sqrt{2}\ell_B} \frac{1}{m\omega_c} (K_x - iK_y), \quad (406)$$

where

$$\ell_B = \sqrt{\frac{\hbar}{m\omega_c}} = \sqrt{\frac{\hbar}{eB}} \quad (407)$$

is the so-called magnetic length. By substituting $\hbar = 1.054571817 \times 10^{-34}$ Js and $e = 1.60217663 \times 10^{-19}$ C we get

$$\ell_B = \frac{25.66}{\sqrt{B [T]}} \text{nm}, \quad (408)$$

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 be expressed in terms of the ladder operators,

$$H = \frac{P^2}{2m} + \frac{1}{2}m\omega_c^2 X^2 + \frac{p_z^2}{2m} = \hbar\omega_c \left(a^+ a + \frac{1}{2} \right) + \frac{p_z^2}{2m} . \quad (409)$$

Following the algebraic derivation of the spectrum of the harmonic oscillator (see Quantum Mechanics 1), the eigenenergies of the system are

$$E_{n,k} = \hbar\omega_c \left(n + \frac{1}{2} \right) + \frac{\hbar^2 k^2}{2m} , \quad (410)$$

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*,

$$\vec{A} = (-By, 0, 0) , \quad (411)$$

which leads to the wavefunction (see Practical course),

$$\psi_{n,k_x,k_z}(x, y, z) \sim \exp(ik_z z) \exp(ik_x x) \exp\left(-\frac{1}{2\ell_B^2} (y - k_x \ell_B^2)^2\right) H_n\left(\frac{y - k_x \ell_B^2}{\ell_B}\right) , \quad (412)$$

where H_n denotes the Hermite polynomials. From here we can see that the characteristic decay constant of the wavefunction in the y direction is $\sqrt{2}\ell_B$. Since the energy doesn't depend on k_x , the *Landau levels are degenerate*. If the planar motion of the electron is confined to finite lengths (L_x, L_y) , k_x becomes quantized. Supposing that the wavefunctions takes the same value at $x = 0$ and $x = L_x$ (Born-Karman boundary condition):

$$k_x = \frac{2\pi}{L_x} m \quad (m \in \mathbb{N}) . \quad (413)$$

Because the distance in y direction between the Landau orbits is $k_x \ell_B^2$, only a finite number M of these orbits can exist on the length L_y ,

$$\underbrace{\frac{2\pi}{L_x} M \ell_B^2}_{\max k_x} = L_y \longrightarrow M = \frac{\ell_x \ell_y}{2\pi \ell_B^2} = \frac{AeB}{h} = \frac{\Phi}{\Phi_0} , \quad (414)$$

where A is the surface of the sample and Φ is the flux of the magnetic field. Clearly, M is the degeneracy of a Landau level. We can interpret this result such that a Landau orbit stands for a unit flux, therefore, the number of the Landau orbits M in any Landau level is proportional with the magnetic flux.

Within quasiclassical approximation, we consider a Landau state as a motion along a circle of radius $r \simeq \sqrt{2}\ell_B$ and we get for the magnetic flux on this circle,

$$\Phi = 2\pi \ell_B^2 B = \frac{hB}{m\omega_c} = \frac{h}{e} = \Phi_0 . \quad (415)$$

A Classical electrodynamics

A.1 Maxwell equations

The Lorentz force acting on a charged particle in electromagnetic fields:

$$\vec{F} = q \left(\vec{E} + \vec{v} \times \vec{B} \right), \quad (416)$$

where $\vec{E}$ is the electric field and $\vec{B}$ is the magnetic field (B-field).

Electrodynamics in presence of matter

$$\rho_{\text{tot}} = \rho_{\text{f}} + \rho_{\text{b}}, \quad \rho_{\text{b}} = -\vec{\nabla} \cdot \vec{P}, \quad (417)$$

$$\vec{j}_{\text{tot}} = \vec{j}_{\text{f}} + \vec{j}_{\text{b}}, \quad \vec{j}_{\text{b}} = \vec{\nabla} \times \vec{M} + \partial_t \vec{P}, \quad (418)$$

where ρ_{tot} , ρ_{f} , and ρ_{b} stand for the total, free and bound electric charge densities, while $\vec{j}_{\text{tot}}$, $\vec{j}_{\text{f}}$, and $\vec{j}_{\text{b}}$ 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

$$\vec{D} = \varepsilon_0 \vec{E} + \vec{P}, \quad (419)$$

where ε_0 is the vacuum permittivity. Relationship between the magnetic H-field $\vec{H}$, B-field $\vec{B}$ and the magnetisation density $\vec{M}$:

$$\vec{H} = \frac{\vec{B}}{\mu_0} - \vec{M}. \quad (420)$$

Maxwell equations:

$$\vec{\nabla} \cdot \vec{E} = \frac{\rho_{\text{tot}}}{\varepsilon_0} = \frac{1}{\varepsilon_0} \left(\rho_{\text{f}} - \vec{\nabla} \cdot \vec{P} \right) \rightarrow \vec{\nabla} \cdot \vec{D} = \rho_{\text{f}}, \quad (421)$$

$$\vec{\nabla} \times \vec{E} = -\partial_t \vec{B}, \quad (422)$$

$$\vec{\nabla} \cdot \vec{B} = 0, \quad (423)$$

$$\vec{\nabla} \times \vec{B} = \mu_0 \vec{j}_{\text{tot}} = \mu_0 \left(\vec{j}_{\text{f}} + \vec{\nabla} \times \vec{M} + \partial_t \vec{P} + \varepsilon_0 \partial_t \vec{E} \right) \rightarrow \vec{\nabla} \times \vec{H} = \vec{j}_{\text{f}} + \partial_t \vec{D}. \quad (424)$$

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

$$\vec{\nabla} \cdot \vec{E} = \frac{\rho}{\varepsilon_0}, \quad (425)$$

$$\vec{\nabla} \times \vec{E} = -\partial_t \vec{B}, \quad (426)$$

$$\vec{\nabla} \cdot \vec{B} = 0, \quad (427)$$

$$\vec{\nabla} \times \vec{B} = \mu_0 \left(\vec{j} + \varepsilon_0 \partial_t \vec{E} \right). \quad (428)$$

A.2 Scalar and vector potentials, gauge transformations

Based on equation (427), we can introduce a vector potential $\vec{A}(\vec{r}, t)$ such that

$$\vec{B} = \vec{\nabla} \times \vec{A}. \quad (429)$$

By using equation (426),

$$\vec{\nabla} \times \vec{E} + \partial_t \vec{B} = \vec{\nabla} \times (\vec{E} + \partial_t \vec{A}) = 0, \quad (430)$$

thus a scalar potential $\phi(\vec{r}, t)$ can be introduced that satisfy

$$-\vec{\nabla} \phi = \vec{E} + \partial_t \vec{A} \rightarrow \vec{E} = -\vec{\nabla} \phi - \partial_t \vec{A}. \quad (431)$$

From equations (425) and (428) we obtain differential equations for the potentials,

$$\Delta \phi + \partial_t \vec{\nabla} \vec{A} = -\frac{\rho}{\varepsilon_0}, \quad (432)$$

$$\Delta \vec{A} - \vec{\nabla}(\vec{\nabla} \vec{A}) = -\mu_0 \left(\vec{j} - \varepsilon_0 \partial_t \vec{\nabla} \phi - \varepsilon_0 \partial_t^2 \vec{A} \right) = -\mu_0 \vec{j} + \frac{1}{c^2} \partial_t \vec{\nabla} \phi + \frac{1}{c^2} \partial_t^2 \vec{A}, \quad (433)$$

where $c = 1/\sqrt{\varepsilon_0 \mu_0}$ is the velocity of light in vacuum.

Using a $\Lambda(\vec{r}, t)$ gauge field, the potentials can be transformed such that the fields remain invariant:

$$\left. \begin{array}{l} \vec{A}' = \vec{A} + \vec{\nabla} \Lambda \\ \phi' = \phi - \partial_t \Lambda \end{array} \right\} \implies \begin{array}{l} \vec{E}' = \vec{E} \\ \vec{B}' = \vec{B} \end{array}. \quad (434)$$

In that case the scalar and vector potentials $(\phi', \vec{A}')$ and $(\phi, \vec{A})$ are said to be equivalent or, in other words, they belong to the same gauge orbit.

A Coulomb gauge is defined by $\vec{\nabla} \vec{A}' = 0$. This implies

$$0 = \vec{\nabla} \vec{A} + \Delta \Lambda \rightarrow \Delta \Lambda = -\vec{\nabla} \vec{A} \quad (435)$$

and for the scalar potential

$$\Delta \phi' = -\frac{\rho}{\varepsilon_0} \rightarrow \phi'(\vec{r}, t) = \frac{1}{4\pi\varepsilon_0} \int d^3r' \frac{\rho(\vec{r}', t)}{|\vec{r} - \vec{r}'|}, \quad (436)$$

where we fixed a space independent constant to zero. The potentials fulfill the equation,

$$\Delta \vec{A}' - \frac{1}{c^2} \partial_t^2 \vec{A}' = -\mu_0 \vec{j} + \frac{1}{c^2} \partial_t \vec{\nabla} \phi'. \quad (437)$$

Taking the divergence of the above expressions,

$$\text{div } \vec{j} - \varepsilon_0 \partial_t \Delta \phi' = 0 \rightarrow \text{div } \vec{j} + \partial_t \rho = 0, \quad (438)$$

which is the continuity equation for the charge current and density. The vector field $\vec{j}(\vec{r}, t)$ can be divided into longitudinal and transversal components,

$$\vec{j} = \vec{j}_l + \vec{j}_t, \quad (439)$$

where

$$\vec{\nabla} \vec{j}_t = 0 \quad \text{and} \quad \vec{\nabla} \times \vec{j}_l = 0. \quad (440)$$

Since the left-hand side of equation (437) is purely transversal, while $\vec{\nabla} \phi$ is purely longitudinal, (437) can be rewritten as

$$\Delta \vec{A}' - \frac{1}{c^2} \partial_t^2 \vec{A}' = -\mu_0 \vec{j}_t. \quad (441)$$

The Lorenz gauge is defined by

$$\vec{\nabla} \vec{A}' + \frac{1}{c^2} \partial_t \phi' = 0.$$

Then we get the following differential equations for the potentials,

$$\Delta \phi' - \frac{1}{c^2} \partial_t^2 \phi' = -\frac{\rho}{\varepsilon_0}, \quad (442)$$

and

$$\Delta \vec{A}' - \frac{1}{c^2} \partial_t^2 \vec{A}' = -\mu_0 \vec{j}. \quad (443)$$

The above equations can be written into Lorentz covariant form:

$$A^\mu = (\phi/c, A_i) \quad (444)$$

$$\partial_\mu = (\partial_t/c, \partial_i) \quad (445)$$

$$j^\mu = (c\rho, j_i) \quad (446)$$

$$\partial_\mu \partial^\mu = \frac{1}{c^2} - \Delta = -\square \quad (447)$$

$$\Downarrow$$

$$\square A^\mu = \mu_0 j^\mu. \quad (448)$$

A.3 Lagrangian formalism

We define the Lagrange function in presence of electric and magnetic fields as

$$L(\vec{r}, \dot{\vec{r}}) = -mc^2 \sqrt{1 - \frac{\dot{\vec{r}}^2}{c^2}} + q\vec{A}(\vec{r}, t) \cdot \dot{\vec{r}} - q\phi(\vec{r}, t). \quad (449)$$

The conjugated *canonical momentum* is then given by

$$\begin{aligned} \vec{p} &= \frac{\partial L(\vec{r}, \dot{\vec{r}})}{\partial \dot{\vec{r}}} = -\frac{mc^2 \left(-2 \frac{\dot{\vec{r}}}{c^2} \right)}{2\sqrt{1 - \frac{\dot{\vec{r}}^2}{c^2}}} + q\vec{A}(\vec{r}, t) = \\ &= \frac{m\dot{\vec{r}}}{\sqrt{1 - \frac{\dot{\vec{r}}^2}{c^2}}} + q\vec{A}(\vec{r}, t) = \vec{K} + q\vec{A}(\vec{r}, t), \end{aligned} \quad (450)$$

where $\vec{K}$ is the so called *kinetic momentum*,

$$\vec{K} = \frac{m\dot{\vec{r}}}{\sqrt{1 - \frac{\dot{\vec{r}}^2}{c^2}}} = \vec{p} - q\vec{A}. \quad (451)$$

Euler-Lagrange equation of motion:

$$\frac{\partial L(\vec{r}, \dot{\vec{r}})}{\partial \vec{r}} - \frac{d}{dt} \frac{\partial L(\vec{r}, \dot{\vec{r}})}{\partial \dot{\vec{r}}} = 0 \quad (452)$$

$$\Downarrow$$

$$\frac{d\vec{p}}{dt} = \frac{\partial L(\vec{r}, \dot{\vec{r}})}{\partial \dot{\vec{r}}} = q(\vec{\nabla} \circ \vec{A})\dot{\vec{r}} - q\vec{\nabla}\phi, \quad (453)$$

where

$$(\vec{\nabla} \circ \vec{A})_{ij} = \partial_i A_j. \quad (454)$$

Using the vector identity,

$$(\vec{a} \circ \vec{b})\vec{c} = \vec{c} \times (\vec{a} \times \vec{b}) + (\vec{c}\vec{a})\vec{b}, \quad (455)$$

we can proceed as

$$(\vec{\nabla} \circ \vec{A})\dot{\vec{r}} = \dot{\vec{r}} \times (\vec{\nabla} \times \vec{A}) + (\dot{\vec{r}} \cdot \vec{\nabla})\vec{A} = \dot{\vec{r}} \times \vec{B} + (\dot{\vec{r}} \cdot \vec{\nabla})\vec{A} \quad (456)$$

$$\Downarrow$$

$$\frac{d\vec{p}}{dt} = q(\dot{\vec{r}} \cdot \vec{\nabla})\vec{A} - q\vec{\nabla}\phi + q(\dot{\vec{r}} \times \vec{B}). \quad (457)$$

The substantial derivative of the vector potential is defined as

$$\frac{d\vec{A}}{dt} = \frac{\partial \vec{A}}{\partial t} + (\dot{\vec{r}} \cdot \vec{\nabla})\vec{A}, \quad (458)$$

by which we obtain

$$\frac{d\vec{p}}{dt} = q\frac{d\vec{A}}{dt} - q\frac{\partial \vec{A}}{\partial t} - q\vec{\nabla}\phi + q(\dot{\vec{r}} \times \vec{B}). \quad (459)$$

Now we can express the time derivative of the kinetic momentum,

$$\frac{d\vec{K}}{dt} = -q\frac{\partial \vec{A}}{\partial t} - q\vec{\nabla}\phi + q(\dot{\vec{r}} \times \vec{B}) = q\vec{E} + q(\dot{\vec{r}} \times \vec{B}), \quad (460)$$

which is the Lorentz force.

A.4 Hamiltonian formalism

The Hamilton function is related to the Lagrange function as

$$\begin{aligned} H &= \dot{\vec{r}}\vec{p} - L(\vec{r}, \dot{\vec{r}}) \\ &= \dot{\vec{r}}\vec{K} + q\vec{A}\dot{\vec{r}} + mc^2\sqrt{1 - \frac{\dot{\vec{r}}^2}{c^2}} - q\vec{A}\dot{\vec{r}} + q\phi \\ &= \frac{m\dot{\vec{r}}^2}{\sqrt{1 - \frac{\dot{\vec{r}}^2}{c^2}}} + mc^2\sqrt{1 - \frac{\dot{\vec{r}}^2}{c^2}} + q\phi = \frac{mc^2}{\sqrt{1 - \frac{\dot{\vec{r}}^2}{c^2}}} + q\phi. \end{aligned} \quad (461)$$

From the relationship,

$$\frac{m^2 c^4}{1 - \frac{\dot{\vec{r}}^2}{c^2}} = m^2 c^2 \left(c^2 + \frac{\dot{\vec{r}}^2}{1 - \frac{\dot{\vec{r}}^2}{c^2}} \right) = \quad (462)$$

$$= m^2 c^4 + c^2 \vec{K}^2 = m^2 c^4 + c^2 (\vec{p} - q\vec{A})^2, \quad (463)$$

we obtain the well-known expression for the Hamilton function,

$$H(\vec{r}, \vec{p}) = \sqrt{(mc^2)^2 + c^2(\vec{p} - q\vec{A})^2} + q\phi . \quad (464)$$

In the non-relativistic limit,

$$\frac{(\vec{p} - q\vec{A})^2}{mc^2} \ll 1 , \quad (465)$$

therefore, we can approach the Hamiltonian by

$$H(\vec{r}, \vec{p}) = \frac{(\vec{p} - q\vec{A})^2}{2m} + q\phi , \quad (466)$$

where we dropped the rest energy mc^2 .

Hamiltonian equations of motion:

$$\frac{d\vec{r}}{dt} = \vec{v} = \frac{\partial H(\vec{r}, \vec{p})}{\partial \vec{p}} = \frac{\vec{p} - q\vec{A}}{m} = \frac{\vec{K}}{m} \quad (467)$$

and

$$\begin{aligned} \frac{d\vec{p}}{dt} &= -\frac{\partial H(\vec{r}, \vec{p})}{\partial \vec{r}} = q(\vec{\nabla} \circ \vec{A}) \frac{\vec{p} - q\vec{A}}{m} - q\vec{\nabla}\phi \\ &= q(\vec{\nabla} \circ \vec{A})\dot{\vec{r}} - q\vec{\nabla}\phi = q(\dot{\vec{r}} \times \vec{B}) + q(\dot{\vec{r}}\vec{\nabla})\vec{A} - q\vec{\nabla}\phi \\ &= q(\dot{\vec{r}} \times \vec{B}) + q\frac{d\vec{A}}{dt} - q\frac{\partial \vec{A}}{\partial t} - q\vec{\nabla}\phi . \end{aligned} \quad (468)$$

From this we again get the Lorentz force as the substantial derivative of kinetic momentum,

$$\begin{aligned} \frac{d\vec{K}}{dt} &= m\frac{d^2\vec{r}}{dt^2} = q(-\vec{\nabla}\phi - \frac{\partial \vec{A}}{\partial t}) + q(\dot{\vec{r}} \times \vec{B}) \\ &= q\vec{E} + q(\dot{\vec{r}} \times \vec{B}) . \end{aligned} \quad (469)$$