TFY4205 :

Quantum Mechanics II

Lecture Notes J.L.

(written originally in 2016)

CHAPTER 6

GENERAL FORMULATION OF QUANTUM MECHANICS

Introductory QM usually utilizes a position-representation where one works with wavefunctions $\psi = \psi(\vec{r})$. This is a special case of a more general theory. The latter is important because some QM systems cannot be treated by wavefunctions in position-space, such as the spin degree of freedom.

6.1 Dirac's bra-ket notation

New formulation: a QM state is described by a state-vector $|\psi\rangle$ in a complex linear vector space $\mathcal{H}$.

$\mathcal{H}$ is known as a Hilbert-space.

There are different notations used for the state-vector: stationary states in a Coulomb-field may be denoted $|n l m\rangle$.

$\mathcal{H}$ may have finite or infinite dimension, usually the latter. We need infinite Hilbert spaces to represent a vector describing a continuous variable (like position).

On the other hand, it would suffice with a 2-dimensional Hilbert space to describe the spin of one particle (spin 1/2): there are just two eigenvalues $\pm \hbar/2$.

The state-vector may depend on time. In what follows, we usually suppress the t-dependence notation-wise unless it is important.

For any state $|a\rangle$ in $\mathcal{H}$, there is assigned a dual vector $\langle a|$ in a dual vector-space. The relation is that the scalar-product $\langle a|\cdot|b\rangle \equiv \langle a|b\rangle$ is defined as a complex number with the property $\langle a|b\rangle = \langle b|a\rangle^*$.

Two states $|a\rangle$ and $|b\rangle$ are orthogonal if $\langle a|b\rangle = 0$.

This type of notation is due to Dirac.

$|\ldots\rangle \equiv$ ket, $\langle\ldots| \equiv$ bra, $\langle \text{bra} | \text{ket} \rangle$.

If a vector is multiplied by a number c, the corresponding dual vector must be multiplied by c^*. Let $|a'\rangle = c|a\rangle$.

It follows that:

$\langle b|a'\rangle = c\langle b|a\rangle$ and thus:

$$\langle a'|b\rangle = \langle b|a'\rangle^* = c^*\langle b|a\rangle^* = c^*\langle a|b\rangle$$

$$\Rightarrow \quad \underline{\langle a'| = c^*\langle a|}.$$

6.2. Completeness

In an n-dimensional vector space, we may choose n linearly independent vectors $|1\rangle, |2\rangle, \ldots |n\rangle$ as basis vectors and expand an arbitrary vector $|\psi\rangle$ in these:

$$|\psi\rangle = \sum_{k=1}^{n} c_k |k\rangle$$

with complex numbers as vector components.

Assume for simplicity that these basis vectors are orthonormal: $\langle k|m\rangle = \delta_{km}$. We allow the dimension n to not necessarily be finite.

It follows that $c_m = \langle m|\psi\rangle$, so we may write:

$$|\psi\rangle = \sum_k \langle k|\psi\rangle |k\rangle .$$

This can be written as:

$$|\psi\rangle = \sum_k |k\rangle\langle k| \cdot |\psi\rangle$$

$$\Rightarrow \sum_k |k\rangle\langle k| = 1 .$$

This is the <u>completeness relation</u> which is very useful.

The corresponding relation for usual vectors can be written in a similar fashion:

$$\sum_k (\vec{e}_k)\vec{e}_k \cdot = (\vec{e}_x)\vec{e}_x \cdot + (\vec{e}_y)\vec{e}_y \cdot + (\vec{e}_z)\vec{e}_z \cdot = 1$$

Using this on a vector $\vec{A}$ gives the identity:

$$\vec{e}_x A_x + \vec{e}_y A_y + \vec{e}_z A_z = \vec{A} .$$

$|a\rangle\langle b|$: outer product of the vectors $|a\rangle$ and $|b\rangle$.
This is in general an operator.

$\langle a|b\rangle$: inner product — " —
This is a complex number.

For instance, $|k\rangle\langle k|$ is a projection operator that projects a vector  onto the $|k\rangle$-axis.

Some basis vector sets $\{|k\rangle\}$ are such that k takes on continuous values. Then, we replace the summation with integration and also a delta function normalization:

$$\langle k|k'\rangle = \delta(k-k').$$

The expansion in basis vectors takes the form

$$|\psi\rangle = \int dk\, c(k)\,|k\rangle$$

Multiplying from the left with $\langle k'|$, we find the expansion coefficients:

$$\langle k'|\psi\rangle = \int dk\, c(k)\langle k'|k\rangle = \int dk\, c(k)\delta(k'-k) = c(k').$$

We can thus write $|\psi\rangle = \int dk\, \langle k|\psi\rangle |k\rangle$.

The completeness relation for continuous variables then takes the form $\int dk\, |k\rangle\langle k| = 1$.

Norm. The length squared for $|f\rangle$ is (as in the case of usual vectors) defined as the scalar product of $|f\rangle$ with itself: $\langle f|f\rangle$. By using the completeness relation we have derived, it follows that

$$\langle f|f\rangle = \sum_k \langle f|k\rangle\langle k|f\rangle = \sum_k |\langle k|f\rangle|^2$$

since $\langle f|k\rangle = \langle k|f\rangle^*$. Thus, $\langle f|f\rangle$ is always real and non-negative. The norm $\|f\|$ is defined as

$$\|f\| = \sqrt{\langle f|f\rangle} \geq 0.$$

6.3 Operators and eigenvectors

An operator in Hilbert-space is an image of $\mathcal{H}$ on itself, since the operator A assigns a vector $|c\rangle$ to any vector $|a\rangle$: $A|a\rangle = |c\rangle$.

The adjoint operator $A^\dagger$ is defined by

$$\langle a|A^\dagger|b\rangle = \langle b|A|a\rangle^* \qquad (\dagger)$$

which must hold for all vectors $|a\rangle$ and $|b\rangle$ in $\mathcal{H}$.

By setting $A|a\rangle = |c\rangle$, we may write $(\dagger)$ as:

$\langle a|A^\dagger|b\rangle = \langle b|c\rangle^* = \langle c|b\rangle$. It then follows that $\langle c| = \langle a|A^\dagger$. We have shown that the dual vector of $A|a\rangle$ is $\langle a|A^\dagger$.

The following properties of the adjoint operation follow from our definitions so far (try to prove them yourself!)

(i) $(A^\dagger)^\dagger = A$

(ii) $(\alpha A)^\dagger = \alpha^* A^\dagger$ where α is a constant

(iii) $(AB)^\dagger = B^\dagger A^\dagger$

An operator is self-adjoint or Hermitian if $A^\dagger = A$.

It follows that for such operators,

$$\langle a|A|a\rangle = \langle a|A|a\rangle^* \Rightarrow \langle a|A|a\rangle \in \mathbb{R}.$$

We define an eigenvector of A to be $|a\rangle$ where:

$A|a\rangle = \lambda_a |a\rangle$. The number λ_a is the eigenvalue.

The collection of eigenvalues for the operator A are known as the spectrum of A.

Eigenvalues of hermitian operators A are real.

Since $A|a\rangle = \lambda_a|a\rangle$, we get $\lambda_a = \dfrac{\langle a|A|a\rangle}{\langle a|a\rangle} \in \mathbb{R}$.

Physical observables are represented by Hermitian operators.

The set of eigenvectors $\{|a\rangle\}$ for an operator corresponding to a physical quantity is assumed to be a complete set

$\Rightarrow$ the eigenvectors may be used as basis vectors.

The total state vector may be expanded as:

$|\psi\rangle = \int dx' \langle x'|\psi\rangle |x'\rangle$. The complex number $\langle x'|\psi\rangle$ is the contribution to the state vector $|\psi\rangle$ from position x'.

Hence, this is in fact nothing but the familiar wavefunction in position space: $\psi(x') = \langle x'|\psi\rangle$.

$\Rightarrow$ $\langle x|\psi\rangle$ are the components of $|\psi\rangle$ with the basis vectors $|x\rangle$.

If x took discrete values, we could have written:

$|\psi\rangle = \begin{bmatrix} \psi(x_1) \\ \psi(x_2) \\ \vdots \end{bmatrix}$. However, since x is a continuous variable we must δ-function normalize the basis vectors: $\langle x''|x'\rangle = \delta(x''-x')$.

The scalar product between $|\psi_1\rangle$ and $|\psi_2\rangle$ may be written as

$$\langle\psi_1|\psi_2\rangle = \int dx \langle\psi_1|x\rangle\langle x|\psi_2\rangle = \int dx \langle x|\psi_1\rangle^* \langle x|\psi_2\rangle = \int dx \psi_1^*(x)\psi_2(x)$$

where we used the completeness relation $\int dx\, |x\rangle\langle x| = 1$.

Let us also consider how to work with operators in this representation. The expectation value of $\hat{F}$ may be written as:

$$\langle \psi | \hat{F} | \psi \rangle = \int dx'' \int dx' \langle \psi | x'' \rangle \langle x'' | \hat{F} | x' \rangle \langle x' | \psi \rangle$$

The first and last factor are wavefunctions, so it remains to clarify what the so-called matrix-elements $\langle x'' | \hat{F} | x' \rangle$ are.

If $\hat{F} = \hat{x}$, it is simple. We have:

$$\langle x'' | \hat{x} | x' \rangle = x' \langle x'' | x' \rangle = x' \delta(x'' - x').$$

More generally, if $\hat{F}$ is a function of $\hat{x}$ [$\hat{F} = F(\hat{x})$].

This follows for any power of $\hat{x}$ since $\hat{x}^n | x' \rangle = (x')^n | x' \rangle$, and thus it follows for any function $F(\hat{x})$ that may be expanded in powers of $\hat{x}$.

What if $\hat{F} = \hat{p}_x \equiv \hat{p}$? We know that $[\hat{x}, \hat{p}] = i\hbar$, and thus:

$$\langle x'' | \hat{x}\hat{p} - \hat{p}\hat{x} | x' \rangle = i\hbar \langle x'' | x' \rangle = i\hbar \delta(x'' - x')$$

The second term on the l.h.s. is

$$\langle x'' | -\hat{p}\hat{x} | x' \rangle = -x' \langle x'' | \hat{p} | x' \rangle$$

The first term on the l.h.s. may be computed as follows:

$$\langle x'' | \hat{x}\hat{p} | x' \rangle = \int dx_1 \langle x'' | \hat{x} | x_1 \rangle \langle x_1 | \hat{p} | x' \rangle$$

$$= \int dx_1 \, x_1 \, \delta(x'' - x_1) \langle x_1 | \hat{p} | x' \rangle = x'' \langle x'' | \hat{p} | x' \rangle$$

Combined, we then have $(x'' - x') \langle x'' | \hat{p} | x' \rangle = i\hbar \delta(x'' - x')$. (X)

An alternative way to show this is as follows.
(explicitly for the 2nd term)

First, note that if $\hat{A}|a\rangle = \lambda |a\rangle$, then $\langle a | \hat{A}^\dagger = \langle a | \lambda^*$.

This follows since $\langle a | \hat{A}^\dagger | b \rangle = \langle b | \hat{A} | a \rangle^* = \langle b | \lambda | a \rangle^*$

$$= \lambda^* \langle b | a \rangle^* = \lambda^* \langle a | b \rangle.$$

We then see that:

$$\langle x'' | \hat{p}\hat{x} | x' \rangle = \langle x' | (\hat{p}\hat{x})^\dagger | x'' \rangle^* = \langle x' | \hat{x}^\dagger \hat{p}^\dagger | x'' \rangle^*$$

But $\hat{x}$ and $\hat{p}$ must be Hermitian $\Rightarrow$ $= \langle x' | \hat{x}\hat{p} | x'' \rangle^*$

Since $\langle x' | \hat{x} = \langle x' | x'$, we get $\Rightarrow$ $= x' \langle x' | \hat{p} | x'' \rangle^*$

(Used that $\hat{p}^\dagger = \hat{p}$). $= x' \langle x'' | \hat{p} | x' \rangle$.

Back to equation (X) now. One can show that $x\delta'(x) = -\delta(x)$.

Let $x = x'' - x' \Rightarrow$ $(x'' - x') \frac{\partial}{\partial x''} \delta(x'' - x') = -\delta(x'' - x')$ [treat x' as a constant].

We can then rewrite $(x''-x')\langle x''|\hat{p}|x'\rangle = i\hbar\delta(x''-x')$ to

$\langle x''|\hat{p}|x'\rangle = \frac{\hbar}{i}\frac{\partial}{\partial x''}\delta(x''-x')$. This can be generalized to a power $\hat{p}^n \Rightarrow \langle x''|\hat{p}^n|x'\rangle = \left(\frac{\hbar}{i}\frac{\partial}{\partial x''}\right)^n \delta(x''-x')$.

Now, we know that for an arbitrary function $F(p)$ we have:

$$\langle x''|F(\hat{p})|x'\rangle = F\left(\frac{\hbar}{i}\frac{\partial}{\partial x''}\right)\delta(x''-x').$$

In the most general case, we then have:

$$\langle x''|F(\hat{p},\hat{x})|x'\rangle = F\left(\frac{\hbar}{i}\frac{\partial}{\partial x''}, x''\right)\delta(x''-x')$$

Now that we know this expectation value, we can finally go back and evaluate:

$$\begin{aligned}\langle\psi|\hat{F}|\psi\rangle &= \int dx'' \int dx' \langle\psi|x''\rangle\langle x''|\hat{F}|x'\rangle\langle x'|\psi\rangle \\ &= \int dx'' \int dx' \, \psi^*(x'') F\left(\frac{\hbar}{i}\frac{\partial}{\partial x''}, x''\right)\delta(x''-x')\psi(x') \\ &= \int dx' \, \psi^*(x') F\left(\frac{\hbar}{i}\frac{\partial}{\partial x'}, x'\right)\psi(x')\end{aligned}$$

In the end, we see that this is precisely how we used to evaluate expectation values in the wavefunction formulation.

Hence, there is consistency between the general formulation and the position representation.

We may also show that the two versions of the Schrödinger equation are consistent. The general formula is: $i\hbar \frac{\partial}{\partial t}|\psi\rangle = \hat{H}|\psi\rangle$ can be brought to the position-representation by multiplying with $\langle x|$ from the left side.

$$i\hbar \frac{\partial}{\partial t}\langle x|\psi\rangle = \langle x|\hat{H}|\psi\rangle = \int dx' \langle x|\hat{H}|x'\rangle\langle x'|\psi\rangle.$$

Here, $\langle x|\psi\rangle = \psi(x)$. For a Hamiltonian operator $\hat{H} = H(\hat{p}, \hat{x})$:

$$i\hbar \frac{\partial}{\partial t}\psi(x) = \int dx' H\left(\frac{\hbar}{i}\frac{\partial}{\partial x}, x\right)\delta(x-x')\psi(x') = H\left(\frac{\hbar}{i}\frac{\partial}{\partial x}, x\right)\psi(x).$$

Summarizing, we see that when the eigenvectors for the position operator are used as basis vectors, the general formulation of QM is reduced to wavemechanics in position space.

Momentum representation

In the same manner as above, the wavemechanics in momentum space is contained in the general formulation of QM. In this case, we want to use the eigenvectors $|p\rangle$ of the momentum operator $\hat{p}$ as basis vectors.

The wave function in the momentum representation is then

$\Phi(p) = \langle p|\psi\rangle$

Matrix mechanics

The matrix mechanics form of QM was actually the representation that was originally developed. Heisenberg did this in 1925, six months before Schrödinger developed the wave mechanics in position space.

In this case, the state vector is projected down on an arbitrary, discrete, orthonormal set of basis vectors $|k\rangle$, $k = 1, 2, \ldots$ A vector $|a\rangle$ may then be expanded as:

$|a\rangle = \sum_k a_k |k\rangle$ where $a_k = \langle k|a\rangle$. These coefficients can be visualized as components of a vector:

$$\vec{a} = \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ \vdots \end{bmatrix}$$ The scalar product $\langle b|a\rangle$ is then:

$$\langle b|a\rangle = \sum_k \langle b|k\rangle\langle k|a\rangle = \sum_k \langle k|b\rangle^* \langle k|a\rangle = \sum_k b_k^* a_k .$$

We see that $\vec{b}^{\dagger}\vec{a} = [b_1^* \; b_2^* \; \dots]\begin{bmatrix} a_1 \\ a_2 \\ \vdots \end{bmatrix} = \sum_k b_k^* a_k$.

With this representation, an operator $\hat{A}$ has an expectation value which is a matrix: $A_{mn} = \langle m|\hat{A}|n\rangle$.

If $|b\rangle = \hat{A}|a\rangle$, we then obtain that:

$\langle m|b\rangle = \langle m|\hat{A}|a\rangle = \sum_n \langle m|\hat{A}|n\rangle\langle n|a\rangle$, $m = 1, 2, \dots$

which can be written as $b_m = \sum_n A_{mn} a_n$. This is the definition of matrix multiplication: $\begin{bmatrix} b_1 \\ b_2 \\ \vdots \end{bmatrix} = \begin{bmatrix} A_{11} & A_{12} & A_{13} \dots \\ A_{21} & A_{22} \dots \\ \vdots \end{bmatrix}\begin{bmatrix} a_1 \\ a_2 \\ \vdots \end{bmatrix}$

<u>In effect</u>: the result of acting with the operator on the state-vector is represented by conventional matrix-mult.

This rep. is commonly used, and its most important application is on the stationary Schrödinger equation $\hat{H}|\psi\rangle = E|\psi\rangle$.

If we knew the eigenvectors $|n\rangle$ (usually we don't: the task is to find them), using them as basis vectors gives:

$\langle m|\hat{H}|n\rangle = E_n\langle m|n\rangle \Rightarrow H_{mn} = E_n\delta_{nm}$

where we used that $\hat{H}|n\rangle = E_n|n\rangle$. The matrix-rep. of $\hat{H}$ is diagonal.

Creation & annihilation operators

Hamilton-operator for a harmonic oscillator:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m}{2}\omega^2\hat{q}^2 \Rightarrow \frac{\hat{H}}{\hbar\omega} = \frac{\hat{p}^2}{2m\hbar\omega} + \frac{m\omega}{2\hbar}\hat{q}^2$$

is the dimensionless version since $[\hbar\omega]$ = energy. Instead of $\hat{q}$ and $\hat{p}$, we introduce new dimensionless operators:

$$a = \sqrt{\frac{m\omega}{2\hbar}}\,\hat{q} + \frac{i}{\sqrt{2m\hbar\omega}}\,\hat{p}, \quad a^+ = \sqrt{\frac{m\omega}{2\hbar}}\,\hat{q} - \frac{i}{\sqrt{2m\hbar\omega}}\,\hat{p}.$$

While $\hat{q}$ and $\hat{p}$ are Hermitian operators, a and a^+ are not ($a \neq a^+$).
It is also useful to note the inverse relations:

$$\hat{q} = \sqrt{\frac{\hbar}{2m\omega}}\,(a + a^+), \quad \hat{p} = i\sqrt{\frac{m\hbar\omega}{2}}\,(a^+ - a). \qquad (*)$$

Keep in mind that $[\hat{q}, \hat{p}] = i\hbar$. It follows from (*) that:

$$a^+a = \frac{m\omega}{2\hbar}\hat{q}^2 + \frac{1}{2m\hbar\omega}\hat{p}^2 + \frac{i}{2\hbar}(\hat{q}\hat{p} - \hat{p}\hat{q}) = \frac{\hat{H}}{\hbar\omega} - \frac{1}{2}.$$

Similarly, one shows that $aa^+ = \frac{\hat{H}}{\hbar\omega} + \frac{1}{2}$. Combining these results, one obtains $[a, a^+] = aa^+ - a^+a = 1$.

We have now found a very simple expression for $\hat{H}$:

$$\hat{H} = \hbar\omega\left(a^+a + \frac{1}{2}\right).$$

The next step is to find the eigenvalues of $\hat{H}$.

This amounts to finding the eigenvalues of $\hat{N} = a^\dagger a$, since $\hat{H} = (\hat{N} + \frac{1}{2})\hbar\omega$. The quantity $\hat{N}$ is known as the number operator, the reason being that the eigenvalues of $\hat{N}$ are $0, 1, 2, 3, \ldots$ We will now prove this.

The following relations will be useful to accomplish this task:

$$[\hat{N}, a] = a^\dagger a a - a a^\dagger a = (a^\dagger a - a a^\dagger)a = -a$$

$$[\hat{N}, a^\dagger] = a^\dagger a a^\dagger - a^\dagger a^\dagger a = a^\dagger (a a^\dagger - a^\dagger a) = a^\dagger$$

For reasons transpiring later, a is the annihilation - and $a^\dagger$ is the creation operator.

Energy spectrum

Let $|n\rangle$ be orthonormal eigenvectors for $\hat{H}$ with eigenvalues E_n: $\hat{H}|n\rangle = E_n|n\rangle$. To identify E_n, let us start with examining $a|n\rangle$. We know that $\hat{H}a - a\hat{H} = -\hbar\omega a$. Thus:

$$\hat{H} a|n\rangle = a\hat{H}|n\rangle - \hbar\omega a|n\rangle = (E_n - \hbar\omega)a|n\rangle$$

We may conclude that as long as $a|n\rangle \neq 0$, $a|n\rangle$ is an eigenvector of $\hat{H}$ with eigenvalue $E_n - \hbar\omega$.

This argument can be generalized : $a^2|n\rangle$ has eigenvalue $E_n - 2\hbar\omega$, and so forth. This cannot continue forever, since the energy of a harmonic oscillator cannot be negative.

To see this, recall that the norm of a vector is always ≥ 0, and we have $\| a|n\rangle \|^2 = \langle n|a^\dagger . a|n\rangle = \langle n| \frac{\hat{A}}{\hbar\omega} - \frac{1}{2}|n\rangle = \frac{E_n}{\hbar\omega} - \frac{1}{2}$.

Thus, $E_n \geq \frac{\hbar\omega}{2}$.

To guarantee this, there must be a final eigenvector $|0\rangle$ so that $a|0\rangle = 0$. The belonging energy to the state $|0\rangle$ must be the lowest energy available :

$$\hat{A}|0\rangle = \hbar\omega\left(a^\dagger a + \frac{1}{2}\right)|0\rangle = \frac{1}{2}\hbar\omega|0\rangle \Rightarrow E_0 = \frac{1}{2}\hbar\omega.$$

Now, since we could reach this state from any higher-energy state by moving downward with energy steps of $\hbar\omega$, we conclude that the general eigenvalues must be :

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega.$$

This is consistent with the known result, but we found it in a quite simple manner.

Eigenvectors

First, note that since $\hat{H} = (\hat{N} + \frac{1}{2})\hbar\omega$ and $E_n = (n + \frac{1}{2})\hbar\omega$, it follows that $\hat{N}|n\rangle = n|n\rangle$. The eigenvalue of $\hat{N}$ thus denotes how many energy quanta $\hbar\omega$ that the energy of the system exceeds the ground-state (lowest energy) by.

We have: $\hat{H}a|n\rangle = (n - \frac{1}{2})\hbar\omega a|n\rangle$. But since $(n - \frac{1}{2})\hbar\omega$ is the eigenvalue of the state $|n-1\rangle$, we must have $|n-1\rangle = C_n a|n\rangle$. Here, C_n is a constant which we may determine through normalization:

$$1 = \langle n-1|n-1\rangle = |C_n|^2 \langle n|a^\dagger a|n\rangle = |C_n|^2 \langle n|\hat{N}|n\rangle = |C_n|^2 n$$

$$\Rightarrow C_n = \frac{1}{\sqrt{n}} e^{i\delta}, \quad \delta \in \mathbb{R}.$$ We set $\delta = 0$ for now and get:

$$\boxed{a|n\rangle = \sqrt{n}\,|n-1\rangle}$$

However, if time-dependence is included in the notation $|n\rangle$ for stationary states, then $|n\rangle \propto e^{-iE_n t/\hbar} = e^{-i(n+\frac{1}{2})\omega t}$, so that δ becomes time-dependent:

$$a|n\rangle = e^{-i\omega t}\sqrt{n}\,|n-1\rangle.$$

To find $a^\dagger|n\rangle$, we operate on the above equation on both sides with $a^\dagger$ to find $e^{-i\omega t}\sqrt{n}\,a^\dagger|n-1\rangle = a^\dagger a|n\rangle = \hat{N}|n\rangle = n|n\rangle$:

$$a^\dagger|n\rangle = e^{i\omega t}\sqrt{n+1}\,|n+1\rangle.$$

The time-dep. is disregarded in the rest of this section ($t=0$)

$$\Rightarrow \boxed{a^\dagger |n\rangle = \sqrt{n+1}\,|n+1\rangle}$$

We can now understand why $a^\dagger$ is a creation operator: $|n\rangle \to |n+1\rangle$ (creates one quantum of energy) while a is the annihilation operator: $|n\rangle \to |n-1\rangle$. Any excited state $|n\rangle$ can then be obtained by acting on the ground-state $|0\rangle$ n times with $a^\dagger$: $|n\rangle = \frac{1}{\sqrt{n!}}(a^\dagger)^n |0\rangle$.

EXAMPLE Compute the expectation value of the potential energy of a harm. osc. in the n'th eigenstate.

$V = \frac{1}{2}m\omega^2 q^2 = \frac{1}{2}m\omega^2 \frac{\hbar}{2m\omega}(a+a^\dagger)^2$. Insert into $\langle n|V|n\rangle$:

$$\langle n| \tfrac{1}{4}\hbar\omega\,(aa + aa^\dagger + a^\dagger a + a^\dagger a^\dagger)|n\rangle = \langle n|\tfrac{1}{4}\hbar\omega\,(aa^\dagger + a^\dagger a)|n\rangle$$

$$\left(\langle n|aa|n\rangle = \langle n|a^\dagger a^\dagger|n\rangle = 0\right) \uparrow$$

$$= \tfrac{1}{4}\hbar\omega\left(\sqrt{n+1}\sqrt{n+1} + \sqrt{n}\sqrt{n}\right)$$

$$= \tfrac{1}{2}\hbar\omega\left(n + \tfrac{1}{2}\right) = \underline{\tfrac{1}{2}E_n}.$$

Average pot. energy = average kin. energy = 50% of total energy.

Note that, in comparison, if we wanted to compute $\langle q^2\rangle$ in the position representation, it would have been necessary to evaluate an integral with the square of a Hermite-polynomial: much more difficult!

Wavefunctions in position space

For completeness, let us show how the wavefunctions are recovered from the eigenstates $|n\rangle = \frac{1}{\sqrt{n!}}(a^\dagger)^n|0\rangle$.

We know that the starting point to find $\psi_n(q)$ (q = position coordinate) is $\psi_n(q) = \langle q|n\rangle$. Using the completeness-relation $\int dq'|q'\rangle\langle q'| = 1$, we obtain:

$$\langle q|n\rangle = \frac{1}{\sqrt{n!}}\int dq' \langle q|(a^\dagger)^n|q'\rangle\langle q'|0\rangle \qquad (*)$$

First, we evaluate:

$$\langle q|(a^\dagger)^n|q'\rangle = \langle q|\left(\sqrt{\frac{m\omega}{2\hbar}}\hat{q} - \frac{i}{\sqrt{2m\hbar\omega}}\hat{p}\right)^n|q'\rangle$$

$$= \left(\sqrt{\frac{m\omega}{2\hbar}}q - \frac{\hbar}{\sqrt{2m\omega\hbar}}\frac{d}{dq}\right)^n \delta(q-q')$$

Inserting this into (*) and using the δ-function, we get:

$$\langle q|n\rangle = \frac{1}{\sqrt{n!}}\left(\sqrt{\frac{m\omega}{2\hbar}}q - \sqrt{\frac{\hbar}{2m\omega}}\frac{d}{dq}\right)^n \langle q|0\rangle.$$

We see that the n'th wavefunction $\psi_n = \langle q|n\rangle$ is expressed via $\psi_0(q) = \langle q|0\rangle$. We determine $\psi_0(q)$ by the criterion that defined $|0\rangle$, namely $a|0\rangle = 0$. Projected onto $|q\rangle$, we get:

$$\langle q|a|0\rangle = \int dq' \langle q|a|q'\rangle\langle q'|0\rangle = 0$$

This yields:

$$\langle q|a|0\rangle = 0 = \int dq' \langle q| \sqrt{\frac{m\omega}{2\hbar}}\,\hat{q} + \frac{i}{\sqrt{2m\hbar\omega}}\,\hat{p}\,|q'\rangle\langle q'|0\rangle$$

$$= \left(\sqrt{\frac{m\omega}{2\hbar}}\,q + \frac{\hbar}{\sqrt{2m\hbar\omega}}\,\frac{d}{dq}\right)\langle q|0\rangle$$

$$\Rightarrow \frac{d}{dq}\langle q|0\rangle = -\frac{m\omega}{\hbar}\,q\,\langle q|0\rangle \quad \text{(diff. equation for } \langle q|0\rangle\text{)}.$$

Solving it gives: $\ln\langle q|0\rangle = -\frac{m\omega}{2\hbar}q^2 + C$ where C is a constant.

$$\Rightarrow \langle q|0\rangle = e^{C} e^{-m\omega q^2/2\hbar} = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} e^{-m\omega q^2/2\hbar}$$

where we determined the constant through normalization.

Now, we put this back into the expression for $\psi_n(q)$:

$$\psi_n = \left(\frac{m\omega}{\pi\hbar}\right)^{1/4} \frac{1}{\sqrt{2^n n!}} \left(x - \frac{d}{dx}\right)^n e^{-\frac{1}{2}x^2}$$

which is the correct result.

We mention in passing that we can now identify the matrix-representation for the operators by using the energy eigenvectors as a basis. From $a|n\rangle = \sqrt{n}\,|n-1\rangle$ and $a^\dagger|n\rangle = \sqrt{n+1}\,|n+1\rangle$, we see that:

$$a = \begin{pmatrix} 0 & \sqrt{1} & 0 & 0 & \cdots \\ 0 & 0 & \sqrt{2} & 0 & \cdots \\ 0 & 0 & 0 & \sqrt{3} & \cdots \\ 0 & 0 & 0 & 0 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \end{pmatrix}, \quad a^\dagger = \begin{pmatrix} 0 & 0 & 0 & 0 & \cdots \\ \sqrt{1} & 0 & 0 & 0 & \cdots \\ 0 & \sqrt{2} & 0 & 0 & \cdots \\ 0 & 0 & \sqrt{3} & 0 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \end{pmatrix}$$

Coherent states

The eigenstates of the annihilation operator a, $|\alpha\rangle$, are known as coherent states: $a|\alpha\rangle \propto |\alpha\rangle$. The reason for this is that the time-evolution of this state does not cause the state to spatially "diffuse" and become delocalized. Instead, the state's spatial distribution oscillates with a preserved width of the oscillation, as we now shall prove.

We expand the eigenstate of a in energy eigenstates: $|\alpha\rangle = \sum_{n=0}^{\infty} c_n |n\rangle$. We showed previously that:

$$a|\alpha\rangle = e^{-i\omega t} \sum_{n=0}^{\infty} c_n \sqrt{n}\, |n-1\rangle.$$

When $c_n\sqrt{n} = \alpha c_{n-1}$, where α is a constant, then $a|\alpha\rangle$ becomes proportional to $|\alpha\rangle$. Using this relation, we have $c_n = c_0 \alpha^n/\sqrt{n!}$, so that

$$|\alpha\rangle = c_0 \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}} |n\rangle = e^{-\frac{1}{2}|\alpha|^2} \sum_{n=0}^{\infty} \frac{\alpha^n}{\sqrt{n!}} |n\rangle$$

We here selected c_0 so that $\langle\alpha|\alpha\rangle = 1$ by using that

$$\sum_{n=0}^{\infty} \frac{(\alpha^*\alpha)^n}{n!} = e^{|\alpha|^2}.$$

These states then satisfy $a|\alpha\rangle = e^{-i\omega t}\alpha|\alpha\rangle$ and the expectation values for a and $a^\dagger$ are:

$$\langle\alpha|a|\alpha\rangle = \alpha e^{-i\omega t} \quad \text{and} \quad \langle\alpha|a^\dagger|\alpha\rangle = \langle\alpha|a|\alpha\rangle^* = \alpha^* e^{i\omega t}$$

To see why these are called coherent states, we want to see how these states behave spatially. Since

$\hat{q} = \sqrt{\frac{\hbar}{2m\omega}}(a+a^\dagger)$, we can show that:

$$|\langle q|\alpha\rangle|^2 = \sqrt{\frac{m\omega}{\pi\hbar}}\, e^{-m\omega[q-q_0\cos(\omega t-\theta)]^2/\hbar}$$

where $\alpha = |\alpha|e^{i\theta}$. This is the distribution of the spatial position, and we see that it describes an oscillating wavepacket which maintains a constant width as time evolves, hence the name coherent state.

Heisenberg-picture | 6.7.

So far, we've described quantum mechanical systems described by a state $|\psi\rangle$ which "moves" in a Hilbert-space where the axes (basis vectors) are time-independent. (Schrödinger-picture)

However, it is fully possible to take the perspective from a rotating coordinate-system. The simplest option is in fact that the rotation of the system is such that the state-vector is at rest: Heisenberg-picture.

Time-evolution

Let us first recap the time-evolution in the position-representation. Since the S-E is linear and 1st order in time, the propagator $U = U(\vec{r}, t; \vec{r}_0, t_0)$ determines the evolution of the wavefunction from t_0 to t:

$$\Psi(\vec{r}, t) = \int U(\vec{r}, t; \vec{r}_0, t_0)\, \Psi(\vec{r}_0, t_0)\, d^3 r_0$$

For a Hamilton-operator that does not depend explicitly on time, we can expand:

$$\Psi(\vec{r}, t) = \sum_n c_n \psi_n(\vec{r})\, e^{-iE_n t/\hbar} \quad \text{where } c_n \text{ are determined by:}$$

$$c_n e^{-iE_n t_0/\hbar} = \int \psi_n^*(\vec{r}_0)\, \Psi(\vec{r}_0, t_0)\, d^3 r_0 .$$

Inserting this c_n into the expression for Ψ gives:

$$U(\vec{r}, t; \vec{r}_0, t_0) = \sum_n \psi_n^*(\vec{r}_0)\, \psi_n(\vec{r})\, e^{-i(t-t_0)E_n/\hbar} .$$

If we instead have a continuous eigenvalue spectrum, the summation is replaced by an integral:

$$U(\vec{r}, t; \vec{r}_0, t_0) = \int_{-\infty}^{\infty} \psi_p^*(\vec{r}_0)\, \psi_p(\vec{r})\, e^{-i(t-t_0)E_p}\, dp$$

where p is the eigenvalue-parameter running from $-\infty$ to ∞.

To be concrete, consider the example of a free one-dimensionally moving particle:

$$\psi_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar}, \quad E_p = \frac{p^2}{2m}.$$

The propagator then turns into:

$$U(x,t,x_0,t_0) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} e^{ip(x-x_0)/\hbar} e^{-i(t-t_0)p^2/2m\hbar} \, dp$$

$$= \sqrt{\frac{m}{2\pi i\hbar(t-t_0)}} \, e^{im(x-x_0)^2/2\hbar(t-t_0)}.$$

Schrödinger- and Heisenberg pictures

Let us now turn to the general formulation. The time-evolution is given by $|\Psi,t\rangle = \hat{U}(t,t_0)|\Psi,t_0\rangle$. If the Hamilton-operator does not contain time explicitly:

$\hat{U}(t,t_0) = e^{-i(t-t_0)\hat{H}/\hbar}$ where the exponential operator should be interpreted via $e^{\hat{x}} = \sum_{n=0}^{\infty} \frac{\hat{x}^n}{n!}$.

We see that $|\Psi,t\rangle = e^{-i(t-t_0)\hat{H}/\hbar}|\Psi,t_0\rangle$ satisfies $i\frac{\partial}{\partial t}|\Psi,t\rangle = \hat{H}|\Psi,t\rangle$. The corresponding bra to the above ket is: $\langle\Psi,t| = \langle\Psi,t_0| e^{i(t-t_0)\hat{H}/\hbar}$.

Normalization is thus preserved: $\langle \Psi, t | \Psi, t \rangle = \langle \Psi, t_0 | \Psi, t_0 \rangle$

We may compute the expectation value of some physical quantity F at the time t in the usual way:

$$\langle F \rangle = \langle \Psi, t | \hat{F} | \Psi, t \rangle = \langle \Psi, t_0 | \hat{F}_H | \Psi, t_0 \rangle$$

where we defined $\hat{F}_H = e^{i(t-t_0)\hat{H}/\hbar} F e^{-i(t-t_0)\hat{H}/\hbar}$. We see that $\langle F \rangle$ can be expressed in two equivalent ways:

① Schrödinger-picture: expectation value of a time-indep. operator $\hat{F}$ in a time-dep. state.

② Heisenberg-picture: expectation value of a time-dep. operator $\hat{F}_H$ in a time-indep. state.

We see that $\hat{F}_H = \hat{U}^\dagger \hat{F} \hat{U}$ where the evolution operator satisfies $\hat{U}^\dagger = \hat{U}^{-1}$: unitary operator.

In the Schrödinger picture, we know that:

$$\frac{d}{dt}\langle F \rangle = \frac{i}{\hbar}\langle [\hat{H}, \hat{F}] \rangle$$

In the Heisenberg picture, we may differentiate

$\hat{F}_H = e^{i(t-t_0)\hat{H}/\hbar}\,\hat{F}\,e^{-i(t-t_0)\hat{H}/\hbar}$ to obtain the equation:

$$\frac{d}{dt}\hat{F}_H = \frac{i}{\hbar}[\hat{H}, \hat{F}_H]. \quad (*)$$

Note that commutator-relations are preserved when making a transition to time-dep. operators. If $[\hat{A}, \hat{B}] = \hat{C}$, then:

$$[\hat{A}_H, \hat{B}_H] = [\hat{U}^+\hat{A}\hat{U}, \hat{U}^+\hat{B}\hat{U}] = \hat{U}^+(\hat{A}\hat{B} - \hat{B}\hat{A})\hat{U} = \hat{U}^+\hat{C}\hat{U} = \hat{C}_H.$$

EXAMPLE

For the creation and annihilation operators a^+ and a of a harmonic oscillator, we get from (*):

$$\frac{da_H}{dt} = -i\omega a_H, \quad \frac{da_H^+}{dt} = i\omega a_H^+.$$

Solution: $a_H(t) = e^{-i\omega t}a_H(0)$ & $a_H^+(t) = e^{i\omega t}a_H^+(0)$.

It is also worth mentioning that it is possible with an approach where only part of the time-dependence is transferred to the operators.

This is the interaction picture, which is often used when the Hamilton-operator $\hat{H} = \hat{H}_0 + \hat{H}_I$ where $\hat{H}_I$ has to be handled via perturbation theory. We may then transform with $\hat{U}_0 = e^{-i(t-t_0)\hat{H}_0/\hbar}$ so that the state vector would be time-indep. if $\hat{H}_I$ could be neglected.

Which picture that one ultimately decides to use, is a matter of convenience: the physics is the same.

CHAPTER 7

APPROXIMATIVE METHODS FOR ENERGY LEVELS

Only rarely is a QM problem exactly solvable. Thus, having a "toolbox" of useful approximative methods is indispensible for a physicist.

7.1 Time independent perturbation theory

Assume that $\hat{H}_0$ corresponds to an exactly solvable problem. Often times, a physical system may be described by a $\hat{H}$

which only slightly deviates from $\hat{H}_0$. Then, $\hat{H} - \hat{H}_0$ is the perturbation of the system.

Assume E_n^0 and $|n\rangle$ are known for $\hat{H}_0$: $\hat{H}_0 |n\rangle = E_n^0 |n\rangle$.

We want to find eigenvalues and eigenstates for the perturbed Hamilton-operator $\hat{H} = \hat{H}_0 + \lambda \hat{H}_1$, where $\hat{H}_1$ is time-independent.

λ is a small expansion parameter. This kind of pert. theory is suitable and commonly used in the context of atomic energy levels influenced by $\vec{E}$ or $\vec{B}$ fields.

Perturbation of a non-degenerate set of states

Assume that the unperturbed energy level is non-degenerate, i.e. only has one eigenstate. Exact eigenvalue problem:

$$\hat{H} |\psi_n\rangle = E_n |\psi_n\rangle \longrightarrow (\hat{H}_0 + \lambda \hat{H}_1 - E_n) |\psi_n\rangle = 0.$$

If the eigenvalues & eigenstates can be expanded:

$$E_n = E_n^0 + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} \ldots \qquad |\psi_n\rangle = |n\rangle + \lambda |n^{(1)}\rangle + \lambda^2 |n^{(2)}\rangle \ldots$$

we obtain: $\left(\hat{H}_0 + \lambda \hat{H}_1 - E_n^0 - \lambda E_n^{(1)} - \ldots\right)\left(|n\rangle + \lambda |n^{(1)}\rangle + \ldots\right) = 0.$

If this is to be valid for all λ, the equation must be fulfilled for each power of λ. We obtain:

$\mathcal{O}(\lambda^0)$: $(\hat{H}_0 - E_n^{(0)})|n\rangle = 0$

$\mathcal{O}(\lambda^1)$: $(\hat{H}_0 - E_n^{(0)})|n^{(1)}\rangle + (\hat{H}_1 - E_n^{(1)})|n\rangle = 0$

$\mathcal{O}(\lambda^2)$: $(\hat{H}_0 - E_n^{(0)})|n^{(2)}\rangle + (\hat{H}_1 - E_n^{(1)})|n^{(1)}\rangle - E_n^{(2)}|n\rangle = 0$.

The 0'th order equation is known to be valid from the outset. Now, multiply the 1'st order equation with $\langle n|$:

$$\langle n|\hat{H}_0 - E_n^0|n^{(1)}\rangle + \langle n|\hat{H}_1|n\rangle - E_n^{(1)} = 0$$

Since $\langle n|\hat{H}_0 - E_n^0|n^{(1)}\rangle = \langle n^{(1)}|\hat{H}_0 - E_n^0|n\rangle^* = 0$, we get

$$\boxed{\lambda E_n^{(1)} = \langle n|\lambda\hat{H}_1|n\rangle}$$

This is the lowest order energy correction. Can also be written as:

$$\lambda E_n^{(1)} = \int \psi_n^{(0)*}\, \lambda\hat{H}_1\, \psi_n^{(0)}\, dV$$

What about the correction to the eigenstates? Multiply the $\mathcal{O}(\lambda^1)$ equation with $\langle m|$, where $m \neq n$, and get:

$$\langle m|\hat{H}_0 - E_n^{(0)}|n^{(1)}\rangle + \langle m|\hat{H}_1|n\rangle = 0$$

Using that:

$$\langle m|\hat{H}_0 - E_n^0|n^{(1)}\rangle = \langle n^{(1)}|\hat{H}_0 - E_n^0|m\rangle^*$$

$$= (E_m^0 - E_n^0)\langle n^{(1)}|m\rangle^* = (E_m^{(0)} - E_n^{(0)})\langle m|n^{(1)}\rangle$$

we obtain $\langle m|n^{(1)}\rangle = \dfrac{\langle m|\hat{H}_1|n\rangle}{E_n^0 - E_m^0}$. It is clear that a problem would arise if the unperturbed eigenvalues were degenerate, since the denominator would go to zero then. If we now expand $|n^{(1)}\rangle$ in the unperturbed eigenstates:

$|n^{(1)}\rangle = \sum_m |m\rangle\langle m|n^{(1)}\rangle$ via the completeness relation,

we end up with:

$$\boxed{|n^{(1)}\rangle = \sum_{m\neq n} \frac{\langle m|\hat{H}_1|n\rangle}{E_n^0 - E_m^0}|m\rangle}$$

Note that $\langle n|n^{(1)}\rangle = 0$ since n is not part of the summation. This means that the normalization of $|n\rangle + \lambda|n^{(1)}\rangle$ is actually satisfied up to first order in λ:

$$(\langle n| + \lambda\langle n^{(1)}| + \dots)(|n\rangle + \lambda|n^{(1)}\rangle + \dots) = 1 + \lambda\underbrace{(\langle n|n^{(1)}\rangle + \langle n^{(1)}|n\rangle)}_{=0} + \dots$$

We have now determined the eigenvalues & eigenstates to $O(\lambda)$. For some applications it turns out that $\langle n|\hat{H}_n|n\rangle = 0$, so then we have to go up to second order in λ.

Following a similar procedure as in the first order case, we get:

$$E_n = E_n^0 + \langle n|\lambda \hat{H}_1|n\rangle + \sum_{m\neq n} \frac{|\langle m|\lambda \hat{H}_1|n\rangle|^2}{E_n^0 - E_m^0} + O(\lambda^3)$$

$$|\psi_n\rangle = |n\rangle + \sum_{m\neq n} \frac{\langle m|\lambda \hat{H}_1|n\rangle}{E_n^0 - E_m^0}|m\rangle + O(\lambda^2)$$

Note that if we are perturbing the ground-state, then $E_m^0 > E_n^0$, which means that $E_n^{(4)}$ is negative.

We see that a criterion for the applicability of this method is that $|\langle m|\lambda \hat{H}_1|n\rangle| \ll |E_n^0 - E_m^0|$, so that the correction to E_n is indeed small.

This type of approximation theory is known as Rayleigh-Schrödinger perturbation theory.

EXAMPLE Relativistic correction to the Coulomb-levels.

Even if the levels above the ground-state have a degeneracy, we can still use our approximation theory because the perturbation matrix elements between degenerate states, $\langle m|\lambda \hat{H}_1|n\rangle$, turn out to vanish.

The relativistic expression for kinetic energy can be expanded in momentum as follows:

$$\sqrt{m^2c^4 + \vec{p}^2c^2} - mc^2 = mc^2\sqrt{1 + \frac{\vec{p}^2}{m^2c^2}} - mc^2 \qquad (\text{assume now } |\vec{p}| \ll mc)$$

$$\simeq mc^2\left(1+\frac{\vec{p}^2}{2m^2c^2}-\frac{(\vec{p}^2)^2}{8m^4c^4}+\dots\right)-mc^2$$

$$=\frac{\vec{p}^2}{2m}-\frac{(\vec{p}^2)^2}{8m^3c^2}+\dots$$

Here, m is the rest mass of the particle. The pertubation is then:

$\lambda\hat{H}_1 = -\frac{\hbar^4}{8m^3c^2}(\nabla^2)^2$. We knew that the first order correction to the energy eigenvalue is the expectation value:

$$\lambda E_n^{(1)} = \langle n|\lambda\hat{H}_1|n\rangle = -\frac{\hbar^4}{8m^3c^2}\int\psi_n^*(\nabla^2)^2\psi_n d^3r$$

$$= -\frac{\hbar^4}{8m^3c^2}\int|\nabla^2\psi_n|^2 d^3r, \qquad (*)$$

obtained by performing two partial integrations. The integral is most easily evaluated by using the S.E. for the Coulomb-potential:

$$-\frac{\hbar^2}{2m}\nabla^2\psi_{nlm} = \frac{Ze^2}{4\pi\varepsilon_0 r}\psi_{nlm} + E_n\psi_{nlm} = \frac{Ze^2}{4\pi\varepsilon_0}\left(\frac{1}{r}-\frac{1}{2an^2}\right)\psi_{nlm}.$$

Inserted into our expression (*), we get:

$$\lambda E^{(1)} = -\frac{1}{2mc^2}\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)^2\left\langle\left(\frac{1}{r}-\frac{1}{2an^2}\right)^2\right\rangle.$$

This expectation value may be computed by using the known form of the hydrogen wavefunction and noting that:

$$\left\langle \frac{a}{r} \right\rangle = \frac{1}{n^2} \,, \left\langle \frac{a^2}{r^2} \right\rangle = \frac{2}{(2l+1)n^3}$$

$$\Rightarrow \left\langle \left(\frac{a}{r} - \frac{1}{2n^2} \right)^2 \right\rangle = \frac{2}{n^4} \left(\frac{n}{2l+1} - \frac{3}{8} \right).$$

Introducing the fine-structure constant $\alpha = e^2/4\pi\varepsilon_0\hbar c$, we obtain

$$E_{nl} = mc^2 \left[1 - \frac{Z^2\alpha^2}{2n^2} - \frac{Z^4\alpha^4}{n^4} \left(\frac{n}{2l+1} - \frac{3}{8} \right) \right]$$

where the term $\propto Z^4$ is the lowest order relativistic correction to the energy level. Importantly, the energy level is now not only dependent on n, but also on the angular momentum quantum number $l \Rightarrow$ the energy spectrum acquires a <u>fine-structure</u>.

This result is correct for a spinless particle. The result is slightly modified for e.g. an electron that has spin $1/2$.

7.2 | Perturbation of a degenerate level.

Consider now the case where the eigenvalue E_n^0 for the unperturbed Hamilton-operator $\hat{H}_0$ is degenerate.

Let there be g orthonormal states $|n_1\rangle, |n_2\rangle, \ldots |n_g\rangle$ with eigenvalue E_n^0. An example is the four states $|200\rangle, |211\rangle, |210\rangle, |21\,{-1}\rangle$ corresponding to the first excited level for the Coulomb potential.

We again expand in powers of λ. For the state-vector:

$$|\Psi_n\rangle = \sum_{r=1}^{g} a_r |n_r\rangle + \lambda |N_1\rangle + \ldots \quad \text{with unknown coefficients } a_r.$$

To first order in λ, $\hat{H}|\Psi_n\rangle = E_n|\Psi_n\rangle$ gives us:

$$(\hat{H}_0 - E_n^0)|N_1\rangle + (\hat{H}_1 - E_n^{(1)}) \sum_{r=1}^{g} a_r |n_r\rangle = 0$$

Multiply from the left with one of the unperturbed states $\langle n_s|$:

$$\sum_{r=1}^{g} \langle n_s| \hat{H}_1 - E_n^{(1)} |n_r\rangle a_r = 0 \qquad (\dagger)$$

where we used that $\langle N_1| \hat{H}_0 - E_n^0 |n_s\rangle^* = 0$.

In $(\dagger)$, all the matrix elements are known: $\langle n_s|\hat{H}_1|n_r\rangle \equiv H'_{sr}$. They are computed via the unperturbed states. Since $\langle n_s|n_r\rangle = \delta_{sr}$, we get:

$$\sum_{r=1}^{g} (H'_{sr} - E_n^{(1)}\delta_{sr}) a_r = 0 \quad , \quad s = 1, 2, \ldots g.$$

This is a homogeneous set of equations for the unknown a_r:

$$\underbrace{\begin{bmatrix} H'_{11} - E_n^{(1)} & H'_{12} & \cdots & H'_{1g} \\ H'_{21} & H'_{22} - E_n^{(1)} & \cdots & H'_{2g} \\ \vdots & \vdots & & \vdots \\ H'_{g1} & H'_{g2} & \cdots & H'_{gg} - E_n^{(1)} \end{bmatrix}}_{M} \begin{bmatrix} a_1 \\ a_2 \\ \vdots \\ a_g \end{bmatrix} = 0 .$$

This only has a non-trivial solution for the coeff. $a_1, a_2, \ldots a_g$ when $\det(M) = 0$. This gives us an equation of the g'th degree for $E_n^{(1)}$. If all g solutions for $E_n^{(1)}$ are different, it means that the perturbation $\lambda \hat{H}_1$ has completely lifted the degeneracy of the energy level:

This method for degenerate levels can and <u>should</u> be used on a level which is not degenerate, but where the criterion $|\langle m|\lambda \hat{H}_1|n\rangle| \ll |E_n^0 - E_m^0|$ is not satisfied, i.e. the energy difference between the level under consideration and another unperturbed level is not large compared to the matrix elements of the perturbation taken between unperturbed states.

Stark-effect in hydrogen

As an application of this framework, consider the Stark-effect: The displacement of energy levels due to an external constant electric field $\vec{\mathcal{E}}$. Choosing $\hat{z}$ as the direction of the field, we get $\lambda \hat{H}_1 = e\mathcal{E}\hat{z}$ where $\vec{\mathcal{E}} = \mathcal{E}\hat{z}$. (potential energy for charged particle in field).

Assume that the particle is an electron in a Coulomb-potential, and that the field is so weak that pert. theory is permissible.

Let the energy states in Coulomb-potential be $|nlm\rangle$.

The ground-state $|100\rangle$ is non-degenerate, and the correction to E becomes: $\lambda E_1^{(1)} = e\mathcal{E}\langle 100|z|100\rangle = e\mathcal{E}\int z|\psi_{100}|^2 d^3r$.

This integral is zero due to symmetry since $\psi_{100} \sim e^{-r/a}$.

For the ground-state, the lowest order non-vanishing correction is thus 2nd order in the perturbation (the field $\mathcal{E}$):

$E_1 = E_1^0 - \text{const.}\,\mathcal{E}^2$.

The constant is evaluated (see appendix C, Hemmer book):

$$E_1 = E_1^0 \left[1 + \frac{9}{8}\left(\frac{e a_0 \mathcal{E}}{E_1^0}\right)^2\right]. \qquad (E_1^0 < 0).$$

The correction to the ground-state is atypical, because it is quadratic in $\mathcal{E}$: for all other levels, the Stark-effect is linear in the field $\mathcal{E}$. It turns out that the reason for this is that all excited energy levels are degenerate.

Consider the $n=2$ level with 4-fold degeneracy: $|200\rangle, |210\rangle, |211\rangle, |21{-1}\rangle$.

To do pert. theory for a degenerate level, we need the matrix elements $e\mathcal{E}\langle 2lm|z|2l'm'\rangle$. Several of these vanish:

- Diagonal elements $\langle 2lm|z|2lm\rangle$ are zero due to symmetry, just like the first-order term for the ground-state.
- All elements where $m \neq m'$ vanish, the reason being that $z = r\cos\theta$ does not contain φ, while $\psi_{nlm} \sim e^{im\varphi}$. It's a result, the φ-integration gives:

$$\int_0^{2\pi} e^{-im\varphi} e^{im'\varphi} d\varphi = 2\pi\delta_{mm'}.$$

In effect, only the matrix elements $\langle 210|z|200\rangle$ and $\langle 200|z|210\rangle = \langle 210|z|200\rangle^*$ are non-zero, and we thus only have to compute:

$$e\mathcal{E}\langle 210|z|200\rangle = e\mathcal{E}\int \psi_{210}^* z\, \psi_{200}\, dV$$

The wavefunctions can be derived or looked up in a table:

$$\psi_{210} = (32\pi a_0^3)^{-1/2} r a_0^{-1} e^{-r/2a_0}\cos\theta \quad , \quad \psi_{200} = (32\pi a_0^3)^{-1/2}(2 - r a_0^{-1})\, e^{-r/2a_0},$$

and inserting these yields:

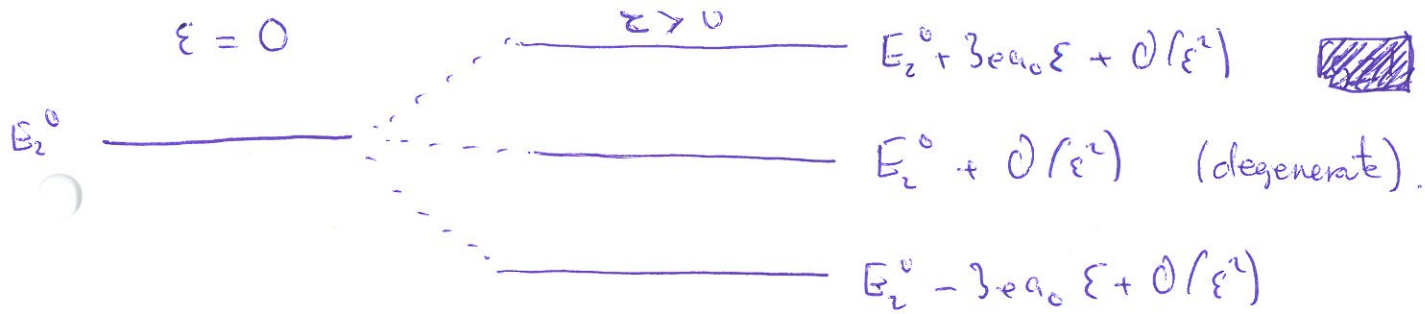
$$e\mathcal{E}\langle 210|z|200\rangle = -3e\mathcal{E}a_0.$$

The determinant that provides us with the first order energy correction is then:

$$\begin{vmatrix} -E_2^{(1)} & -3ea_0\mathcal{E} & 0 & 0 \\ -3ea_0\mathcal{E} & -E_2^{(1)} & 0 & 0 \\ 0 & 0 & -E_2^{(1)} & 0 \\ 0 & 0 & 0 & -E_2^{(1)} \end{vmatrix} = \left(E_2^{(1)}\right)^2 \cdot \left[\left(E_2^{(1)}\right)^2 - \left(3ea_0\mathcal{E}\right)^2\right].$$

The solutions are: $E_2^{(1)} = 0, 0, \pm 3ea_0\mathcal{E}$.

We see that the degeneracy is not completely lifted: the field splits the $n=2$ level into three levels (instead of four).



We have assumed that the field $\mathcal{E}$ is weak in order to use perturbation theory, but what does this quantitatively mean? Let us compare it with the distance to the next unperturbed energy level:

$$E_3^0 - E_2^0 = \left(\frac{1}{4} - \frac{1}{9}\right)|E_1^0| = 1.89\,eV.$$

The ratio between field-splitting of the levels and the above distance is then:

$$\frac{3ea_0\mathcal{E}}{E_3^0 - E_2^0} = \frac{\mathcal{E}}{1.2\cdot 10^{10}\ V/m}. \qquad (a_0 = 0.529\cdot 10^{-10}\ m)$$

The conclusion is then that our approach is valid so long as $\mathcal{E} \ll 10^{10}\ V/m$ (which is very large).

It is instructive to consider the state belonging to the lowest energy level $E_2^{(1)} = -3ea_0\mathcal{E}$. The state is specified by computing the $\{a_j\}$ coefficients (see previous notes).

One finds that $|4_-\rangle = \frac{1}{\sqrt{2}}(|200\rangle - |210\rangle)$. This state has a finite dipole-moment along the z-axis, namely:

$$d = \langle 4_- | -ez | 4_- \rangle = \frac{1}{2e}\left(\langle 200|z|210\rangle + \langle 210|z|200\rangle\right) = 3a_0 e.$$

We can now interpret the energy shift due to the electric field $\mathcal{E}$ physically: it is simply the <u>dipole-energy</u> $-\vec{d}\cdot\vec{\mathcal{E}}$.

7-3 Variational method

There are problems where one cannot split $\hat{H}$ into an exactly solvable part + a small perturbation. In those events, perturbation theory is not applicable and we may instead employ a <u>variational method</u> (Rayleigh-Ritz).

Ground-state

This method is particularly useful to determine the lowest-lying eigenvalue E_0. It is based on the fact that the expectation value of $\hat{A}$ in any state f is $\geq E_0$:

$$\frac{\langle f|\hat{A}|f\rangle}{\langle f|f\rangle} \geq E_0$$

Let us prove this, using the wave-mechanics formulation.

Expand the states f in the eigen functions of $\hat{H}$:
$f = \sum_n c_n \psi_n$. Using the orthonormality of the set $\{\psi_n\}$, we obtain:
$\int f^* f \, dV = \sum_n |c_n|^2$. Thus, $\int f^* \hat{H} f \, dV = \sum_n |c_n|^2 E_n$.

Since $E_n \geq E_0$ per definition, we get:

$$\int f^* \hat{H} f \, dV \geq E_0 \sum_n |c_n|^2 = E_0 \int f^* f \, dV \quad \square.$$

The equality sign is obtained if the state f is the ground state ψ_0.
In other words:

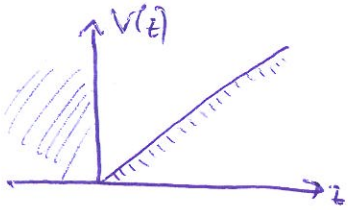
$$E_0 = \min_f E[f] \quad \text{with} \quad E[f] = \frac{\int f^* \hat{H} f \, dV}{\int f^* f \, dV}$$

The variational method then consists of selecting trial functions f that depend on one or more parameters, computing $E[f]$, and then minimizing it w.r.t. f. The result will be an upper limit for E_0 and the lowest value obtained will always be the best.

To be successful, one should ideally try to guess on a trial function form f which seems physically reasonable for the system.

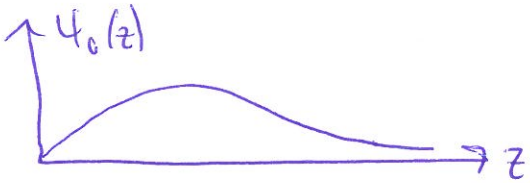
EXAMPLE Triangular well.

We use the variational method to estimate E_0 for a triangular well $V(z) = \begin{cases} \infty & z<0 \\ Fz & z>0 \end{cases}$.



Physically, this could be realized by pushing an electron with an electric field $\mathcal{E}$ toward a hard potential wall (the force being $F = e\mathcal{E}$). This is a commonly encountered situation in experimental electronics when one wants to create artificial 2D electron systems.

What kind of wavefunction should we expect in this system? It should be zero in the $V=\infty$ region and also fall off as z increases. Thus, something like:



could be a reasonable guess.

A possible choice is then: $f(z) = z e^{-\frac{1}{2}az}$. We get:

$$E[f] = \frac{\int_0^\infty \left(-\frac{\hbar^2}{2m}\right) f f'' dz + F \int_0^\infty z f^2 dz}{\int_0^\infty f^2 dz}$$

All integrals may be evaluated analytically.

- $\int_0^\infty f^2\,dz = \int_0^\infty z^2 e^{-\alpha z}\,dz = \frac{2}{\alpha^3}$

- $-\frac{\hbar^2}{2m}\int_0^\infty f f''\,dz = -\frac{\hbar^2}{2m}\int_0^\infty \left(-\alpha z + \frac{1}{4}\alpha^2 z^2\right) e^{-\alpha z}\,dz = \frac{\hbar^2}{2m}\,\frac{1}{2\alpha}$

- $F\int_0^\infty z f^2\,dz = F\int_0^\infty z^3 e^{-\alpha z}\,dz = \frac{6F}{\alpha^4}$.

In total, we get: $E[f] = \frac{\hbar^2}{2m}\cdot\frac{\alpha^2}{4} + \frac{3F}{\alpha}$.

α is here a free parameter that we may adjust to obtain as good a guess that is possible for E_0. In effect, we want to minimize $E[f]$ w.r.t. α. Setting $\frac{\partial E[f]}{\partial \alpha} = 0$ gives $\alpha = \left(6F\cdot\frac{2m}{\hbar^2}\right)^{1/3}$. The minimum value of $E[f]$ for our particular trial function is then:

$$\min_\alpha E[f] \approx 2.48\left(\frac{\hbar^2}{2m}\right)^{1/3} F^{2/3}.$$

We don't know how good this result is, i.e. how far away from the true ground-state energy it is. In this particular case, however, we are lucky because the triangular well problem can actually be solved exactly.

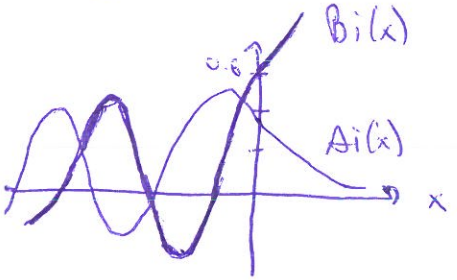
Consider the SE for $z > 0$: $-\frac{\hbar^2}{2m}\frac{d^2\psi}{dz^2} + Fz\psi = E\psi$.

Introduce the quantities $k = \left(\frac{\hbar^2}{2mF}\right)^{1/3}$ and $x = z/k$ to bring the equation to dimensionless form:

$$\frac{d^2\psi}{dx^2} - (x - \tilde{E})\psi = 0 \quad , \text{where } \tilde{E} = E/Fk.$$

Now, the equation $y'' - xy = 0$ is Airys differential equation and has two known independent solutions $y = Ai(x)$ and $y = Bi(x)$.

While $Bi(x)$ diverges for large x, and thus is physically unacceptable in our system, $Ai(x - \tilde{E})$ has an acceptable behavior as it decreases with x:



The solution of our diff. equation is then $\psi(x) = Ai(x - \tilde{E})$ where:

$$Ai(x) = \frac{1}{\pi}\int_0^\infty \cos\left(xz + \tfrac{1}{3}z^3\right)dz$$

Since $\psi(0) = 0$ due to the infinite wall potential, we obtain the energy eigenvalues from $Ai(-\tilde{E}) = 0$. The smallest value of $\tilde{E}$ must be the ground-state, which is found numerically to occur at $\tilde{E} = 2.33811$. Since $\tilde{E} = E/Fk$, we get

$$E_0 = 2.33811\left(\frac{\hbar^2}{2m}\right)^{1/3} F^{2/3}$$

Comparing with the result we obtained with the variational method, we see now that it was quite good : 6% deviation from the exact result!

Excited states

The variational method can also be used for the lowest-lying excited level E_1, granted that we can choose a trial function that is orthogonal to the ground state.

To see this, expand $f = \sum_{n=1}^{\infty} c_n \psi_n$, thus excluding $n=0$ since f has to be orthogonal to ψ_0. It follows, proceeding as we did before, that for this f:

$$\frac{\langle f|\hat{A}|f\rangle}{\langle f|f\rangle} \geq E_1.$$

Symmetry can be used as a guideline to ensure orthogonality between f and ψ_0. For instance, in a 1D symmetric potential, the first excited state is antisym. while the ground-state is sym.

If symmetry arguments are not available, another option is to compute the ground-state as accurately as we can, and then ensure that f is orthogonal to that function.

7.5 | WKB - approximation

Whereas the variational method is useful for approximating the ground-state of a system, it is useless for the purpose of determining highly excited states.

In contrast, the WKB-method (Wentzel, Kramers, Brillouin) is particularly accurate for highly excited states, and also reasonably useful for lower states. This method is also known as a semiclassical approach or the Liouville-Green approximation

WKB wavefunctions

The basic idea is simple to grasp. Consider 1D SE with a general potential $V(x)$:

$$\frac{d^2}{dx^2}\psi(x) + \frac{2m}{\hbar^2}[E - V(x)]\psi(x) = 0 .$$

We now try to solve this with the ansatz $\psi(x) = e^{iS(x)/\hbar}$.

For $V(x) = V_0$, this is indeed a solution with $S(x) = \pm\sqrt{2m(E-V)}\,x$.

We may thus view $\psi(x) = e^{iS(x)/\hbar}$ as a wavefunction with variable wavelength. Inserting it into the SE gives:

$$(S')^2 - 2m[E-V(x)] - i\hbar S'' = 0 \qquad (*)$$

If $V(x) = V_0$, then $S'' = 0$. Thus, for a slowly varying potential $V(x)$ it seems reasonable to solve (*) iteratively while treating $i\hbar S''$ as a small perturbation. Let us use $\hbar$ as a book-keeping expansion parameter (similarly to what we did with λ in previous perturbation theory). We expand

$$S(x) = S_0(x) + \hbar S_1(x) + \hbar^2 S_2(x) + \dots$$

Insert this into (*). The $O(\hbar^0)$ terms are:

$$(S_0')^2 = 2m[E-V(x)].$$

Integrating provides: $S_0(x) = \pm \int_{x_0}^{x} \sqrt{2m[E-V(y)]}\, dy + C_{1,\pm}$

where $C_{1,\pm}$ is a constant. Next, the $O(\hbar)$ terms give:

$$2 S_0' S_1' = i S_0'' \implies S_1'(x) = \frac{1}{2} i S_0''/S_0'.$$

Integrating provides:

$$S_1(x) = \frac{1}{2} i \ln S_0'(x) + C_{2,\pm} = \frac{1}{2} i \ln\left(\pm \sqrt{2m[E-V(x)]} \right) + C_{2,\pm}$$

where $C_{2,\pm}$ is a new integration constant.

Since we now have identified S_0 and S_1, we find:

$$\psi(x) = e^{iS(x)/\hbar} \simeq e^{i(S_0 + \hbar S_1)/\hbar} = e^{iS_0/\hbar} \cdot e^{iS_1}$$

$$= e^{\pm \frac{i}{\hbar} \int_{x_0}^{x} \sqrt{2m[E-V(y)]}\, dy} \cdot e^{C_{1,\pm}} \cdot e^{-\frac{1}{2}\ln\left(\pm\sqrt{2m[E-V(x)]}\right)} \cdot e^{iC_{2,\pm}}$$

We rename the constants: $A_\pm \equiv e^{iC_{1,\pm}} \cdot e^{iC_{2,\pm}}$ and thus obtain:

$$\boxed{\psi(x) = \frac{A_\pm}{[E-V(x)]^{1/4}}\, e^{\pm (i/\hbar) \int_{x_0}^{x} \sqrt{2m[E-V(y)]}\, dy}}$$

This is the WKB-approximation for the solution $\psi(x)$.

Note that if $V(x) > E$ (classically forbidden area), $\psi(x)$ exponentially increases or decreases:

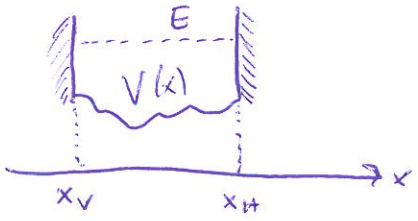
$$\psi(x) = \frac{B_\pm}{[V(x)-E]^{1/4}}\, e^{\pm (1/\hbar) \int_{x_0}^{x} \sqrt{2m[V(y)-E]}\, dy}$$

where we absorbed some numerical constants, $(-1)^{1/4}$, into $A_\pm \to B_\pm$.

For a bound-state, one of the coefficients $B_\pm$ thus has to be zero in order to prevent $\psi(x)$ from diverging.

Application #1: quantization with hard walls

Consider a potential containing two hard walls at $x = x_V$ and $x = x_H$.



$$V(x) = \infty \quad \text{for } x < x_V \text{ and } x > x_H$$

Since the wave function is zero outside $x_V < x < x_H$, we must have $\psi(x_V) = \psi(x_H) = 0$. We then need a linear combination of the solutions $\psi(x) = \frac{A_\pm}{[E - V(x)]^{1/4}} e^{\pm (i/\hbar) \int_{x_0}^{x} \sqrt{2m[E - V(y)]}\, dy}$ which vanishes at those points. One combination that does this is:

$$\psi(x) = A\,[E - V(x)]^{-1/4} \sin\left[(1/\hbar) \int_{x_V}^{x} \sqrt{2m\,[E - V(y)]}\, dy\right]$$

if we demand that:

$$\frac{1}{\hbar} \int_{x_V}^{x_H} \sqrt{2m\,[E - V(y)]}\, dy = n\pi, \quad n = \text{integer}.$$

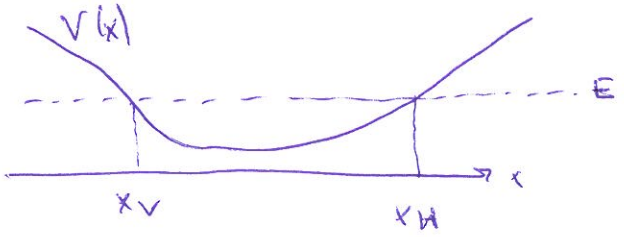
This is effectively a quantization condition for the energy, which may be written as (using $\frac{1}{\hbar} = \frac{2\pi}{h}$):

$$\boxed{2 \int_{x_V}^{x_H} \sqrt{2m\,[E_n - V(y)]}\, dy = nh.}$$

In the simple limit that $V(y) = 0$, we get $2\sqrt{2mE_n}\,(x_H - x_V) = nh$, which is an exact result.

Application #2: quantization with continuous potential

Consider a continuously varying potential with a minimum:



We should then expect to have oscillating WKB-solutions for $x_V < x < x_H$, but decaying solutions for $x < x_V$ and $x > x_H$ since those areas are classically forbidden.

A problem arises at the points where $E = V(x)$ ($x = x_V$ and $x = x_H$) since the WKB-solution diverges there due to $\sim \frac{1}{(E-V)^{1/4}}$.

How do we then connect the inner solution ($x_V < x < x_H$):

$$\psi(x) = [E-V(x)]^{-1/4}\left[A_+ e^{(i/\hbar)\int_{x_V}^{x}\sqrt{2m[E-V(y)]}\,dy} + A_- e^{-(i/\hbar)\int_{x_V}^{x}\sqrt{2m[E-V(y)]}\,dy}\right]$$

with the outer solutions:

$$\psi(x) = B_-[V(x)-E]^{-1/4} e^{(1/\hbar)\int_{x_V}^{x}\sqrt{2m[V(y)-E]}\,dy} \qquad x < x_V$$

$$\psi(x) = B_+[V(x)-E]^{-1/4} e^{-(1/\hbar)\int_{x_H}^{x}\sqrt{2m[V(y)-E]}\,dy} \qquad x > x_H.$$

?

Our strategy will be to treat the areas close to $x = x_V$ and $x = x_H$ exactly, since the potential can then be approximated as linear (via e.g. a Taylor expansion), and then use this exact solution to connect the inner and outer solutions.

Close to the right turning point, we have

$V(x) - E \simeq c(x - x_{tp})$, with $c > 0$.

The SE for this linear potential: $\frac{d^2\psi}{dx^2} - \frac{2mc}{\hbar^2}(x - x_{tp})\psi = 0$

becomes Airy's differential equation: $\frac{d^2\psi}{d\xi^2} - \xi\psi = 0$ with

$\xi = (2mc/\hbar^2)^{1/3} \cdot (x - x_{tp})$.

We have previously looked at the solutions $Ai(x)$ and $Bi(x)$, and the non-divergent solution $Ai(\xi)$ has the following asymptotic behaviour:

$$Ai(\xi) \simeq \begin{cases} \frac{1}{2\sqrt{\pi}}\,\xi^{-1/4} \cdot e^{-\frac{2}{3}\xi^{3/2}} & \text{for large positive } \xi \\ \frac{1}{\sqrt{\pi}}(-\xi)^{-1/4} \cdot \cos\left[\frac{2}{3}(-\xi)^{3/2} - \frac{1}{4}\pi\right] & \text{for large negative } \xi \end{cases}$$

If we use the linear potential $c(x - x_{tp})$ in the WKB-wavefunction, then for $x < x_{tp}$ we obtain:

$$\frac{1}{\hbar}\int_x^{x_{tp}} \sqrt{2m[E - V(y)]}\,dy = \frac{2}{3}(2mc/\hbar^2)^{\frac{1}{2}}(x_{tp} - x)^{3/2} = \frac{2}{3}(-\xi)^{3/2}.$$

We then see that we can [illegible] write the asymptotic $Ai(\xi)$ function as:

$$Ai(\xi) = \frac{1}{\sqrt{\pi}} \cdot \left[-\left(\frac{2mc}{\hbar^2}\right)^{1/3} (x - x_{tp}) \right]^{-1/4} \cdot \cos\left[\frac{1}{\hbar} \int_{x}^{x_{tp}} \sqrt{2m[E - V(y)]}\, dy - \frac{\pi}{4} \right]$$

for large negative ξ. Since $E - V(x) \propto (x - x_{tp})$, we see that

$$Ai(\xi) \propto [E - V(x)]^{-1/4} \cos\left[(1/\hbar) \int_{x}^{x_{tp}} \sqrt{2m[E - V(y)]}\, dy - \frac{\pi}{4} \right]$$

and this is precisely the WKB wavefunction for suitably chosen coefficients $A_\pm$. In other words, by choosing $A_\pm$ so that the WKB-wavefunction becomes the asymptotic part of $Ai(\xi)$, we may then connect the inner wavefunction for $x_v < x < x_{tp}$ to the outer one for $x > x_{tp}$. ~~To get cos [ ] we see that we need $A_+ = A_-$.~~

Performing the same procedure at the left interface gives us

$$\psi(x) \propto [E - V(x)]^{-1/4} \cos\left[\frac{1}{\hbar} \int_{x_v}^{x} \sqrt{2m[E - V(y)]}\, dy - \frac{\pi}{4} \right].$$

We now have two expressions for the inner wavefunction which should be equal for consistency. Using that $\int_{x_v}^{x} = \int_{x_v}^{x_{tp}} - \int_{x}^{x_{tp}}$, we can write:

$$\psi(x) \propto [E - V(x)]^{-1/4} \cos\left[\frac{1}{\hbar} \int_{x}^{x_{tp}} \sqrt{2m[E - V(y)]}\, dy - \frac{1}{\hbar} \int_{x_v}^{x_{tp}} \sqrt{2m[E - V(y)]}\, dy + \frac{1}{4}\pi \right].$$

For the two wavefunctions to be equal, we thus obtain the criterion that:

$$\frac{1}{\hbar}\int_{x_V}^{x_H}\sqrt{2m[E-V(y)]}\,dy = n\pi - \frac{1}{2}\pi.$$

Here, n is an integer. We may rewrite this as:

$$\boxed{2\int_{x_V}^{x_H}\sqrt{2m[E-V(y)]}\,dy = (n-\tfrac{1}{2})\,h\,,\quad n=1,2,3,\ldots} \qquad (*)$$

This determines the energy eigenvalues $E=E_n$.

Since the classical energy-momentum relation is $E=\frac{p^2}{2m}+V$, we can write the above result as:

$$\oint p(x)\,dx = (n+\tfrac{1}{2})\,h,$$

where the integral is taken over one period of the classical motion (starting and ending up with the same momentum).

This is Bohr-Sommerfelds quantization condition.

The quantization condition (*) gives better results the larger n is, but decent results may also be obtained for lower-lying levels n as well. For a harmonic oscillator, (*) gives the exact eigenvalues for all n.

We previously treated the case with two hard walls.

If the potential instead has one hard wall, e.g. at $x = x_V$, the wavefunction must vanish at $x = x_V$. From our expression for the inner wavefunction obtained from the asymptotic behaviour at $x = x_H$ ($\psi(x) \propto [E - V(x)]^{-1/4} \cos\left[\frac{1}{\hbar} \int_x^{x_H} \sqrt{2m[E - V(y)]}\, dy - \frac{1}{4}\pi\right]$), we see that the quantization condition becomes:

$$2 \int_{x_V}^{x_H} \sqrt{2m[E - V(y)]}\, dy = (n - \tfrac{1}{4})h.$$

It is then possible to summarize our WKB-results for the energy eigenvalues in the presence of hard walls as follows:

0 hard walls: $2 \cdot \int_{x_V}^{x_H} \sqrt{2m[E - V(y)]}\, dy = (n - \frac{1}{2})h.$

1 hard wall: $\quad -\!\!\cdot\!\!- \quad = (n - \frac{1}{4})h$

2 hard walls: $\quad -\!\!\cdot\!\!- \quad = (n - 0)h.$

EXAMPLE Let us apply the WKB-method to the triangular well problem to see how well it approximates the eigenvalues. We have $V(z) = \begin{cases} \infty & \text{for } z < 0 \\ Fz & \text{for } z > 0 \end{cases}$.

This problem has one hard wall and to use the quantization condition we have to set $z_1 = 0$ and $z_{tt} = E/F$, since z_{tt} was assumed to be located at the classical turning point. We get:

$$2\int_0^{E/F} \sqrt{2m[E - Fz]}\, dz = (n - \tfrac{1}{4})h. \quad \text{Introduce } z = x\,E/F:$$

$$2E^{3/2}\sqrt{2m/F}\int_0^1 \sqrt{1-x}\, dx = (n - \tfrac{1}{4})2\pi\hbar.$$

The integral equals $2/3$. Solving for E gives:

$$E_n = \left[\frac{3}{2}\pi(n - \tfrac{1}{4})\right]^{2/3}\left(\frac{\hbar^2}{2m}\right)^{1/3} F^{2/3}$$

The numerical coefficients for $n = 1, 2, 3$ are 0.8%, 0.15% and 0.08% off the exact result: very good approximations!

CHAPTER 11

TIME-DEPENDENT PERTURBATION THEORY

We have studied weak or slowly (spatially) varying perturbations of a QM system so far; but now we take the step to time-dependent perturbations. Important applications include EM radiation, spectroscopy, and laser physics.

11.1 - Weak perturbations

Differential equations for the state-coefficients

Let $\hat{V}(\vec{r},t)$ be a weak time-dependent perturbation:

$$\hat{H}(\vec{r},t) = \hat{H}^0(\vec{r}) + \hat{V}(\vec{r},t).$$

Assume that the stationary states $\Psi_n^0(\vec{r},t) = \psi_n(\vec{r})\, e^{-iE_n t/\hbar}$ for the unperturbed system $\hat{H}^0(\vec{r})$ are known. We thus have

$$\hat{H}^0(\vec{r})\,\psi_n = E_n \psi_n.$$

The time-evolution of the time-dependent, non-stationary states Ψ are governed by:

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi = (\hat{H}^0 + \hat{V})\Psi$$

We are not able to solve this in its exact form, and thus look for a perturbation method valid for weak $\hat{V}$.

Since the eigenstates for the unperturbed system is, as usual, assumed to be a complete and orthonormal set, we may expand:

$$\Psi(\vec{r},t) = \sum_k a_k(t)\,\psi_k(\vec{r})\,e^{-iE_k t/\hbar} \qquad (*)$$

Note that the coefficients $\{a_k\}$ have to be time-dependent.

Due to the normalization of $\Psi(\vec{r},t)$, we get:

$$1 = \int \Psi^*(\vec{r},t)\,\Psi(\vec{r},t)\,d^3r = \sum_k a_k^* a_k \Rightarrow \sum_k |a_k(t)|^2 = 1.$$

Inserting $(*)$ into the S.E. provides:

$$\sum_k i\hbar\left(\frac{da_k}{dt} - \frac{i}{\hbar}E_k a_k\right)\psi_k(\vec{r})\,e^{-iE_k t/\hbar} = \sum_k a_k\left(\hat{H}_0 + \hat{V}(\vec{r},t)\right)\psi_k(\vec{r})\,e^{-iE_k t/\hbar}.$$

$$\Rightarrow \sum_k i\hbar\frac{da_k}{dt}\psi_k(\vec{r})\,e^{-iE_k t/\hbar} = \sum_k a_k\hat{V}(\vec{r},t)\,\psi_k(\vec{r})\,e^{-iE_k t/\hbar} \qquad (\dagger)$$

We used that $\hat{H}^0\psi_k = E_k\psi_k$ to cancel two terms. Now, multiply $(\dagger)$ with $\psi_n^*(\vec{r})$ and integrating over the entire space, we get:

$$i\hbar\frac{da_n}{dt}\,e^{-iE_n t/\hbar} = \sum_k V_{nk}(t)\,e^{-iE_k t/\hbar}$$

where we defined:

$$V_{nk}(t) \equiv \int \psi_n^*(\vec{r})\,\hat{V}(\vec{r},t)\,\psi_k(\vec{r})\,d^3r = \langle n|\hat{V}|k\rangle .$$

This is a known quantity since it can be computed (ψ_n and $\hat{V}$ are both known). With the short-hand notation $\omega_{nk} \equiv \frac{E_n - E_k}{\hbar}$, we may then write the result as:

$$\boxed{\frac{da_n(t)}{dt} = \frac{1}{i\hbar}\sum_k V_{nk}\, e^{i\omega_{nk}t}\, a_k(t)} \qquad (n = 1, 2, 3, \ldots)$$

Note that so far, we haven't made any approximations: this coupled set of equations is fully equivalent to SE.

Perturbation expansion

If we now assume that $\hat{V}$ is weak, a_n will have only a weak time-dependence, and we can approximate the solution by neglecting the time-dependence of $a_k(t)$ on the r.h.s.

Doing so and integrating w.r.t. t gives:

$$a_n(t) = a_n(t_0) + \frac{1}{i\hbar}\sum_k a_k(t_0)\int_{t_0}^{t} V_{nk}(\tau)\, e^{i\omega_{nk}\tau}\, d\tau$$

If we know that the system was in state b at $t=t_0$, then $a_k(t_0) = \delta_{kb}$ and we obtain

$$\boxed{a_s(t) = \frac{1}{i\hbar}\int_{t_0}^{t} V_{sb}(\tau)\, e^{i\omega_{sb}\tau}\, d\tau \qquad (s \neq b)}$$

This is a key result. It tells us that the probability that the system at a time t has made a transition from state b to s is: $P_{b\to s}(t) = |a_s(t)|^2$. Note that $P_{b\to b} = 1 - \sum_{s\neq b} P_{b\to s}$.

Detailed balance

Let us compare the probabilities for the transitions $b\to s$ and $s\to b$. The first one was calculated above. The second one is:

$$a_{s\to b}(t) = \frac{1}{i\hbar}\int_{t_0}^{t} V_{bs}(\tau)\, e^{i\omega_{bs}\tau}\, d\tau$$

Since $\omega_{bs} = \dfrac{(E_b - E_s)}{\hbar} = -\omega_{sb}$ and $V_{bs} = \langle b|\hat{V}|s\rangle = \langle s|\hat{V}|b\rangle^* = V_{sb}^*$, the amplitudes satisfy: $a_{b\to s}(t) = -a^*_{s\to b}(t)$.

Taking $|\ldots|^2$, we see that $\boxed{P_{s\to b}(t) = P_{b\to s}(t)}$.

To first order in time-dependent perturbation theory, the probability for a transition is equal to the probability for the opposite transition. This result is known as detailed balance.

Transient perturbations

Assume that we're dealing with a perturbation that is transient, such as a charged particle passing by an atom and exciting the electrons in the atom (this is actually the dominant mechanism that causes deceleration of individual charged particles injected into a material).

Since the coefficients $\{a_s\}$ stop changing after the perturbation has ceased, we may set $t = \infty$ and use $t = -\infty$ as the initial time. The transition probability from state b to s then takes the form:

$$P_{b\to s} = \left| \frac{1}{i\hbar} \int_{-\infty}^{\infty} e^{i\omega_{sb}\tau} V_{sb}(\tau)\, d\tau \right|^2$$

In the special case where $\hat{V}(\vec{r},t)$ varies slowly in time compared to the period $\omega_{sb}^{-1} = \hbar/(E_s - E_b)$, the integrand oscillates rapidly around zero and the integral becomes very small.

If instead the perturbation varies in the same way as the "eigen frequency" ω_{sb} of the system, a <u>resonance</u> can occur which strongly influences the system. We now proceed to consider such a scenario.

11.2 - Harmonic perturbations

An important special case is when the perturbation varies harmonically: $\hat{V}(\vec{r},t) = V_+(\vec{r})e^{i\omega t} + V_-(\vec{r})e^{-i\omega t}$

The interaction between an atomic system and a radiation field in the form of EM waves has this form.

The limit $\omega \to 0$ corresponds to a constant perturbation.

In order for $\hat{V}$ to be Hermitian, we need $V_+^* = V_-$.

Inserting this $\hat{V}$ into our result for the transition coefficients, we obtain:

$$a_{b\to s}(t) = \frac{1}{i\hbar}(V_+)_{sb}\int_0^t e^{i(\omega_{sb}+\omega)\tau}\,d\tau + \frac{1}{i\hbar}(V_-)_{sb}\int_0^t e^{i(\omega_{sb}-\omega)\tau}\,d\tau$$

$$= (V_+)_{sb}\cdot\frac{1-e^{i(\omega_{sb}+\omega)t}}{\hbar\omega_{sb}+\omega\hbar} + (V_-)_{sb}\cdot\frac{1-e^{i(\omega_{sb}-\omega)t}}{\hbar\omega_{sb}-\hbar\omega}, \qquad (*)$$

having set $t_0 = 0$ as the reference point. To obtain the transition probability, we need $|a_{sb}|^2$. This gives $|\ldots|^2$ of the individual terms in (*) and a cross-term

Consider the last term first. $|\ldots|^2$ gives:

$$4|(V_-)_{sb}|^2 \quad \frac{\sin^2[(E_s - E_b - \hbar\omega)t/2\hbar]}{(E_s - E_b - \hbar\omega)^2}$$

We see that this contribution peaks (with a height $\propto t^2$) at energy $E_s = E_b + \hbar\omega$. The width of the peak, on the other hand, goes like t^{-1}. As a crude approximation, we may then write:

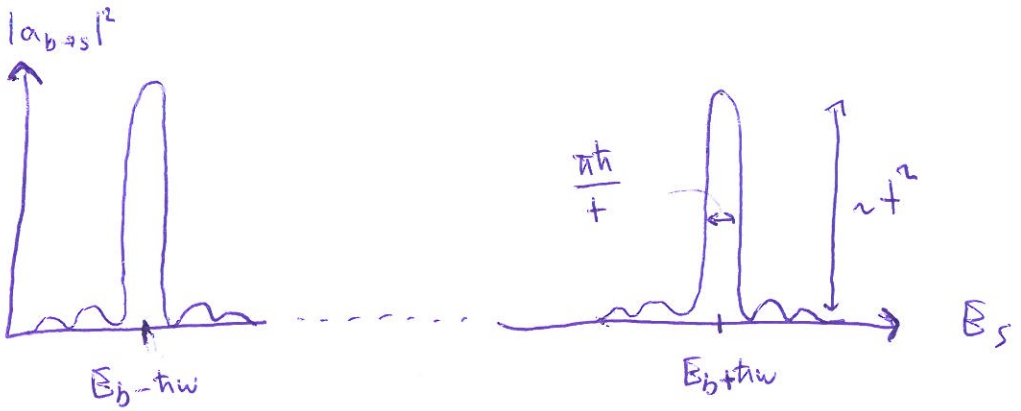
$$4|(V_-)_{sb}|^2 \frac{\sin^2[(E_s - E_b - \hbar\omega)t/2\hbar]}{(E_s - E_b - \hbar\omega)^2} \simeq |(V_-)_{sb}|^2 \frac{2\pi t}{\hbar} \delta(E_s - E_b - \hbar\omega).$$

The other $|\ldots|^2$ gives a sharp maximum at $E_s = E_b - \hbar\omega$.

The cross-term, however, has no sharp maximum and thus for large times t we have the following transition probability per unit time:

$$w_{b\to s} = \frac{|a_{b\to s}(t)|^2}{t} \simeq \frac{2\pi}{\hbar}|(V_-)_{sb}|^2 \delta(E_s - E_b - \hbar\omega) + \frac{2\pi}{\hbar}|(V_+)_{sb}|^2 \delta(E_s - E_b + \hbar\omega)$$

A sketch of the true behaviour of $|a_{b\to s}|^2$ would look like this:



The formula for $w_{b\to s}$ is useful when the energy spectrum (or frequencies) are continuous so that $E_b \pm \hbar\omega = E_s$ can indeed be satisfied.

EXAMPLE Continuous ω: an EM field (e.g. visible light, X-rays) with a broad spectrum of frequencies causes transitions between discrete atomic or molecular states. The resulting absorption spectrum consists of sharp lines.

Continuous E_s: a laser beam with fixed frequency ω can ionize an atom, causing a transition from a discrete bound state to a state in the continuous spectrum. This is the photoelectric effect.

Continuous E_b and E_s: a typical scattering experiment consists of particles in a beam being perturbed by some target potential (i.e. potential) and changing direction. Such scattering is a transition between different states in continuous spectra.

Transition to continuum states

Assume that we start out with a state with fixed E_b, and that the perturbation has a specific ω, while the final state s lies in a continuum of final-states.

Let there be $\rho(E) \cdot dE$ energy states in the range $(E, E+dE)$, such that $\rho(E)$ is the density of states. For instance, in previous QM courses you may have shown that the DOS for a free particle in a volume V_0 is: $\rho(E) = 2\pi \left(\frac{2m}{\hbar^2}\right)^{3/2} \cdot V_0 \, E^{1/2}$.

We may then compute the total transition probability to a state with energy close to E_s. This is obtained by $\boxed{w_{b\to s} = \frac{2\pi}{\hbar} |V_{sb}|^2 \rho(E_s)}$. The formula expresses that the transition rate w increases both with the "overlap" $|V_{sb}|$ element between the states and the amount of available states $\rho(E_s)$.

This is known as the golden rule.

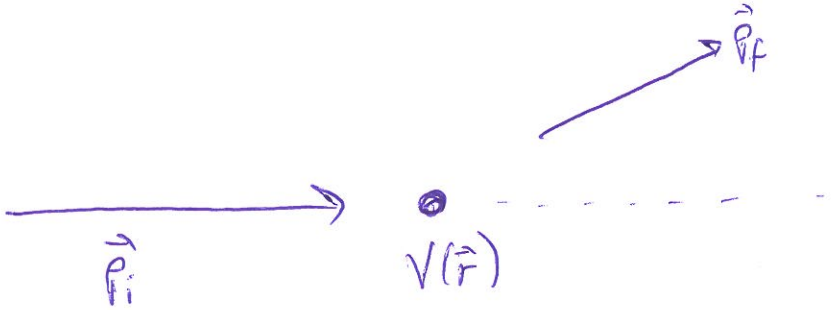
If one is interested in only a subset of the states with energy E_s, e.g. particles moving in a certain direction which a detector can pick up, one simply uses the density of states for that subset. For a free particle, it would be the fraction $\frac{d\Omega}{4\pi}$ of the total DOS : $\rho = 2\pi \left(\frac{2m}{\hbar^2}\right)^{3/2} V_0 E^{1/2} \cdot \frac{d\Omega}{4\pi} = V_0 \frac{m p_f}{\hbar^3} d\Omega$

where $E = \frac{p_f^2}{2m}$.

11.3 Application on scattering

We consider a scattering potential $V(\vec{r})$ as a perturbation on a particle-beam $\psi_i(\vec{r}) = \frac{1}{\sqrt{V_0}} e^{i\vec{p}_i \cdot \vec{r}/\hbar}$. The aim is to find the probability per unit time for a transition to the final state $\psi_f(\vec{r}) = \frac{1}{\sqrt{V_0}} e^{i\vec{p}_f \cdot \vec{r}/\hbar}$. Here, V_0 is the volume under consideration.

We may treat this process as stationary (corresponding to $\omega = 0$) and the energy before and after is thus the same : $|\vec{p}_f| = |\vec{p}_i| = p$.



To obtain $w_{b\to s}$ via the golden rule, we need the matrix-element:

$$V_{fi} = \frac{1}{V_0}\int e^{i(\vec{p}_i-\vec{p}_f)\cdot\vec{r}/\hbar}\, V(\vec{r})\, d^3r$$

It follows that:

$$w_{i\to f} = \frac{2\pi}{\hbar}\,\frac{1}{V_0^2}\cdot\left|\int e^{i(\vec{p}_i-\vec{p}_f)\cdot\vec{r}/\hbar}\, V(\vec{r})\, d^3r\right|^2 \cdot V_0\,\frac{mp}{h^3}\,d\Omega$$

A common way to measure scattering is the scattering cross section $d\sigma$:

$$d\sigma = \frac{\text{number of particles scattered into } d\Omega \text{ pr. unit time}}{\text{incident particle intensity}}$$

Quantitatively, the nominator is $w_{i\to f}$ and the inc. part. int. is the product of the particle density $|\psi_i|^2 = \frac{1}{V_0}$ and the velocity p/m, so that: $d\sigma = w_{i\to f}\cdot\frac{mV_0}{p}$.

With our expression for $w_{i\to f}$, we end up with:

$$\boxed{\frac{d\sigma}{d\Omega} = \left|\frac{m}{2\pi\hbar^2}\int V(\vec{r})\, e^{i(\vec{p}_i-\vec{p}_f)\cdot\vec{r}/\hbar}\, d^3\sigma\right|^2}$$

Later, we will regain this result using a different method.

The above formula is the so-called Born approximation for the scattering cross section. In chapter 13, we will also examine the range of validity for this result.

Next up:

- Adiabatic approximation
- Berry phase
- Sudden approximation

(BJ 9.4-9.5)

The adiabatic approximation

The perturbation methods we've considered so far have been based on the assumption that the magnitude of the time-dependent part of H has been small.

We now present a new approximation method where the key parameter is the rate of change of H. Start by assuming that H varies very slowly with time. One can then expect that the approximate solutions of $i\hbar \frac{\partial \Psi}{\partial t} = H(t)\Psi$ can be obtained in terms of the eigenfunctions $\psi_k(t)$ of the "instantaneous" Hamiltonian $H(t)$ so that: $H(t)\psi_k(t) = E_k(t)\psi_k(t)$ at any given time t.

Physically, what we are stating here is that if $H(t)$ changes very slowly, a system which at $t=t_0$ is in a discrete non-degenerate state $\psi_a(t_0)$ with $E_a(t_0)$ is very likely to go over to the state $\psi_a(t)$ with energy $E_a(t)$ at a later time t, i.e. without making any transition.

We now proceed to prove this adiabatic theorem, using the method of Born & Fock in 1928.

Assume that Ψ is known at $t = t_0$. Now, expand for $t > t_0$ in the instantaneous eigenfunctions $\psi_n(t)$:

$$\Psi = \sum_n C_n(t)\,\psi_n(t)\,\exp\left[-\frac{i}{\hbar}\int_{t_0}^{t} E_n(t')\,dt'\right]$$

We assume ψ_n form an orthonormal and complete set. The energies $E_n(t)$ are non-degenerate and form a discrete spectrum. Note that "energy levels" is just a formal name, since energy is not conserved for a time-dependent H. Insert into S-E:

$$i\hbar \sum_n \left(\dot{C}_n \psi_n + C_n \frac{\partial \psi_n}{\partial t} - \frac{i}{\hbar} C_n \psi_n E_n\right) \exp\left[-\frac{i}{\hbar}\int_0^t E_n(t')dt'\right]$$
$$= H(t) \sum_n C_n \psi_n \exp\left[-\frac{i}{\hbar}\int_0^t E_n(t')\,dt'\right]$$

There is a cancellation of the last term on the l.h.s. Now, do the following:

- Multiply with $\psi_b^*(t)$ (it is part of the set $\{\psi_n(t)\}$)
- Integrate over the coordinates of the system
- Use that $\langle \psi_b | \psi_n \rangle = \delta_{bn}$.

This gives: $$\dot{C}_b(t) = -\sum_n C_n(t) \exp\left\{\frac{i}{\hbar}\int_0^t [E_b(t') - E_n(t')]\,dt'\right\} \left\langle \psi_b \middle| \frac{\partial \psi_n}{\partial t} \right\rangle$$

This is a set of coupled first-order diff. equations for all the coefficients $C_k(t)$.

The diagonal terms can be removed as follows:

Consider $\alpha_k(t) = \langle \psi_k | \frac{\partial \psi_k}{\partial t} \rangle$. Use normalization $\langle \psi_k(t) | \psi_k(t) \rangle = 1$ and differentiate it w.r.t. time:

$$\langle \frac{\partial \psi_k}{\partial t} | \psi_k \rangle + \langle \psi_k | \frac{\partial \psi_k}{\partial t} \rangle = \alpha_k^*(t) + \alpha_k(t) = 0$$

Thus, $\alpha_k(t)$ is purely imaginary : $\alpha_k(t) = i\beta_k(t)$ where $\beta_k \in \mathbb{R}$.

Now, define : $C_k'(t) = C_k(t) \exp\left[i \int_{t_0}^{t} \beta_k(t')dt' \right]$

Differentiating C_b' to get $\dot{C}_b'$, we obtain :

$$\dot{C}_b' = - \sum_{k \neq b} C_k'(t) \exp\left\{ \frac{i}{\hbar} \int_0^t [E_b'(t') - E_k'(t')]dt' \right\} \langle \psi_b | \frac{\partial \psi_k}{\partial t} \rangle \quad (*)$$

where $E_k'(t) = E_k(t) + \hbar\beta_k(t)$. Note that

$$C_k(t)\psi_k(t) = C_k(t) e^{i\int_{t_0}^{t} \beta_k(t')dt'} \cdot \psi_k(t) e^{-i\int_{t_0}^{t} \beta_k(t')dt'} \equiv C_k'(t)\psi_k'(t)$$

If we assume that the phases of the eigenfunctions ψ_k are arbitrary at each instant of time, we can do this change on all ψ_k. Assume from now on that this change has already been made and omit ' notation. Note: this assumption is not valid for the case of cyclic systems, but we return to this issue later.

Looking at (*) again, we examine $\langle \psi_b | \frac{\partial \psi_k}{\partial t} \rangle$ for $k \neq b$.

Differentiate w.r.t. time for $H(t)\psi_k(t) = E_k(t)\psi_k(t)$ and get:

$$\frac{\partial H}{\partial t}\psi_k + H\frac{\partial \psi_k}{\partial t} = \frac{\partial E_k}{\partial t}\psi_k + E_k\frac{\partial \psi_k}{\partial t}$$

Using the notation $\langle \psi_a | \psi_b \rangle \equiv \int \psi_a^*(r)\,\psi_b(r)\,d^3r$ and taking the scalar product with ψ_b:

$$\langle \psi_b | \frac{\partial H}{\partial t} | \psi_k \rangle + \langle \psi_b | H | \frac{\partial \psi_k}{\partial t} \rangle = E_k \langle \psi_b | \frac{\partial \psi_k}{\partial t} \rangle \qquad (*)$$

Using that H is Hermitian, we obtain for the 2nd term:

$$\langle \psi_b | H | \frac{\partial \psi_k}{\partial t} \rangle = \langle H\psi_b | \frac{\partial \psi_k}{\partial t} \rangle = E_b \langle \psi_b | \frac{\partial \psi_k}{\partial t} \rangle .$$

Plugging it back into $(*)$ gives:

$$\langle \psi_b | \frac{\partial \psi_k}{\partial t} \rangle = -\frac{\left(\frac{\partial H}{\partial t}\right)_{bk}}{E_b(t) - E_k(t)} = -\frac{\left(\frac{\partial H}{\partial t}\right)_{bk}}{\hbar\omega_{bk}(t)}, \quad b \neq k \qquad (\dagger)$$

where we introduced the notation $\left(\frac{\partial H}{\partial t}\right)_{bk} = \langle \psi_b | \frac{\partial H}{\partial t} | \psi_k \rangle$

and $\omega_{bk}(t) = \frac{E_b(t) - E_k(t)}{\hbar}$, $b \neq k$. Thus, $\omega_{bk} \neq 0$ always since we assumed that the energy levels are non-degenerate.

If we now use our result in $(\dagger)$ and plug it back into our expression for the coupled equations for the $C_k(t)$ coefficients, we obtain (keep in mind that we omit the primes)

$$\dot{C}_b(t) = \sum_{k \neq b} \frac{C_k(t)}{i\hbar\, \omega_{bk}(t)} \left(\frac{\partial H}{\partial t}\right)_{bk} \exp\left[i \int_{t_0}^{t} \omega_{bk}(t')\,dt'\right] \qquad (x)$$

This system of equations then determine C_b - coefficients, which in turn determine the wave function:

$$\Psi = \sum_k C_k(t)\,\psi_k(t) \exp\left[-\frac{i}{\hbar} \int_{t_0}^{t} E_k(t')\,dt'\right]$$

This is a convenient starting point to make approximations, especially when $\frac{\partial H}{\partial t}$ is small (slowly varying Hamiltonian).

If $\frac{\partial H}{\partial t} = 0 \Rightarrow C_b =$ constant for all b. If $\frac{\partial H}{\partial t}$ is finite, but small, we can try to solve (x) by setting all C_k on the r.h.s. to be constants.

Assuming that the system initially ($t = t_0$) is in state a, we substitute the values $C_k = \delta_{ka}$ on the r.h.s. and get:

$$\dot{C}_b(t) = \hbar^{-1}\, \omega_{ba}^{-1}(t) \left(\frac{\partial H}{\partial t}\right)_{ba} \exp\left[i \int_{t_0}^{t} \omega_{ba}(t')\,dt'\right], \quad b \neq a.$$

For $b = a$, we get $\dot{C}_a = 0$ in this approximation.

Now integrate this equation with initial condition $C_b(t \leq t_0) = 0$ $(b \neq a)$, and obtain: $\longrightarrow$

$$\dot{c}_b(t) = i\hbar^{-1} \int_{t_0}^{t} dt' \, \omega_{ba}^{-1}(t') \left(\frac{\partial H(t')}{\partial t'}\right)_{ba} \exp\left[i \int_{t_0}^{t'} \omega_{ba}(t'')dt''\right] \qquad (b \neq a)$$

This is the result for the adiabatic approximation for the probability amplitude $c_b(t)$.

We should expect this result to yield a small $|c_b(t)|$ in order to be valid. Thus, $P_{ba}(t) = |c_b(t)|^2$ denotes the transition probability from the initial state a to state b, and we must have $P_{ba}(t) \ll 1$.

A crude estimate: assume ω_{ba} and $\partial_t H$ being time-indep.

$$\Rightarrow c_b(t) \simeq (i\hbar)^{-1} \omega_{ba}^{-2} \left(\frac{\partial H}{\partial t}\right)_{ba} \left(e^{i\omega_{ba}(t-t_0)} - 1\right)$$

$$\Rightarrow P_{ba}(t) \simeq 4\hbar^{-2} \omega_{ba}^{-4} \left|\left(\frac{\partial H}{\partial t}\right)_{ba}\right|^2 \sin^2\left[\omega_{ba}(t-t_0)/2\right].$$

This behaves reasonably as time increases since it merely oscillates, and the upper bound is (since $\sin^2 x \leq 1$):

$$P_{ba}(t) \leq \frac{4\left|(\partial_t H)_{ba}\right|^2}{\hbar^2 \omega_{ba}^4}.$$

The adiabatic approximation is thus valid if:

$$\left|\left(\frac{\partial H}{\partial t}\right)_{ba}\right|^2 \ll \frac{\hbar^2 \omega_{ba}^4}{4}.$$

EXAMPLE Charged harmonic oscillator in a time-dependent electric field.

We now witness the adiabatic approximation in action.
Consider a charged particle subject to a linear harm. osc. potential and a spatially uniform, time-dependent electric field $\mathcal{E}(t)$.

Hamiltonian: $H(t) = -\frac{\hbar^2}{2m}\partial_x^2 + \frac{1}{2}kx^2 - q\mathcal{E}(t)x$

$$= -\frac{\hbar^2}{2m}\partial_x^2 + \frac{1}{2}k[x-a(t)]^2 - \frac{1}{2}ka^2(t),$$

where $a(t) \equiv \frac{q}{k}\mathcal{E}(t)$.

We can identify this $H(t)$ as, at a given time t, describing a standard harm.osc. with frequency $\omega = \sqrt{\frac{k}{m}}$, but displaced equilibrium position to $x = a(t)$. The term $-\frac{1}{2}ka^2(t)$ is just a constant.

Instantaneous energy eigenfunctions thus obtained as:

$$\psi_n = \left(\frac{\alpha}{\sqrt{\pi}2^n n!}\right)^{1/2} \exp\left[-\alpha^2(x-a)^2/2\right] H_n[\alpha(x-a)]$$

with $\alpha \equiv \sqrt{\frac{m\omega}{\hbar}}$. Corresponding instantaneous energy eigenvalues:

$$E_n(t) = \left(n+\tfrac{1}{2}\right)\hbar\omega - \frac{1}{2}ka^2(t), \quad n = 0, 1, 2, \ldots$$

The angular frequencies $\omega_{nn'} = \frac{E_{n'}(t) - E_n(t)}{\hbar} = (n'-n)\omega$

are thus indep. of time and equal to the unperturbed value.

Assume:

- $\mathcal{E}(t)$ applied at $t=t_0$ and that it varies slowly
- The harm. osc. is initially in its ground state ($n=0$).

We want to compute the probability that the system is in an excited state at $t=t_1$.

First, note that $\frac{\partial H}{\partial t} = -k\dot{a}x$ with $\dot{a} = \frac{da}{dt} = \frac{q}{ic}\frac{d\mathcal{E}}{dt}$.

To find the transition probabilities, we will need (as we've derived previously) $\langle \psi_b | \frac{\partial H}{\partial t} | \psi_0 \rangle = \left(\frac{\partial H}{\partial t}\right)_{b0}$. In effect, we need to compute matrix elements of the type $x_{b0} = \langle \psi_b | x | \psi_0 \rangle$.

It can be shown that all these matrix elements vanish when $b \neq 1$, while for $b=1$ we have $x_{10} = \sqrt{\frac{\hbar}{2m\omega}}$.

Since $P_{ba}(t) = \hbar^{-2}\omega_{ba}^{-2}\left|\int_{t_0}^{t}\left(\frac{\partial H(t')}{\partial t'}\right)_{ba}\exp(i\omega_{ba}t')\,dt'\right|^2$,

the only non-vanishing transition probability is $0 \to 1$.

Inserting our expression for $\frac{\partial H}{\partial t}$ and $\omega_{10} = \omega$, we get

$$P_{10}(t_1) = |C_1(t_1)|^2 = \frac{q^2}{2m\hbar\omega^3}\left|\int_{t_0}^{t_1}\frac{d\mathcal{E}(t)}{dt}\exp(i\omega t)\,dt\right|^2$$

The slower the $\mathcal{E}$-field varies, the smaller the transition probability $0 \to 1$.

The Berry phase

When we discussed the adiabatic approximation, it was assumed that the phases of the eigenfunctions $\psi_k(t)$ are arbitrary at each instant of time. This was in fact generally accepted up to 1984 when M. V. Berry showed that:

> In a cyclic system where the Hamiltonian at time t_f is the same as at time t_0, there is a relative change in the phase between $\psi_k(t_0)$ and $\psi_k(t_f)$ which cannot be removed by a phase transformation and thus has observable consequences.

To show this, consider the case where $H(t)$ varies so slowly that the system remains in its initial non-degenerate state with energy $E_a(t)$ and eigenfunction $\psi_a(t)$.

According to our previous treatment, the approximate solution of $i\hbar \frac{\partial \Psi}{\partial t} = H(t)\Psi(t)$ is then:

$$\Psi(t) = c_a(t)\,\psi_a(t)\exp\left[-\frac{i}{\hbar}\int_{t_0}^{t} E_a(t')\,dt'\right].$$

Since $\Psi(t)$ is in the state $\psi_a(t)$ at $t=t_0$, we can set $C_a(t_0)=1$. Moreover, since $\psi_a(t)$ should also be normalized to unity, we can write generally at $t \neq t_0$ that

$$C_a(t) = \exp[i\gamma_a(t)]. \quad \left(\gamma_a(t) \in \mathbb{R} \text{ and } \gamma_a(t_0)=0\right).$$

Now, $\exp\left[-\frac{i}{\hbar}\int_{t_0}^{t} E_a(t')dt'\right]$ is the usual dynamical phase factor whereas the SE gives us the following equation for $\gamma_a(t)$.

$$i\dot{\gamma}_a(t)\,\psi_a(t) = -\partial_t \psi_a(t),$$

with the solution $\gamma_a(t) = i\int_{t_0}^{t} \langle \psi_a(t') \mid \frac{\partial \psi_a(t')}{\partial t'} \rangle dt'$.

If the system is cyclic, then $H(t_f) = H(t_0)$ since the Hamiltonian returns to its value at $t=t_0$ at a later time $t=t_f$.
This also implies that $E_a(t_f) = E_a(t_0)$ and $\psi_a(t_0) = \psi_a(t_f)$.

The Berry phase is the accumulated phase change from t_0 to t_f:

$$\bar{\gamma}_a \equiv i\int_{t_0}^{t_f} \langle \psi_a(t') \mid \frac{\partial \psi_a(t')}{\partial t'} \rangle dt'$$

This turns out to be a physically observable quantity, thus with experimentally verifiable quantities. Importantly, the Berry-phase is gauge-invariant and a key message in the 1984 paper by Berry was that any gauge-invariant quantity is in principle observable.

In fact, let us see what happens when we try to eliminate $\bar{\gamma}_a$ by transforming $\psi_a \to \psi_a' = \psi_a \cdot e^{i\eta(t)}$. Under this transformation, the Berry phase becomes: $\bar{\gamma}_a'$; where:

$$\bar{\gamma}_a' = i \int_{t_0}^{t_f} \langle \psi_a'(t') | \frac{\partial \psi_a'(t')}{\partial t'} \rangle dt'$$

$$= i \int_{t_0}^{t_f} \langle \psi_a(t') | \frac{\partial \psi_a(t')}{\partial t'} \rangle dt' - \int_{t_0}^{t_f} \frac{d\eta(t')}{dt'} dt'$$

$$= \bar{\gamma}_a - \eta(t_f) + \eta(t_0).$$

Since $\psi_a(t_f) = \psi_a(t_0)$, it follows that $\eta(t_f) - \eta(t_0) = 2\pi n$, $n = 0, 1, 2, \ldots$ Thus, $\exp(i\bar{\gamma}_a) = \exp(i\bar{\gamma}_a')$ cannot be removed by a phase transformation.

Strictly speaking, the Berry phase $\bar{\gamma}_a$ is gaugeinvariant up to an integer multiple of 2π, whereas $\exp(i\bar{\gamma}_a)$ is absolutely gauge inv. and thus related to physical observables.

The $H(t)$ may be time dependent through a number of parameters, each of which slowly vary with time.

A common example: components of an external electric or magnetic field which interact with the system.

Consider the case where $H(t)$ depends on t via three parameters $R_1(t), R_2(t), R_3(t)$: $\quad H(t) = H[R_i(t)], \; i = 1, 2, 3.$

$H(t_f) = H(t_i) \Rightarrow R_i(t_f) = R_i(t_i)$. In vector notation $\vec{R} = (R_1, R_2, R_3)$, we can then write the Berry phase as:

$$\gamma_a = i \oint_C \langle \psi_a(\vec{R}) \,|\, \nabla_{\vec{R}} \, \psi_a(\vec{R}) \rangle \cdot d\vec{R}$$

where $\nabla_{\vec{R}}$ is the gradient in parameter space and the closed integral is taken along the curve C in parameter space.

We define the Berry connection:

$$\vec{A}(\vec{R}) \equiv i \langle \psi_a(\vec{R}) \,|\, \nabla_{\vec{R}} \, \psi_a(\vec{R}) \rangle .$$

Since it depends on the closed curve C, it is often called a geometrical phase (the Berry phase, that is). Such phases arise also in a number of non-adiabatic situations as well - not only the strictly adiabatic context discussed here.

In fact, a generalization of Berry's phase is the Aharonov-Anandan phase. Suppose a system evolves according to the SE, but that the change in $\mathcal{H}$ is neither adiabatic or cyclic. The system can then still exhibit a geometrical phase: all that is needed is a cyclic evolution of the state of the system. Such a cyclic evolution defines a closed path C in the Hilbert space of the state.

Regardless of whether this evolution is adiabatic or not, it leaves the system with a dynamical phase, which depends on the Hamiltonian, and a geometrical phase, which depends on the path C.

We also remark that by applying Stokes' theorem, we have:

$$\gamma_a = \oint_C \vec{A}(\vec{R}) \cdot d\vec{R} = \iint \vec{B} \cdot d\vec{S}$$

where S is the surface bound by the closed path C and

$\vec{B} = \nabla_{\vec{R}} \times \vec{A}(\vec{R})$. $\equiv$ Berry curvature.

When treating the Aharonov-Bohm effect, we will see a concrete example of the physical consequences of these kind of geometrical phases.

Closing remarks: is the concept of a Berry / geometrical phase reconcilable with the fact that the overall phase of a quantum system is unobservable? Yes: because the Berry phase expresses the total phase accumulated during a cycle (either a cyclic evolution of the state or the Hamiltonian) change

We assumed for simplicity in our derivation that we know that the phase at $t = t_0$ was $\gamma_a(t=t_0) = 0$, but generally the Berry phase expresses the phase difference:

$$\bar{\gamma}_a \equiv \gamma_a(t=t_f) - \gamma_a(t=t_0) = i \int_{t_0}^{t_f} \left\langle \psi_a(t') \middle| \frac{\partial \psi_a(t')}{\partial t'} \right\rangle dt'.$$

And phase differences are certainly observable, even if the phase at a given time is not.

EXAMPLES A quantum system may be in a superposition of states: then, the relative phase between the states is observable.

$$\psi = \psi_A + \psi_B = |\psi_A| e^{i\alpha_A} + |\psi_B| e^{i\alpha_B}$$

$$= \left(|\psi_A| e^{i(\alpha_A - \alpha_B)} + |\psi_B| \right) e^{i\alpha_B}$$

$\Rightarrow |\psi|^2$ depends on $\Delta\varphi \equiv \alpha_A - \alpha_B$.

More generally, consider two paths $\vec{R}(t)$ and $\vec{R}'(t)$ with the same end-points : $\vec{R}(t_0) = \vec{R}'(t_0)$ and $\vec{R}(t_f) = \vec{R}'(t_f)$.

If the system now evolves in a superposition of states $|\psi_i(\vec{R}(t))\rangle$ and $|\psi_i(\vec{R}'(t))\rangle$. When $t = t_f$, the relative phase of this superposition (analogue to $\Delta\alpha$ above) contains two parts

- Relative dynamical phase
- The Berry phase : the difference between the Berry connection $\vec{A}$ integrated along $\vec{R}$ and $\vec{A}$ integrated along $\vec{R}'$. In effect, it is the circular integral $\oint_C \vec{A}(\vec{r}) \cdot d\vec{r}$ where C is the closed path comprised of $\vec{R}$ and $\vec{R}'$.

The sudden approximation

Let's now consider the opposite scenario of adiabaticity: we switch on a large disturbance abruptly!

Consider first the case where H changes abruptly from H_0 to H_1 at $t=0$. (H_0 and H_1 are both constants in time).

$\underline{t<0}$: $H_0 \psi_k^{(0)} = E_k^{(0)} \psi_k^{(0)}$

$\psi_n^{(0)}$ are orthonormal and form a complete set (not necessarily discrete).

$\underline{t>0}$: $H_1 \varphi_n^{(1)} = E_n^{(1)} \varphi_n^{(1)}$. ($\varphi_n^{(1)}$ also orthonormal and complete).

General solution of time-dependent S.E:

$\underline{t<0}$: $\Psi(t) = \sum_k c_k^{(0)} \psi_k^{(0)} \exp(-i E_k^{(0)} t/\hbar)$

$\underline{t>0}$: $\Psi(t) = \sum_n d_n^{(1)} \varphi_n^{(1)} \exp(-i E_n^{(1)} t/\hbar)$

Assume $\Psi(t)$ normalized to unity: $c_k^{(0)}$ and $d_n^{(1)}$ are the usual probability coefficients for finding system in state $\psi_k^{(0)}$ and $\varphi_n^{(1)}$ at $t<0$ and $t>0$.

Time-dep. S.E. is first order in time $\rightarrow \Psi(t)$ must be a continuous function of t. Thus, at $t=0$:

$$\sum_k c_k^{(0)} \psi_k^{(0)} = \sum_n d_n^{(1)} \varphi_n^{(1)}$$

Take scalar product with $\varphi_n^{(1)}$:

$$d_n^{(1)} = \sum_k c_k^{(0)} \langle \varphi_n^{(1)} | \psi_k^{(0)} \rangle \qquad (*)$$

We now have a way to obtain the prob. coefficients after the sudden change at $t=0$, given that $c_k^{(0)}$ are known.

In practice, the change from H_0 to H_1 will take place over a short time interval τ rather than being instantaneous. The simplest way to approximate this scenario is to use $(*)$, but how large can τ be and still expect $(*)$ to be useful?

We derive a simple criterion of validity. Let:

$$H = \begin{cases} H_0 & t<0 \\ H_i & 0<t<\tau \\ H_1 & t>\tau \end{cases}$$

where $H = H_i$ is time-independent during the intermediate period τ.

If $\{\chi_i^{(i)}\}$ denotes a complete, orthonormal set of eigenfunctions of H_i ($H_i \chi_i^{(i)} = E_i^{(i)} \chi_i^{(i)}$), then the general solution

of time-dep. SE is:

$$\Psi(t) = \begin{cases} \sum_k c_k^{(0)} \psi_k^{(0)} \exp(-i E_k^{(0)} t/\hbar) & t<0 \\ \sum_l a_l^{(i)} \chi_l^{(i)} \exp(-i E_l^{(i)} t/\hbar) & 0<t<\tau \\ \sum_n d_n^{(1)} \varphi_n^{(1)} \exp(-i E_n^{(1)} t/\hbar) & t>\tau \end{cases}$$

where the coefficients $a_l^{(i)}$ must also be time-independent.

Since $\Psi(t)$ is continuous at $t=0$, $\sum_k c_k \psi_k^{(0)} = \sum_l a_l^{(i)} \chi_l^{(i)}$, so that:

$$a_l^{(i)} = \sum_k c_k^{(0)} \langle \chi_l^{(i)} | \psi_k^{(0)} \rangle \qquad (*)$$

Continuity at $t=\tau$ yields:

$$\sum_l a_l^{(i)} \chi_l^{(i)} \exp(-i E_l^{(i)} \tau/\hbar) = \sum_n d_n^{(1)} \varphi_n^{(1)} \exp(-i E_n^{(1)} \tau/\hbar).$$

Taking the scalar product with one particular $\varphi_n^{(1)}$:

$$d_n^{(1)} = \sum_l a_l^{(i)} \langle \varphi_n^{(1)} | \chi_l^{(i)} \rangle \exp[i (E_n^{(1)} - E_l^{(i)}) \tau/\hbar]$$

Inserting $(*)$ gives:

$$d_n^{(1)} = \sum_k \sum_l c_k^{(0)} \langle \varphi_n^{(1)} | \chi_l^{(i)} \rangle \langle \chi_l^{(i)} | \psi_k^{(0)} \rangle \exp[i (E_n^{(1)} - E_l^{(i)}) \tau/\hbar]$$

Compare this with the result we obtained in the sudden approx.:

$$d_n^{(1)} = \sum_k c_k^{(0)} \langle \varphi_n^{(1)} | \psi_k^{(0)} \rangle.$$

At $\tau = 0$, they are equivalent (as expected). If $\tau \neq 0$, the difference arises since $\exp[i(E_n^{(1)} - E_i^{(i)})\tau/\hbar]$ is not unity. If the sudden approximation is to be valid, we thus need τ to be small compared to all the quantities $\hbar/|E_n^{(1)} - E_i^{(i)}|$, so that $\exp[\ldots] \simeq 1$.

An interesting special case of the sudden approximation is when the system initially ($t<0$) is in a particular stationary state $\psi_a^{(0)} \exp(-iE_a^{(0)}t/\hbar)$ where $\psi_a^{(0)}$ is an eigenstate of H_0. Then, $c_n^{(0)} = \delta_{na}$, and the probability amplitude of finding the system in eigenstate $\varphi_n^{(1)}$ of H_1 after the sudden change in the Hamiltonian has occurred is: $d_n^{(1)} = \langle \varphi_n^{(1)} | \psi_a^{(0)} \rangle$.

EXAMPLE Beta decay of the tritium nucleus.

Tritium atom: a nucleus ^3H (one proton + two neutrons) and one electron.

It is unstable and decays into the nucleus ^3He (two protons + one neutron):

$$^3H \rightarrow {}^3He + e^- + \bar{\nu}_e .$$

Assume that the tritium atom is in its ground state before the β-decay of ^3H takes place.

Question: what is the influence of the decay on the atomic electron?

We first note that in the β-decay process above, the electron is emitted from the tritium nucleus with, in most cases, an energy of order several keV. This means that its resulting velocity v is much higher than the velocity $V_0 \simeq c/137$ of the atomic electron in the ground-state of tritium. If $a_0 \equiv$ Bohr radius, the electron will leave the atom in a time $\tau \simeq a_0/v$. This is much shorter than the period $T = \frac{2\pi a_0}{V_0}$ associated with the motion of the atomic electron.

Thus, we can justify a scenario where the nuclear charge "seen" by the atomic electron changes instantaneously from Ze to $Z'e$ where $Z=1$, $Z'=2$.

$H(t<0)$ for ${}^3H+e^-$: $H = H_0 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Ze^2}{(4\pi\varepsilon_0)r}$, $Z=1$

$H(t>0)$ for ${}^3He+e^-$ ion : $H = H_1 = -\frac{\hbar^2}{2m}\nabla^2 - \frac{Z'e^2}{(4\pi\varepsilon_0)r}$, $Z'=2$.

with m being the mass of the atomic electron. We neglected the recoil effect on the nucleus, since its mass $M \gg m$.

The eigenfunctions of H_0 and H_1 are hydrogenic wavefunctions. Since the tritium atom is assumed to initially be in its ground state (quantum numbers $n=1, l=0, m=0$),

The prob. coeff. $d^{(1)}_{n'l'm'}$ of finding the atomic electron in a discrete eigenstate $(n'l'm')$ of H_1 at $t>0$ is

$$d^{(1)}_{n'l'm'} = \langle \psi^{(Z'=2)}_{n'l'm'} | \psi^{(Z=1)}_{100} \rangle = \int \left(\psi^{(Z'=2)}_{n'l'm'}\right)^{*} (\vec{r})\, \psi^{(Z=1)}_{100}(\vec{r})\, d\vec{r}$$

where $\psi^{(Z)}_{nlm}(\vec{r})$ is a hydrogenic wavefunction with atomic number Z.

We know that $\psi^{(Z)}_{nlm}(\vec{r}) = R^{(Z)}_{nl}(r)\, Y_{lm}(\theta,\varphi)$, and from the orthonormality properties of Y_{lm}, one may verify that the only non-vanishing prob. coefficients $d^{(1)}_{n'l'm'}$ are those belonging to the s-states $(l'=m'=0)$:

$$d^{(1)}_{n'00} = \int_0^\infty R^{(Z'=2)}_{n'0}(r)\, R^{(Z=1)}_{10}(r)\, r^2 dr \qquad (\dagger)$$

For the particular case $n'=1$, we get:

$$d^{(1)}_{100} = \int_0^\infty R^{(Z'=2)}_{10}(r)\, R^{(Z=1)}_{10}(r)\, r^2 dr$$

$$= 2^{7/2} a_0^{-3} \int_0^\infty dr\, r^2 \exp(-3r/a_0) = \frac{16\sqrt{2}}{27}.$$

Hence, the probability that the $(^3He^{++}e^-)$ ion is found in its ground state is $P^{(1)}_{100} = |d^{(1)}_{100}|^2 = \frac{512}{729} \simeq 0.702$.

Thus, the total probability for $(^3He^{++}e^-)$ ion to be either excited or even ionised is $1 - P^{(1)}_{100} \simeq 0.298$.

More generally, the integral (†) may be performed for any n', and the resulting probability of finding $(^3He^+ + e^-)$ in an S-state with principal quantum number n' is:

$$p^{(1)}_{n'00} = |d^{(1)}_{n'00}|^2 = \frac{2^9 n'^5 (n'-2)^{2n'-4}}{(n'+2)^{2n'+4}}$$

This allows us to compute the ionisation probability explicitly:

$$p^{(1)}_{ion} = 1 - \sum_{n'=1}^{\infty} p^{(1)}_{n'00} \simeq 0.026. \qquad \text{(can be evaluated numerically)}$$

CHAPTER 13

SCATTERING THEORY

Particles that are incident toward a scattering center - e.g. a different particle - will in general be deflected due to the interaction. The distribution of angles of deflection will depend on the details of the setup.

Experimentally measuring this distribution will provide us with information about the type of interaction that is in play.

We distinguish between

- Elastic scattering : k. energy of the scattered particles is preserved.
- Inelastic scattering: k. energy is not preserved, e.g. due to photon taking off with part of the energy

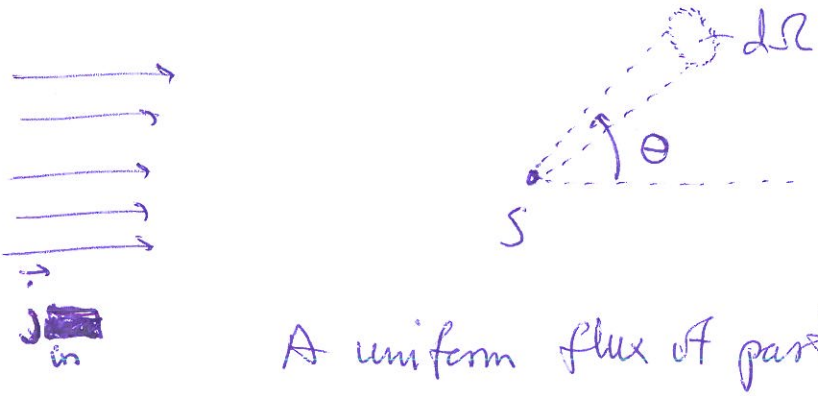
We will consider elastic scattering with the two same particles before and after.

13.1 | Scattering cross section

Consider scattering between two particles. For a potential $V(\vec{r}_1 - \vec{r}_2)$, we know that this is equivalent to a one-particle problem in the potential $V(\vec{r})$ and with a particle mass $m = \frac{m_1 m_2}{m_1 + m_2}$.

We shall initially consider the scattering problem in the center-of-mass (CoM) frame and later see how the results are expressed in the lab-frame (where the scattering potential is at rest).

Consider the following idealized model:



A uniform flux of particles with density $\vec{j}_{in}$ is incident on a scattering center S. Detector counts particles scattered into solid angle $d\Omega = \sin\theta\, d\theta d\varphi$ enclosing the direction (θ, φ). The incident axis is $\theta = 0$.

We have previously defined:

$$\frac{d\sigma}{d\Omega} = \frac{\#\text{ particles scattered into } d\Omega \text{ pr. unit time}}{d\Omega \cdot j_{in}}$$

Since j_{in} is the # of particles incident per time and area, inspection shows that $\frac{d\sigma}{d\Omega}$ has dimension area.

Total scattering cross section:

$$\sigma = \int \frac{d\sigma}{d\Omega} d\Omega = \int_{\varphi=0}^{2\pi} \int_{\theta=0}^{\pi} \frac{d\sigma}{d\Omega} \sin\theta \, d\theta \, d\varphi$$

$[\sigma]$ = area as well. It corresponds to the total area that incident particles pass through which will cause scattering.

Put differently: imagine an area of size σ in the incident flux of particles. The number of particles passing through this area will be equally large as the number of particles that ultimately are scattered in some direction.

For instance, for a hard sphere: $\sigma = 4\pi R^2$.

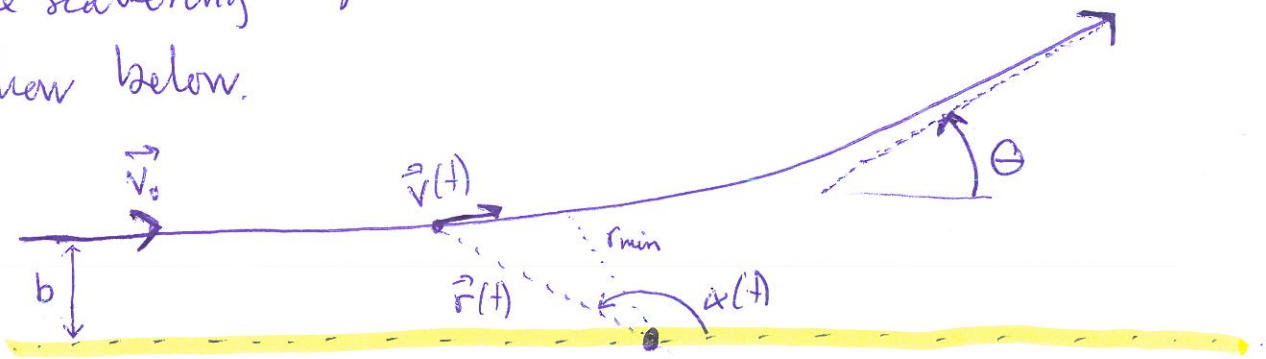
We will primarily stick to central potentials $V(\vec{r}) = V(|\vec{r}|)$, which thus do not depend on the azimuthal angle φ due to symmetry.

13.2 Classical scattering theory

We will look at the classical case prior to the QM treatment. For a central potential (spherically symmetric), the trajectory of the particle will lie in a plane and is characterized by two quantities:

- The velocity v_0 far away from the scatt. center
- The impact parameter b (see figure below).

The scattering angle Θ is determined by v_0 and b, as we show below.



Assuming that $V(r \to \infty) = 0$, energy conservation gives:

$$E = \frac{1}{2} m v_0^2 = \frac{1}{2} m v(t)^2 + V(r(t)) = \frac{1}{2} m (\dot{r}^2 + r^2 \dot{\alpha}^2) + V(r)$$

and conservation of angular momentum (due to rot. symmetry) gives: $L = m b v_0 = m |\vec{r} \times \vec{v}| = m r^2 \dot{\alpha}$

where α characterizes the angle of the instantaneous point along the trajectory.

Now, express E via L: $E = \frac{1}{2} m \dot{r}^2 + \frac{L^2}{2mr^2} + V(r)$

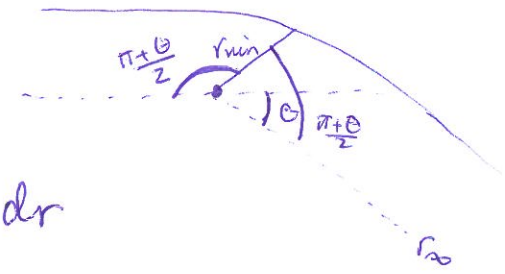
and use that $\dot{r} = \frac{dr}{dt} = \frac{dr}{d\alpha} \cdot \frac{d\alpha}{dt} = \frac{dr}{d\alpha} \cdot \frac{L}{mr^2}$. Combine:

$$d\alpha = \frac{L/r^2}{\sqrt{2mE - 2mV(r) - L^2/r^2}}\, dr$$

We integrate this expression from $r = r_{min}$ to $r = \infty$.

Since r_{min} by definition is given by $\frac{dr}{d\alpha} = 0$, the $\sqrt{\ldots}$ must be zero there.

For repulsive forces (as shown in our previous figure), the change in α when going from r_{min} to $r = \infty$ is then $(\pi - \Theta)/2$, while for attractive forces it would be $(\pi + \Theta)/2$.



The integration thus provides:

$$\frac{1}{2}(\pi \pm \Theta) = \int_{r_{min}}^{\infty} \frac{L/r^2}{\sqrt{2mE - 2mV - L^2/r^2}}\, dr$$

Using $L = mbv_0$ and $E = \frac{1}{2} m v_0^2$, we get:

$$\frac{1}{2}(\pi \pm \Theta) = \int_{r_{min}}^{\infty} \frac{b/r^2}{\sqrt{1 - V(r) E^{-1} - b^2 r^{-2}}}\, dr$$

This relation defines the connection between b and Θ:
knowing b of the incident particle, we can compute Θ.

A certain interval db corresponds to an interval $d\Theta$ according to:

$$db = \left|\frac{db(\Theta)}{d\Theta}\right| d\Theta = \left|\frac{db(\Theta)}{d\Theta}\right| \frac{d\Omega}{2\pi \sin\Theta}$$

Abs. value has been introduced since $\frac{db}{d\Theta}$ is often negative:
larger impact parameter $\rightarrow$ smaller scattering angle.

To compute the cross section, we note that there is an area $2\pi b\,db$ contained between the impact parameters b and $b+db$.
The # of part. passing through this area pr. unit time is $j_{in} \cdot 2\pi b\,db$. According to our above treatment, the # of part. scattered into $d\Omega$ pr. unit time is then

$$j_{in} \cdot 2\pi b\,db = j_{in} \cdot b \cdot \left|\frac{db}{d\Theta}\right| \cdot \frac{d\Omega}{\sin\Theta}$$

Using our definition of the differential scattering cross section, we obtain:

$$\boxed{\frac{d\sigma}{d\Omega} = \frac{b(\Theta)}{\sin\Theta}\left|\frac{db(\Theta)}{d\Theta}\right|.}$$

To compute $\frac{d\sigma}{d\Omega}$, we thus have to identify $b = b(\theta)$.

EXAMPLE Coulomb-potential.

Two charges ze and $z'e$ interact via the well-known $V(r) = \frac{zz'e^2}{4\pi\varepsilon_0 r}$.

To find $b(\theta)$, we then have to compute:

$$\frac{1}{2}(\pi \pm \theta) = \int_{r_{min}}^{\infty} \frac{b/r^2}{\sqrt{1 - b^2/r^2 - zz'e^2/(4\pi\varepsilon_0 Er)}}\, dr$$

Upper sign: attraction ($zz' < 0$) Lower sign: repulsion ($zz' > 0$).

Introducing $x = \frac{b}{r}$ and $g \equiv \frac{zz'e^2}{8\pi\varepsilon_0 E b}$, we obtain:

$$\frac{1}{2}(\pi \pm \theta) = \int_0^{x_{max}} \frac{dx}{\sqrt{1 - x^2 - 2gx}} = \int_0^{\sqrt{1+g^2}-g} \frac{dx}{\sqrt{1 + g^2 - (x+g)^2}}$$

As commented on previously, x_{max} (or equivalently r_{min}) is determined by $\sqrt{\ldots} = 0$. This integral can be evaluated and yields:

$$\frac{1}{2}(\pi \pm \theta) = \frac{1}{2}\pi - \sin^{-1}\left(\frac{g}{\sqrt{1+g^2}}\right).$$

This can be rearranged to $g = \mp \tan\frac{\theta}{2}$, and inserting g:

$b = \mp \frac{zz'e^2}{8\pi\varepsilon_0 E} \cot\frac{\theta}{2}$. We finally end up with the scattering cross section (known as the Rutherford cross section):

$$\frac{d\sigma}{d\Omega} = \left(\frac{zz'e^2}{16\pi\varepsilon_0 E}\right)^2 \frac{1}{\sin^4\left(\frac{\theta}{2}\right)}$$

For small angles θ, $\frac{d\sigma}{d\Omega} \sim \frac{1}{\theta^4}$, causing the integral to diverge:

$$\sigma = \int_0^\pi \frac{d\sigma}{d\Omega} 2\pi \sin\theta \, d\theta \to \infty.$$

Small θ corresponds to large impact parameter b, and so this result reflects the fact that the Coulomb-potential has infinite range, causing scattering of <u>all</u> incident particles.

<u>More generally</u>: a potential $V(r) \neq 0$ for $r \leq a$ and $V(r) = 0$ for $r > a$ will have $\sigma = \pi a^2$ classically. In QM, this is different: σ can be infinite or finite when the range $a \to \infty$, depending on how fast the potential $V(r)$ goes to zero when $r \to \infty$.

The Coulomb-interaction is the most important interaction in physics, and we will treat it quantum mechanically in what follows.

13.3 Scattering as a stationary problem

We have seen an example of this in elementary QM courses: scattering on a potential barrier in 1D. We thus seek the solution of the time-independent SE:

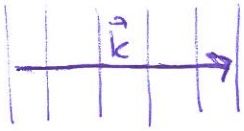
$$\left[-\frac{\hbar^2}{2m}\vec{\nabla}^2 + V(\vec{r})\right]\psi(\vec{r}) = E\psi(\vec{r})$$

and use appropriate boundary conditions for the solution ψ in order to describe an incident flux of particles and an outgoing stream of scattered particles.

Let $E \equiv \frac{\hbar^2 k^2}{2m}$ and $U(\vec{r}) \equiv \frac{2m}{\hbar^2}V(\vec{r}) \Rightarrow (\vec{\nabla}^2 + k^2)\psi = U\psi$.

Near the scattering center S, the behaviour of ψ may be complicated. However, for $r \to \infty$ we can neglect $U(\vec{r})$ and the resulting free-particle solution should then describe an incident plane-wave and radially outgoing particles:

$$\psi \simeq \psi_{in} + \psi_{scatt} \quad \text{for } r \to \infty$$



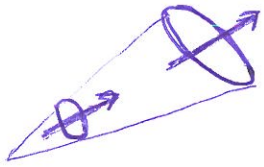
$r = 0$ • S

The incident wave: $\psi_{in} = Ce^{i\vec{k}\cdot\vec{r}}$ where C = constant and $\hbar k = p_i = \sqrt{2mE}$.

The scattered wave: must be a spherical wave with the same energy (wavenumber k) as the incident one,

$$\psi_{scatt} = C f(\theta, \varphi) \frac{e^{ikr}}{r}.$$

The factor $\frac{1}{r}$ ensures that the outgoing current density j_{scatt} is proportional to $\frac{1}{r^2}$. Now, since the surface element corresponding to a solid angle element $d\Omega$ increases with distance as $r^2 d\Omega$, this means for large distances it is the same number of particles passing through any cross-section of the given solid angle element, as expected:



The factor $f(\theta, \varphi)$ determines the angular distribution and is known as the scattering amplitude, which is determined by $V(\vec{r})$. We shall return to this issue.

Let us now determine the diff. scatt. cross section expressed in terms of $f(\theta,\varphi)$. We know that $\vec{j} = \mathrm{Re}\{\psi^* \frac{\hbar}{im} \nabla\psi\}$.

The definition of $d\sigma$ is: $d\sigma = \dfrac{j_{scatt} \cdot r^2 d\Omega}{j_{in}}$.

We obtain: $j_{in} = \mathrm{Re}\{\psi_{in}^* \frac{\hbar}{im} \nabla\psi_{in}\} = \frac{\hbar k}{m} |C|^2$.

Similarly: $j_{scatt} = |C|^2 |f(\theta,\varphi)|^2 \cdot \frac{\hbar k}{m r^2}$

$$\longrightarrow \boxed{\frac{d\sigma}{d\Omega} = |f(\theta,\varphi)|^2}$$

Since C turned out to be insignificant, we set $C=1$ in what follows for simplicity.

Note how we have obtained an expression for $\frac{d\sigma}{d\Omega}$ using only the asymptotic (large r) form of the wavefunction.

Summarizing the idea so far:

We seek a solution of the time-indep. SE

$$(\nabla^2 + k^2)\psi(\vec{r}) = U(\vec{r})\psi(\vec{r})$$

which for large r has the form

$$\psi(\vec{r}) \simeq e^{i\vec{k}\cdot\vec{r}} + f(\theta,\varphi)\frac{e^{ikr}}{r}.$$

The diff. scatt. cross section is then

$$\frac{d\sigma}{d\Omega} = |f(\theta,\varphi)|^2.$$

The remaining task is to determine f. First, a few comments:

(1) We have here assumed elastic scattering, thus neglecting the possibility of the particles making energy transitions during the collision.

(2) We have assumed free-particle behaviour at $r \to \infty$. For potentials with infinite range, it is essential how fast $V \to 0$ when $r \to \infty$. It turns out that $r \cdot V(r) \to 0$ for $r \to \infty$, we obtain the free-particle asymptotic behaviour. The Coulomb-potential does not satisfy this and we shall later see how this influences the asymptotic form.

(3) In a real experiment, one does not send in an infinite plane-wave toward S, but rather a beam that is collimated in space. The localized nature (let l_i be the width of the beam in i-direction) causes an uncertainty in the momentum: $\Delta p_i \simeq \hbar / l_i$. However, l_i will be much larger than atomic distances, and the lack of precision in momentum should be negligible compared to the change in momentum (direction) caused by the potential. We may thus disregard the finite-size effect of the beam and model it with a plane-wave.

④ In practice, one scatters particle on a macroscopic collection of particles rather than a single scattering center S, e.g. a gas of particles. To use our approach, the thickness of the target has to be large enough to cause sufficient scattering intensity, but small enough to keep multiple scattering at a minimum.

13.4 Integral equation for the scattering amplitude

Our strategy here will be to transform the SE into an integral equation in order to incorporate the correct asymptotic behaviour $\psi(\vec{r}) \simeq e^{i\vec{k}\cdot\vec{r}} + f(\theta,\varphi)\frac{e^{ikr}}{r}$.

This transformation is done with the aid of the Green function $G(\vec{r}-\vec{r}')$, defined by:

$$(\nabla^2 + k^2)\, G(\vec{r}-\vec{r}') = \delta(\vec{r}-\vec{r}').$$

If G is known, then the SE is equivalent to:

$$\psi(\vec{r}) = \psi_0(\vec{r}) + \int G(\vec{r}-\vec{r}')\, U(\vec{r}')\, \psi(\vec{r}')\, d^3r' \qquad (*).$$

where ψ_0 is a general solution of the homogeneous equation $(\nabla^2 + k^2)\psi_0 = 0$. To establish this equivalence, operate with $\nabla^2 + k^2$ on (*):

$$(\nabla^2+k^2)\psi = 0 + \int \delta(\vec{r}-\vec{r}')\, U(\vec{r}')\psi(\vec{r}')\, d^3r' = U(\vec{r})\psi(\vec{r})$$

which is precisely the SE.

The second-order diff. equation for G has two independent solutions:

$$G(\vec{r}-\vec{r}') = -\frac{e^{\pm ik|\vec{r}-\vec{r}'|}}{4\pi|\vec{r}-\vec{r}'|}$$

To show this, it is sufficient to demonstrate that $G(\vec{r}) = -\frac{e^{\pm ikr}}{4\pi r}$ satisfies $(\nabla^2 + k^2)\, G(\vec{r}) = \delta(\vec{r})$.

Since $\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}$ + angular derivatives, we get for $r>0$:

$$\frac{d}{dr}\frac{e^{\pm ikr}}{r} = \left(\frac{\pm ik}{r} - \frac{1}{r^2}\right)e^{\pm ikr} \quad \text{and} \quad \frac{d^2}{dr^2}\frac{e^{\pm ikr}}{r} = \left(-\frac{k^2}{r} \mp \frac{2ik}{r^2} + \frac{2}{r^3}\right)e^{\pm ikr}$$

which yields:

$$(\nabla^2+k^2)\frac{e^{\pm ikr}}{r} = \left(\frac{d^2}{dr^2} + \frac{2}{r}\frac{d}{dr} + k^2\right)\frac{e^{\pm ikr}}{r} = 0$$

This is consistent since $\delta(\vec{r}) = 0$ for $\vec{r} \neq 0$. To justify the presence of the δ-function, we integrate $(\nabla^2 + k^2) G$ over a spherical volume with radius R by using the formula:

$$\int_V \nabla^2 G \, d^3r = \int_{f(V)} \nabla G \cdot d\vec{f} = 4\pi R^2 \left(\frac{dG}{dr}\right)_{r=R}$$

where $f(V)$ is the surface of the volume V. We then get:

$$\int_{r \leq R} (\nabla^2 + k^2) G = \int_{r \leq R} (\nabla^2 + k^2) \frac{e^{\pm ikr}}{(-4\pi r)} d^3r$$

$$= 4\pi R^2 \left(\frac{\pm ike^{\pm ikR}}{-4\pi R} + \frac{e^{\pm ikR}}{4\pi R^2} \right) + k^2 \int_0^R \frac{e^{\pm ikr}}{-4\pi r} 4\pi r^2 dr$$

$$= \mp ikRe^{\pm ikR} + e^{\pm ikR} + k^2 \left[\frac{\mp r}{ik} e^{\pm ikr} - \frac{e^{\pm ikr}}{k^2} \right]_0^R = 1$$

Since the integral over $(\nabla^2 + k^2) G$ is 1 for <u>any</u> finite radius R, we must have $(\nabla^2 + k^2) G = \delta(\vec{r})$, which completes the proof.

Now that we know exactly what $G(\vec{r} - \vec{r}')$ is, we can insert it into (*) in order to find $\psi(\vec{r})$.

The choice of $\psi_0(\vec{r})$ is dictated by the b.c. and the fact that it has to satisfy $(\nabla^2 + k^2)\psi_0 = 0$. We set $\psi_0(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}$ since $U=0$ should give precisely $\psi = \psi_0 = e^{i\vec{k}\cdot\vec{r}}$ since there is no scattering in this case.

Secondly, we choose the + solution for G so that we recover the correct form $\frac{e^{+ikr}}{r}$ for large r. With these two choices, the solution for $\psi(\vec{r})$ then becomes:

$$\boxed{\psi(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} - \frac{1}{4\pi}\int \frac{e^{ik|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|} U(\vec{r}')\psi(\vec{r}')\,d^3r'}$$

($|\vec{r}-\vec{r}'| \simeq r$ for large r). If we now look at the behaviour of the above equation in the large-r limit, we will be able to identify $f(\theta,\varphi)$ by comparing directly with the form

$$\psi(\vec{r}) \simeq e^{i\vec{k}\cdot\vec{r}} + \frac{e^{ikr}}{r}\cdot f(\theta,\varphi).$$

First, we do the large-r expansion more accurately:

$$k|\vec{r}-\vec{r}'| = k\sqrt{r^2 - 2\vec{r}\cdot\vec{r}' + r'^2} = kr\sqrt{1 - \frac{2\vec{r}\cdot\vec{r}'}{r^2} + \frac{r'^2}{r^2}}$$

$$= kr\left(1 - \frac{\vec{r}'\cdot\vec{r}}{r^2} + O\left(\frac{1}{r^2}\right)\right) = kr - \vec{k}'\cdot\vec{r}' + O\left(\frac{1}{r}\right)$$

where $\vec{k}' \equiv k\frac{\vec{r}}{r}$.

$\vec{k}'$ points in the direction that the particle has after scattering.

The momentum of the final state is thus $\vec{p}_s = \hbar \vec{k}'$.

Note that $|\vec{p}_s| = \hbar |\vec{k}| = \hbar |\vec{k}'|$: conservation of momentum.

Using our expansion, the integral equation takes the form:

$$\psi(\vec{r}) \simeq e^{i\vec{k}\cdot\vec{r}} - \frac{1}{4\pi} \frac{e^{ikr}}{r} \int e^{-i\vec{k}'\cdot\vec{r}'} U(\vec{r}') \psi(\vec{r}') d^3r'$$

Now, we can finally read out the scattering amplitude:

$$\boxed{f(\theta,\varphi) = -\frac{1}{4\pi} \int e^{-i\vec{k}'\cdot\vec{r}'} U(\vec{r}') \psi(\vec{r}') d^3r'}$$

It may appear as if we still haven't accomplished much since this expression still depends on the unknown $\psi(\vec{r})$. However, it turns out that our formulation is still very useful. The reason is that we have now set up our problem in a manner which is suitable for an iterative treatment.

13.5 Born-approximation

If the scattering potential is weak (and we'll later specify what this means quantitatively), we can solve our integral equation for ψ by iteration: the n'th approximation is obtained by using the $(n-1)$'th approximation on the r.h.s. of

$$\psi(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} - \frac{1}{4\pi}\int \frac{e^{ik|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|} U(\vec{r}')\psi(\vec{r}')\, d^3r'.$$

The most basic approximation, $\psi^{(0)}(\vec{r})$, is simply to set it to the incident plane-wave. Thus, we get:

$$\psi^{(0)}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}$$

$$\psi^{(1)}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} - \frac{1}{4\pi}\int \frac{e^{ik|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|} U(\vec{r}') \underbrace{e^{i\vec{k}\cdot\vec{r}'}}_{\psi^{(0)}(\vec{r}')} d^3r'$$

$$\psi^{(2)}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}} - \frac{1}{4\pi}\int \frac{e^{ik|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|} U(\vec{r}')\psi^{(1)}(\vec{r}')\, d^3r$$

etc. In the same way, we can obtain better and better approximations for $f(\theta,\varphi)$ by inserting approximations for $\psi(\vec{r})$.

This expansion is known as the Born-approximation and one often settles for the lowest order correction. We now examine this in more detail.

First order Born-approximation

Using $\psi^{(0)} = e^{i\vec{k}\cdot\vec{r}}$, we get:

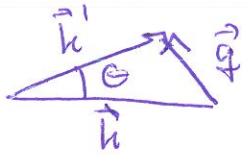
$$f^B(\theta,\varphi) = -\frac{1}{4\pi}\int e^{i(\vec{k}-\vec{k}')\cdot\vec{r}}\, U(\vec{r})\, d^3r$$

This first-order approx. is usually referred to as the Born-approx.
With $q \equiv \vec{k}'-\vec{k}$ and reinstating $U = 2mV/\hbar^2$, we get

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

In other words, f^B is essentially the Fourier-transform of the potential. The physical meaning of $\vec{q}$ is that it is the momentum-transfer during the collision (after-before):

$$q = 2k\sin\frac{\theta}{2}$$



Note that so far, we have not made any assumption about the potential being spherically symmetric. If it is, however, we may simplify the expression for f^B as follows.

Let $V(\vec{r}) = V(r)$ and $\vec{r}$ is the polar axis. We then obtain:

$$\int_{\nu=0}^{\pi}\int_{\tilde{\varphi}=0}^{2\pi} e^{-i\vec{q}\cdot\vec{r}}\, d\tilde{\varphi}\sin\nu\, d\nu = 2\pi\left[\frac{e^{-iqr\cos\nu}}{iqr}\right]_{\nu=0}^{\nu=\pi} = \frac{4\pi\sin(qr)}{qr}$$

The result for f^B is then:

$$f^B(\theta) = -\frac{2m}{\hbar^2 q}\int_0^\infty V(r)\sin(qr)\, r\, dr$$

where $q = 2k\sin\frac{\theta}{2}$. Note that $\tilde{\varphi}$ and ν are just integration variables without any special significance.

In the forward-scattering case ($\theta = 0$), f^B becomes independent on q and thus the energy of the particle. For other directions $\theta \neq 0$, the oscillating term $\sin(qr)$ renders the integral small when $qa \gg 1$ where a is a measure for the spatial range of the potential. This means that for high energies (large k), the diff. scatt. cross section is very small except when

$qa = 2ka\sin\frac{\theta}{2} \simeq 1$, which for large k means $\theta \simeq \frac{1}{ka}$.

We then conclude that high-energy particles do not change their direction much, keeping their trajectory $\theta \simeq 0$.

Total Scatt. cross section

We have $\sigma^B = \int \frac{d\sigma^B}{d\Omega} d\Omega = \int |f^B(\theta,\varphi)|^2 d\Omega$

For a spherically symmetric potential, we obtain:

$$d\Omega = 2\pi \sin\theta \, d\theta = 4\pi \sin\frac{\theta}{2}\cos\frac{\theta}{2} d\theta = \frac{2\pi}{k^2} q\, dq$$

where we utilized $2k\sin\frac{\theta}{2} = q \Rightarrow dq = k\cos\frac{\theta}{2} d\theta$.

σ^B can then be obtained by integrating over q:

$$\sigma^B = \frac{2\pi}{k^2} \int_0^{2k} |f^B(q)|^2 q\, dq$$

Since the integral grows as $E = \frac{\hbar^2 k^2}{2m}$ increases, σ^B cannot decrease faster than $\frac{1}{E}$. More precisely, if the integral converges at high energies, one obtains $\sigma^B \propto \frac{1}{E}$.

We're treating this problem non-relativistically, so "high energies" still means $E \ll mc^2$.

When is the Born-approx. valid?

The iteration procedure that we have utilized is based on the assumption that the incident plane-wave is not severely altered. In effect, $|\psi(\vec{r}) - e^{i\vec{k}\cdot\vec{r}}| \ll 1$.

Using our expression for ψ in the Born-approx. provides:

$$\left| \frac{1}{4\pi} \int \frac{e^{ik|\vec{r}-\vec{r}'|}}{|\vec{r}-\vec{r}'|} U(\vec{r}') e^{i\vec{k}\cdot\vec{r}'} d^3r' \right| \ll 1.$$

The modification of the incident wave is expected to be largest at the scattering center $\vec{r}=0$, so the strictest requirement is:

$$\left| \frac{1}{4\pi} \int \frac{e^{ikr'}}{r'} U(\vec{r}') e^{i\vec{k}\cdot\vec{r}'} d^3r \right| \ll 1$$

If we want an even stricter requirement, we take the absolute value of all factors in the integrand:

$$\int_0^\infty |U(\vec{r})|\, r\, dr \ll 1 \qquad [\text{used } d^3r = 4\pi r^2 dr \text{ for } U(\vec{r}) = U(r)]$$

When this equation (inequality) is satisfied, the Born-approx. is expected to be good for all energies.

EXAMPLE

For a constant potential V_0 with range R, the criterion of validity takes the form:

$$m|V_0|R^2/\hbar^2 \ll 1.$$

At the same time, we know that a negative potential $-|V_0|$ can bind states if $m|V_0|R^2 > \pi^2\hbar^2/8$ (see problem 5.2 in PC(A)). This is in agreement with the criterion: we expect the Born-approx. to be valid only when $|V_0|$ is sufficiently weak to be unable to bind a particle with mass equal to the incident particles.

For a finite-range potential with finite magnitude, one can always use the Born-approx. at sufficiently high energies.

To see this, let us go back to the k-dependent criterion $\left| \frac{1}{4\pi} \int \frac{e^{ikr'}}{r'} U(\vec{r}') e^{i\vec{k}\cdot\vec{r}'} d^3r' \right| \ll 1$. Assume a spherically symmetric potential $U(\vec{r}) = U(r)$, in which case we can perform the angular integration:

$$\int_0^{\pi} e^{ikr'\cos\nu} \sin\nu \, d\nu = \left[-\frac{e^{ikr'\cos\theta}}{ikr'} \right]_0^{\pi} = \frac{e^{ikr'} - e^{-ikr'}}{ikr'} = \frac{2\sin(kr')}{kr'}$$

This gives: $\left| \frac{1}{k} \int_0^{\infty} U(r') e^{ikr'} \sin(kr') \, dr' \right| \ll 1$

Since $|e^{ikr'}\sin(kr')| \leq 1$, the criterion:

$k \gg \int_0^\infty |U(r)|\,dr$ is sufficient to guarantee that the original k-dependent criterion is fulfilled. We conclude that for large enough k, we can always fulfil the above equation.

Note that using the Born-approx., we have actually obtained the same result for $\frac{d\sigma}{d\Omega}$ for a weak potential V as we did using time-dependent perturbation theory in chapter 11 ($d_\Omega\sigma = \left|\frac{m}{2\pi\hbar}\int V(\vec{r})\, e^{i(\vec{p}_i-\vec{p}_f)\cdot\vec{r}/\hbar}\, d^3r\right|^2$), which is reasonable since Born-approx. is good when the potential is weak or the particle energy is high.

EXAMPLE Let us apply this on a screened Coulomb-potential (known as Yukawa-potential): $V(r) = \frac{ZZ'e^2}{4\pi\varepsilon_0 r} e^{-\alpha r}$

α determines the screening radius. Using our derived result for the Born scattering amplitude gives:

$$f^B(\theta) = -\frac{2m}{\hbar^2 q}\frac{ZZ'e^2}{4\pi\varepsilon_0}\int_0^\infty e^{-\alpha r}\sin(qr)\,dr.$$

$$= -\frac{2m}{\hbar^2}\frac{ZZ'e^2}{4\pi\varepsilon_0}\frac{1}{\alpha^2+q^2}$$

Using the relations introduced previously:

$$q = 2k\sin\frac{\theta}{2} \quad \text{and} \quad k = p/\hbar = \sqrt{2mE}/\hbar$$

we can write down the diff. scatt. cross section:

$$\frac{d\sigma^B}{d\Omega} = |f|^2 = \left(\frac{zz'e^2/(4\pi\varepsilon_0)}{q^2\hbar^2(2m)^{-1} + 4E\sin^2\frac{\theta}{2}} \right)^2$$

It is interesting to note that since $\frac{d\sigma^B}{d\Omega}$ is finite for all angles when $\alpha \neq 0$, the total σ^B will also be finite – in contrast to the classical σ for this potential, which becomes infinite.

In the limit $\alpha \to 0$, we obtain the usual unscreened Coulomb-potential:

$$\frac{d\sigma^B}{d\Omega} = \left(\frac{zz'e^2}{16\pi\varepsilon E} \right)^2 \frac{1}{\sin^4\frac{\theta}{2}}$$

which is identical to the classical (Rutherford) result.

Remarkably, the QM Born-result for $\frac{d\sigma}{d\Omega}$ is not only identical to the classical result, but it is even identical to the exact QM Coulomb cross section!

See appendix E PCH for its derivation:

$$f_c(\theta) = \frac{n}{2k\sin^2\frac{\theta}{2}} e^{-2i\eta\ln\sin\frac{\theta}{2} + i\delta} \quad \text{with} \quad n = \frac{m}{k\hbar^2}\frac{Zz'e^2}{4\pi\varepsilon_0}$$

and where δ is a constant (independent on θ). Since $|e^{i\delta}| = 1$, this phase-factor has no consequence for the cross section.

However, we will later show that when scattering identical particles on each other, it will have an effect.

The result that $\frac{d\sigma^{classical}}{d\Omega} = \frac{d\sigma^{B}}{d\Omega} = \frac{d\sigma^{exact}}{d\Omega}$ for the Coulomb-potential must be regarded as coincidence, since the criteria we listed for the Born-approx. are not expected to be valid for the Coulomb-potential.

Elastic scattering on atoms

If the electrons are fast (energetic), we can treat scattering on neutral atoms via the potential:

$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r} + \frac{e^2}{4\pi\varepsilon_0}\int \frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} d^3r'$$

This consists of the Coulomb repulsion from the core $+Ze$ in addition to the potential from the electron distribution $-en(\vec{r})$. Charge neutrality $\Rightarrow \int n(\vec{r})d^3r = Z$.

We use Born-approximation, meaning that incident electron E satisfies $13.6\,Z^2\,eV \ll E \ll 500\,000\,eV$:
much larger than typical potential energy scale while still non-rel. ($m_e c^2 \simeq 0.5\,MeV$).

Now, we seek the scattering amplitude $f^B = -\frac{m}{2\pi\hbar^2}\int V(\vec{r})e^{-i\vec{q}\cdot\vec{r}}d^3r$.

Introducing $\vec{s} = \vec{r} - \vec{r}'$ and using our result for Yukawa-potential without screening ($\alpha = 0$):

$$\int \frac{e^{-i\vec{q}\cdot\vec{r}}}{|\vec{r}-\vec{r}'|}d^3r = e^{-i\vec{q}\cdot\vec{r}'}\int \frac{e^{-i\vec{q}\cdot\vec{s}}}{s}d^3s = e^{-i\vec{q}\cdot\vec{r}'}\frac{4\pi}{q^2}.$$

It follows: $f^B = \frac{e^2}{4\pi\varepsilon_0}\frac{2m}{\hbar^2}\frac{Z - F(\vec{q})}{q^2}$ with $F(\vec{q}) = \int n(\vec{r})e^{-i\vec{q}\cdot\vec{r}}d^3r$.

F, known as the atom-form factor, is the Fourier transformation of the electron distribution.

If $n(\vec{r})$ is spherically symmetric, then $F(\vec{q}) = F(q)$.

With $q = 2k\sin\frac{\theta}{2}$ and $E = \frac{\hbar^2 k^2}{2m}$ as usual, the diff. scatt. cross section becomes:

$$\frac{d\sigma}{d\Omega}^B = |f|^2 = \left(\frac{e^2}{16\pi\varepsilon_0 E}\right)^2 \cdot \frac{1}{\sin^4\frac{\theta}{2}} \left[Z - F(2k\sin\tfrac{\theta}{2})\right]^2.$$

By measuring $\frac{d\sigma}{d\Omega}^B$, we can thus obtain information about $F(q)$ and, in turn, the electronic distribution of the atom!

The idea is thus to scatter a simple particle on a complex structure (potential) to gain info about the complex structure.

Two limiting cases of interest:

1) When the scattering angle θ is <u>not small</u>, $q = 2k\sin\frac{\theta}{2}$ is sizable when k is large (energetic electrons).

The result is that F becomes small since the integrand oscillates around zero. Quantitatively, this requires that $\frac{1}{q} \ll$ atomic dimensions, i.e. $\lesssim 1\,\text{Å}$. If we thus can neglect F compared to Z, $\frac{d\sigma}{d\Omega}$ is essentially the Rutherford cross section. This result makes sense physically: a particle with high E can only scatter a large angle θ if it comes close to the core.

2) In the opposite regime, for very small angles, we can expand F in powers of q:

$$F(q) = \int n(r)\left[1 - i\vec{q}\cdot\vec{r} + \frac{1}{2}(\vec{q}\cdot\vec{r})^2 + \dots\right] d^3r = Z - \frac{1}{6}q^2\int r^2 n(r)\, d^3r$$

The second term $\sim i\vec{q}\cdot\vec{r}$ vanishes due to symmetry. For the third term, we used that the integral with $q_x^2x^2 + q_y^2y^2 + q_z^2z^2$ is $1/3$ of the integral with $(q_x^2 + q_y^2 + q_z^2)r^2 = q^2r^2$.

Define the average atomic radius R:

$$R^2 = \frac{\int r^2 n(r)\, d^3r}{\int n(r)\, d^3r} = \frac{1}{Z}\int r^2 n(r)\, d^3r.$$

This yields $Z - F(q) \simeq \frac{1}{6}ZR^2q^2$. This is $\ll Z$ for small angles (small q), so that:

$$\frac{d\sigma^B}{d\Omega} \simeq \left(\frac{ZR^2}{3a_0}\right)^2 \quad \text{with} \quad a_0 = \frac{4\pi\varepsilon\hbar^2}{me^2}.$$

The scattering is then independent on θ and small when θ is small. This may be interpreted as the electron cloud effectively screening the core Ze at small scattering angles (classically, this corresponds to large impact parameters).

13.6 The method of partial waves.

So far: Born-approx. is good when E of the incident particle is large.

Now: Partial waves method is good in the opposite case, namely low energies. Useful for scattering of e.g. sound and developed in 1927 by Holtsmark and Faxén.

Scattering amplitude

We knew that the energy eigenfunctions for a spherically symmetric potential $V(r)$ can be written generally as:

$$\psi(r,\theta,\varphi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} c_{lm} R_l(r) Y_{lm}(\theta,\varphi) \qquad (*)$$

where $k^2 = 2mE/\hbar^2$ and $U(r) = 2m\hbar^{-2}V(r)$ where R satisfies:

$$\frac{d^2}{dr^2}(rR_l) + \left[k^2 - U(r) - \frac{l(l+1)}{r^2}\right](rR_l) = 0$$

We're interested in $E>0$ (continuous part of the spectrum) and cylinder symmetric (no φ-dependence) solutions, as is often the case in scattering problems.

Choose $\hat{z}$ as incident axis: $(*)$ independent on φ when $m=0$.

$Y_{lm}(\theta,\varphi)$ then reduces to Legendre-polynomials $P_l(\cos\theta)$.

These form a complete set for cylinder-symmetric functions, so that: $\psi(r,\theta) = \sum_{l=0}^{\infty} C_l R_l(r) P_l(\cos\theta)$ where C_l are constants.

We may then also express $f(\theta) = \sum_{l=0}^{\infty} f_l P_l(\cos\theta)$ where f_l are constants. This is the announced expansion in "partial waves", each characterized by a quantum number l.

Keep in mind that $P_l(\cos\theta)$ is an eigenfunction for $\vec{L}^2$ with eigenvalue $\hbar^2 l(l+1)$. We recall that the scattering amplitude $f(\theta)$ is defined from the asymptotic behaviour:

$$\psi(\vec{r}) - e^{i\vec{k}\cdot\vec{r}} \simeq f(\theta)\frac{e^{ikr}}{r} \quad \text{for } r\to\infty .$$

To expand f in partial waves, we must first expand $\psi(\vec{r})$ and $e^{i\vec{k}\cdot\vec{r}}$ in Legendre polynomials.

Start with the incident wave: $e^{i\vec{k}\cdot\vec{r}} = e^{ikr\cos\theta} = \sum_{l=0}^{\infty} d_l(kr) P_l(\cos\theta)$

Introduce $x = \cos\theta$ and use orthogonality of P_l:

$$\int_{-1}^{1} P_l(x) P_n(x)\, dx = \frac{2}{2l+1}\delta_{ln}$$

This gives: $e^{ikrx} = \sum_{l=0}^{\infty} d_l(kr) P_l(x) \Rightarrow \int_{-1}^{1} dx\, P_n(x) e^{ikrx}$

$$= \sum_{l=0}^{\infty} \int_{-1}^{1} dx\, d_l(kr) P_l(x) P_n(x)$$

$$\Rightarrow \quad d_\ell(kr) = \frac{2\ell+1}{2} \int_{-1}^{1} e^{ikrx} P_\ell(x)\,dx \qquad \text{by multiplying}$$

with $P_n(x)$ on both sides and integrating. We now want to see how this behaves for large r. To do so, consider general integrals of the form: $I = \int_{-1}^{1} e^{isx} g(x)\,dx$ for large s.

Consecutive partial integrations, integrating the expenential fenction, provides:

$$I = \left[g(x) \frac{e^{isx}}{is} \right]_{-1}^{1} - \int_{-1}^{1} g'(x) \frac{e^{isx}}{is}\,dx$$

$$= \left[g(x) \frac{e^{isx}}{is} - g'(x) \frac{e^{isx}}{(is)^2} \right]_{-1}^{1} + \int_{-1}^{1} g''(x) \frac{e^{isx}}{(is)^2}\,dx$$

and so forth. Seince s is presumed to be large, we obtain smaller anel smaller terms. The dominating term for large s is then:

$$I = \int_{-1}^{1} e^{isx} g(x)\,dx = g(1) \frac{e^{is}}{is} - g(-1) \frac{e^{-is}}{is} + O(s^{-2})$$

In our case, $s = kr$ and $g(x) = P_\ell(x)$. Moreover, $P_\ell(1) = 1$ and $P_\ell(-1) = (-1)^\ell$ by definition. Hence, the asymptotic behaviour of d_ℓ is:

$$d_\ell \approx \frac{2\ell+1}{2ikr} \left(e^{ikr} - (-1)^\ell e^{-ikr} \right)$$

Using $(-1)^l = e^{i\pi l}$ and $2i\sin y = e^{iy} - e^{-iy}$, we rewrite this to:

$$d_l(kr) \simeq (2l+1)\, i^l \, \frac{\sin\left(kr - \frac{1}{2}l\pi\right)}{kr} \quad \text{for large } r.$$

We have now managed to identify how $e^{i\vec{k}\cdot\vec{r}}$ is expanded for large $\vec{r}$. It remains to find the asymptotic behaviour of $\psi(\vec{r})$.

We have $\psi(r,\theta) = \sum_{l=0}^{\infty} c_l R_l(r) P_l(\cos\theta)$ where the equation determining R_l in the limit $r \to \infty$ reads:

$$\frac{d^2}{dr^2}(rR_l) + k^2(rR_l) = 0. \qquad (*)$$

Here, we disregarded $\frac{l(l+1)}{r^2}$ and $U(r)$ [this is ok when $U(r)$ drops faster than $\frac{1}{r}$ for large r].

The solution of $(*)$ is sine and cosine functions. With two arbitrary constants c_l and δ_l, we can write the general solution as:

$$rR_l \simeq (2l+1)\, i^l c_l \sin\left(kr - \tfrac{1}{2}l\pi + \delta_l\right) \quad \text{for large } r.$$

We've written the solution in this form to look as similar as possible to the expansion of $e^{i\vec{k}\cdot\vec{r}}$ obtained previously.

The quantity δ_l is the phase picked up by the wavefunction as a consequence of the scattering potential and is referred to as the l'th scattering phase. In the absence of any potential $U(r)$, one finds $\delta_l = 0$.

To determine δ_ℓ in the general case, one has to solve the radial equation for all r and then inspect R_ℓ for large r.

Inserting our expansions, we have found:

$$\psi(\vec{r}) - e^{i\vec{k}\cdot\vec{r}} \simeq \sum_{\ell=0}^{\infty} P_\ell(\cos\theta)(2\ell+1) i^\ell \left[c_\ell \sin\left(kr - \tfrac{1}{2}\ell\pi + \delta_\ell\right) - \sin\left(kr - \tfrac{1}{2}\ell\pi\right)\right] \frac{1}{kr}$$

In order to finally identify $f(\theta)$, we should now enforce the condition that the above expression should only contain spherical waves of the form e^{ikr}/r. This is accomplished by noting that:

$$[\ldots] = \frac{1}{2i}\left(c_\ell e^{i\delta_\ell} - 1\right) e^{i\left(kr - \frac{1}{2}\ell\pi\right)} - \frac{1}{2i}\left(c_\ell e^{-i\delta_\ell} - 1\right) e^{-i\left(kr - \frac{1}{2}\ell\pi\right)}$$

It is clear that we must choose $c_\ell = e^{i\delta_\ell}$ to remove the e^{-ikr} term, which leaves us with:

$$\psi(\vec{r}) - e^{i\vec{k}\cdot\vec{r}} \simeq \frac{e^{ikr}}{2ikr} \sum_{\ell=0}^{\infty} (2\ell+1)\left(e^{2i\delta_\ell} - 1\right) P_\ell(\cos\theta).$$

Since $e^{2i\delta_\ell} - 1 = 2ie^{i\delta_\ell}\sin\delta_\ell$, we can now identify $f(\theta)$:

$$\boxed{f(\theta) = \frac{1}{k} \sum_{\ell=0}^{\infty} (2\ell+1) e^{i\delta_\ell} \sin\delta_\ell \, P_\ell(\cos\theta)}$$

and, as usual, $\frac{d\sigma}{d\Omega} = |f(\theta)|^2$.

We have not solved the problem entirely yet, but we've established a connection between the solution of the radial equation (i.e. determining δ_l) and $f(\theta)$. Will look at a concrete application later where δ_l is determined and hence solving the problem.

Total scattering cross section

Our expression for $f(\theta)$ determines σ:

$$\sigma = \int_0^\pi |f(\theta)|^2 2\pi \sin\theta \, d\theta = \frac{2\pi}{k^2} \sum_{l,l'} (2l+1)(2l'+1) e^{i\delta_l - i\delta_{l'}} \times \sin\delta_l \sin\delta_{l'} \int_{-1}^{1} P_l(x) P_{l'}(x) \, dx$$

Using the aforementioned orthogonality of $P_l(x)$, we get:

$$\boxed{\sigma = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2\delta_l}$$

We may note an interesting relation between σ and the forward-scattering amplitude ($\theta = 0$). Setting $\theta = 0$ in $f(\theta) = \frac{1}{k} \sum_{l=0}^{\infty} (2l+1) e^{i\delta_l} \sin\delta_l P_l(\cos\theta)$ and using $P_l(1) = 1$, we get

$$f(0) = \frac{1}{k} \sum_{l=0}^{\infty} (2l+1) e^{i\delta_l} \sin\delta_l$$

It follows that we can write:

$$\boxed{\sigma = \frac{4\pi}{k} \operatorname{Im}\{f(0)\}}$$

This relation is known as the optical theorem.

We will later give a general proof of this theorem. The fact that $f(0)$ appears is related to that in order to cause scattering, the incident beam must be weakened. This can be achieved via destructive interference between incident beam and outgoing forward-scattered beam, described precisely via $f(0)$.

Number of significant phases

If particles with momentum $\hbar k$ approach a potential with range R, only particles with angular momentum $\hbar kR$ or less will be scattered.

Angular momentum size $\hbar\sqrt{l(l+1)} \Rightarrow \boxed{\sqrt{l(l+1)} \leq kR}$

For low energies $kR \ll 1$ (particle wavelength $\frac{2\pi}{k} \gg R$), only $l=0$ contributes. In this case, $f \simeq k^{-1} e^{i\delta_0} \sin\delta_0$ as only the $l=0$ partial wave contributes and we obtain isotropic scattering since:

$$\frac{d\sigma}{d\Omega} \simeq k^{-2}\sin^2\delta_0 \qquad \text{and} \qquad \sigma = \frac{4\pi}{k^2}\sin^2\delta_0 .$$

This shows why the partial wave method is so useful at low energies.

The scattering amplitude has dimension length.

The low-energy limit for f, which for finite-range potentials is independent on angle, is often called the scattering length a:

$$\lim_{k\to 0} f = -a. \qquad \text{It results in } \sigma = 4\pi a^2.$$

To be more specific about what "low energies" means, note that $kR \ll 1$ gives:

$$E = \frac{\hbar^2 k^2}{2m} \ll \frac{\hbar^2}{2mR^2} = \frac{m}{m_e}\left(\frac{a_0}{R}\right)^2 \times 13.6 \text{ eV}.$$

(by using the energy expression for the $n=1$ Coulomb potential).

Ramsauer-Townsend effect: sign of the phase-change

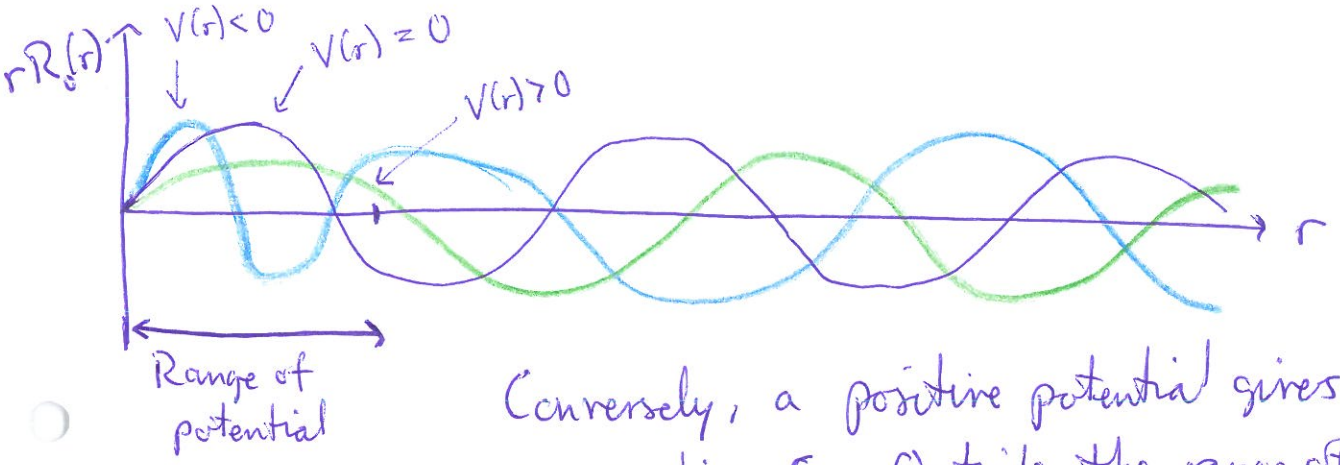
The phase-change δ_0 determines the scattering cross section at low energies. $\text{sign}(\delta_0)$ is related to the sign of the potential $U(r)$. To see this, recall that δ_0 was defined by writing the solution of ($u_0 \equiv r R_0(r)$)

$$\frac{d^2}{dr^2} u_0 + [k^2 - U(r)] u_0 = 0 \quad \text{on the form } u_0 \propto \sin(kr + \delta_0)$$

for large r.

If $U < 0$, the effective wavenumber $\sqrt{k^2 - U(r)}$ is larger than

for $U<0 \Rightarrow$ the particle wavelength λ inside the potential becomes shorter, so that ψ_0 will have a stronger curvature. The wave function is then "pulled" closer to $r=0$, corresponding to a positive phase-change:



Conversely, a positive potential gives a negative δ_0. Outside the range of U, the wavelength is of course the same in all cases.

If the attractive potential is sufficiently strong to "pull in" the partial wave $l=0$ to the extent that $\delta_0 = \pi$, then $\sin\delta_0 = \pi$ and $\sigma \to 0$: scattering cross section vanishes.

For a given potential, this effect (Ramsauer-Townsend) requires a specific energy.

Experimentally observed: extremely low minimum in the cross section of electrons scattering on noble gas atoms (Xe, Kr, Ar) at energies $E \sim 0.7$ eV.

Low-energy scattering on a hard-sphere potential

Consider a hard-sphere potential with range R, such that the wave function $u_0(r) = 0$ for $r \leq R$ while it is a free particle for $r > R$: $\quad u_0(r) \propto \begin{cases} 0 & r \leq R \\ \sin(kr - kR) & r > R \end{cases}$

(note that $u_0(r) = 0$ for $r = R$).

The phase shift $\delta_0 = -kR$ is negative as expected for positive potentials.

Thus, the total cross section (contribution from $l=0$, valid for any energy) is:

$$\sigma_0 = \frac{4\pi}{k^2} \sin^2\delta_0 = \frac{4\pi}{k^2} \sin^2(kR).$$

For low energies, the partial wave $l=0$ gives the dominant contribution. In this case, $k \ll \frac{1}{R}$ so that $\sin(kR) \simeq kR$

$$\Rightarrow \quad \underline{\sigma \simeq 4\pi R^2}.$$

It is interesting to note that this QM expression is four times as large as the classical result for this potential, $\sigma_{classical} = \pi R^2$.

For the opposite limit, high energies, one obtains $\sigma = 2\pi R^2$: still different from $\sigma_{classical}$. Can you figure out why the QM result is different, physically?

Resonant scattering

To illustrate this phenomenon, consider low-energy scattering on a well-potential: $V(r) = \begin{cases} -V_0 & \text{for } r \leq R \\ 0 & \text{for } r > R \end{cases}$.

We know by now that at low energies $kR \ll 1$, only the partial wave $l=0$ contributes significantly to the cross section σ, according to $\sigma = \frac{4\pi}{k^2} \sin^2\delta_0$.

The task is to determine δ_0. To do so, we must relate the solution for $r \leq R$: $u_0(r) = A \sin(\chi r)$ with $\chi = \sqrt{2m(E+V_0)/\hbar^2}$ with the solution for $r > R$: $u_0(r) = B \sin(kr + \delta_0)$ with $k = \sqrt{2mE/\hbar^2}$.

This is accomplished by continuity of u_0 and u_0' (usual boundary conditions) at $r = R$, which yields:

$$\tan(\delta_0 + kR) = \frac{k}{\chi} \tan(\chi R)$$

Neglecting the small term kR compared to δ_0, we get $\tan\delta_0 = \frac{k}{\chi} \tan(\chi R)$ so that:

$$\sin^2\delta_0 = \frac{\tan^2\delta_0}{1+\tan^2\delta_0} = \frac{k^2 \tan^2(\chi R)}{\chi^2 + k^2 \tan^2(\chi R)}$$

The total cross section now takes the form:

$$\sigma = \frac{4\pi}{k^2}\sin^2\delta_0 = \frac{4\pi}{k^2+\xi^2} \quad \text{where} \quad \xi = \frac{\kappa}{\tan(\kappa R)}.$$

For a given k, the cross section is maximal when $\xi = 0$, i.e. when $\kappa R = (n+\frac{1}{2})\pi$ (n = integer), Inserting the definition of κ, we get:

$$E = -V_0 + \frac{\hbar^2\pi^2}{2mR^2}(n+\tfrac{1}{2})^2 \qquad (*)$$

Physically, this means that when the incident particle has the right resonant energy according to (*), it will have a tendency to be bound by the potential and remain at $r \leq R$, thus causing a major disturbance of the wavefunction $\rightarrow$ large σ.

13.7 The optical theorem

We previously proved the relation $\sigma = \frac{4\pi}{k}\mathrm{Im}\{f(0)\}$ for a spherically symmetric potential $V(r)$. Now, we will demonstrate that this theorem is in fact a direct consequence of particle conservation: for a stationary problem, the net flux (of particles) into any volume [redacted] has to equal the net flux out.

Choosing the volume as a sphere centered around the scattering center with radius r, then $\int j_r r^2 d\Omega = 0$, where j_r is the radial probability current density. We know that this is given by $j_r = \mathrm{Re}\{\psi^* \frac{\hbar}{im} \frac{\partial}{\partial r} \psi\}$. To compute this, we choose r to be so large that we can use the asymptotic expression

$$\psi = e^{i\vec{k}\cdot\vec{r}} + f(\theta,\varphi)\, e^{ikr}/r \quad \text{for the wave function.}$$

We begin by computing $r^2 \psi^* \frac{\partial \psi}{\partial r} = r^2 \left[e^{-ikr\cos\theta} + f^* \frac{e^{-ikr}}{r}\right] \cdot$

$$\left[ik\cos\theta e^{ikr\cos\theta} + \left(\frac{ik\, e^{ikr}}{r} - \frac{e^{ikr}}{r^2}\right) f\right] = ikr^2\cos\theta + ikr\, e^{-ikr(1-\cos\theta)} \cdot$$

$$\cos\theta f^* + (ikr - 1)\, e^{ikr(1-\cos\theta)} f + (ik - \tfrac{1}{r})|f|^2. \qquad (*)$$

By:

- Multiplying with $\hbar/im$
- Taking the real part of the expression
- Integrating over all angles θ

we should obtain 0, according to $\int j_r r^2 d\Omega = 0$.

Now, the last term $\left(\frac{\hbar}{imr}|f|^2\right)$ in (*) becomes purely imaginary and gives no contribution. The first term ($\propto \cos\theta$) gives zero upon integrating since $\int_0^\pi \cos\theta \sin\theta\, d\theta = 0$. Finally, we also get rid off the term $\propto k|f|^2$ by using $\int |f|^2 d\Omega = \sigma$.

Dividing the remaining terms in the equation by $\hbar k/m$ gives:

$$\mathrm{Re}\left\{\int_{\varphi=0}^{2\pi}\int_{\theta=0}^{\pi}\left[re^{-ikr(1-\cos\theta)}\cos\theta\, f^{*}+\left(r+\frac{i}{k}\right)e^{ikr(1-\cos\theta)}f\right]d\varphi\sin\theta\, d\theta\right\}+\sigma=0.$$

Introducing $\cos\theta=x$ and using that $1+\frac{i}{kr}\simeq 1$ for large r, this equation becomes:

$$\sigma=-\frac{1}{r}\,\mathrm{Re}\left\{\int_{0}^{2\pi}\int_{-1}^{1}\left[e^{-ikr+ikrx}\,f^{*}+e^{ikr-ikrx}f\right]dx\,d\varphi\right\}\qquad(\dagger)$$

We now make use of a previously derived result (section 13.6), namely that for large s:

$$\int_{-1}^{1}e^{isx}g(x)\,dx=g(1)\,\frac{e^{is}}{is}-g(-1)\,\frac{e^{-is}}{is}+\mathcal{O}(s^{-2}).$$

This expansion can be used with $s=kr$ in the first term of the r.h.s. in $(\dagger)$ and $s=-kr$ for the second term.

The result is:

$$\sigma=-\mathrm{Re}\left\{\frac{1}{ik}\int_{0}^{2\pi}\left[e^{-2ikr}f^{*}(\pi,\varphi)+f^{*}(0,\varphi)+e^{2ikr}f(\pi,\varphi)-f(0,\varphi)\right]d\varphi\right\}$$

where we used that $x=1$ corresponds to $\theta=0$ and $x=-1$ to $\theta=\pi$.

Using that $f^* - f = -2i\,\mathrm{Im}\,f$, we obtain:

$$\sigma = \frac{1}{k}\int_0^{2\pi} 2\,\mathrm{Im}\,f(0,\varphi)\,d\varphi = \frac{4\pi}{k}\,\mathrm{Im}\,f(0)$$

We here used that in the forward-scattering direction $\Theta = 0$, there can be no φ-dependence $\Rightarrow$ φ-integration merely gives a factor 2π. Thus, we have proven the optical theorem:

$$\boxed{\sigma = \frac{4\pi}{k}\,\mathrm{Im}\{f(0)\}}$$

Please note that:

1) In contrast to our previous derivation using the method of partial waves, we now did not make any assumption about the potential being spherically symmetric.

2) The expression we found in the Born-approximation for a spherically symmetric potential, $f^B(\Theta) = -\frac{2m}{\hbar^2 q}\int_0^\infty V(r)\sin(qr)\,r\,dr$, is real: cannot be used in the optical theorem (gives $\sigma = 0$).

Can you think of why the Born-approx. seems to be incompatible with the optical theorem?

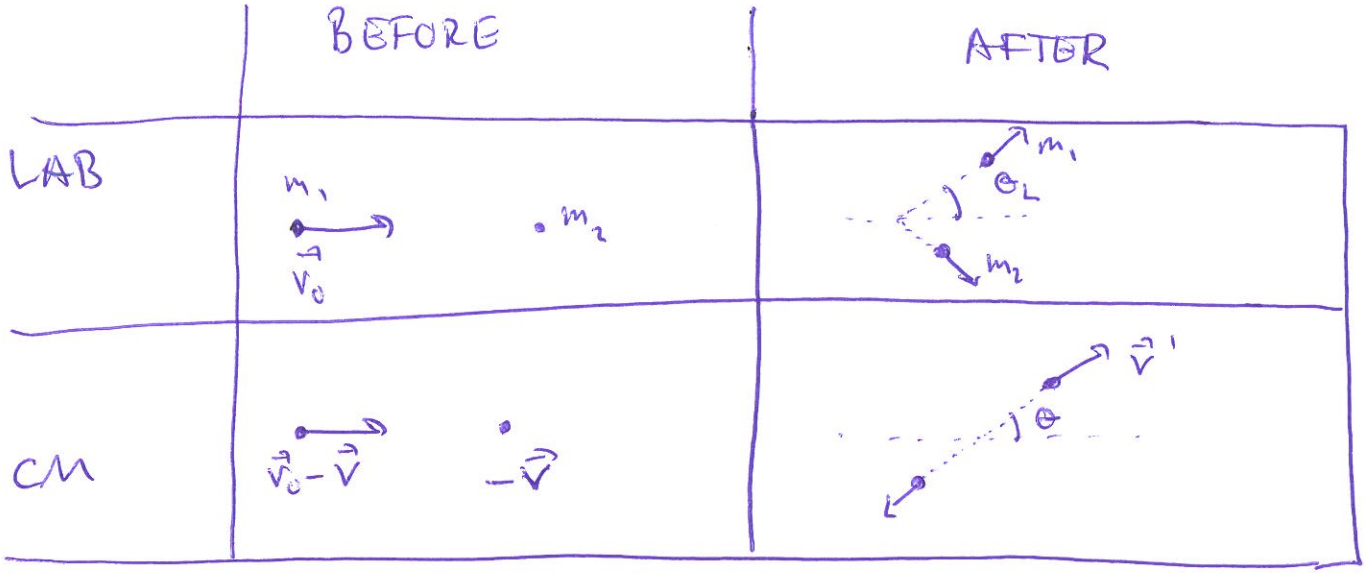
3) We've assumed elastic scattering. If inelastic processes occur, e.g. exciting internal degrees of freedom in the particle or fragmentation of particles, the net current through a volume is no longer zero.
Instead, it must be negative since inelastic scattering processes remove particles (in the original state).
In this more general case, the optical theorem reads:

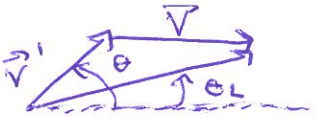
$$\sigma_{el.} + \sigma_{inel.} = \frac{4\pi}{k} \operatorname{Im}\{f_{el}(0)\}.$$

13.8 Lab- and CM-System

(*) As previously remarked, this corresponds to the CM frame of a two-particle problem with potential $V(\vec{r}_1 - \vec{r}_2)$.

In our scattering theory so far, we have considered a particle scattering on a stationary potential.(*) We now want to analyze the difference between the Lab and CM frames for two particles scattering off each other, defined as follows:



Note the following geometrical relations: 

Consider the lab-frame where particle 1 with mass m_1 and velocity v_0 scatters on mass m_2 with zero velocity.

The center-of-mass velocity in the lab-frame is then:

$$V = \frac{m_1 \cdot v_0 + m_2 \cdot 0}{m_1 + m_2} = \frac{m_1 v_0}{m_1 + m_2}$$

We seek the relation between scattering angles Θ and Θ_L in the CM and lab frame, respectively. The above figure shows that:

$$\tan \Theta_L = \frac{v' \sin \Theta}{v' \cos \Theta + V}$$

Note that $v' = |\vec{v}'| = v_0 - V$ (magnitude of velocity of the scattered and incident particle in the CM frame is the same).

Inserting v' and V into the above expression yields:

$$\boxed{\tan \Theta_L = \frac{\sin \Theta}{\cos \Theta + m_1/m_2}}$$

Thus, when the target mass $m_2 \to \infty$, we obtain $\Theta_L = \Theta$ as expected.

Hence, we find:

$$\frac{d\sigma_L}{d\Omega_L} = \frac{d\sigma}{d\Omega}\,\frac{(1+2\gamma\cos\theta+\gamma^2)^{3/2}}{1+\gamma\cos\theta} \qquad \left(\gamma = \frac{m_1}{m_2}\right)$$

13.9 Scattering of identical particles

We now consider what happens when two identical particles are scattered on each other. It is known that the two-particle state satisfies: $\psi(1,2) = \begin{cases} \psi(2,1) & \text{bosons} \\ -\psi(2,1) & \text{fermions} \end{cases}$

where $1 = (\vec{r}_1, s_1)$ and $2 = (\vec{r}_2, s_2)$. Consider only the spatial part of the wavefunction to begin with and focus on the CM frame.

In this case, a two-particle ψ that is symmetric (antisymmetric) in $\vec{r}_1$ and $\vec{r}_2$ must be an even (odd) function of the relative-coordinate $\vec{r} = \vec{r}_1 - \vec{r}_2$. In spherical coordinates, $\vec{r} \to -\vec{r}$ means

$$(r, \theta, \varphi) \to (r, \pi - \theta, \varphi + \pi).$$

Now, our asymptotic wavefunction $\psi \simeq e^{i\vec{k}\cdot\vec{r}} + f(\theta)\frac{e^{ikr}}{r}$ is neither symmetric nor antisymmetric.

$\Longrightarrow$ For identical particles, it must be replaced with:

$$\psi(1,2) \approx e^{i\vec{k}\cdot\vec{r}} \pm e^{-i\vec{k}\cdot\vec{r}} + [f(\theta) \pm f(\pi-\theta)]\frac{e^{ikr}}{r}$$

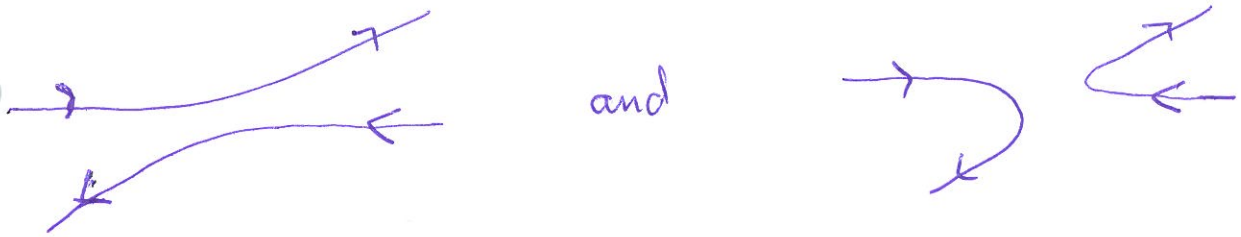
Upper sign: sym. Lower sign: antisym.

Note how the spherical part $\sim \frac{e^{ikr}}{r}$ accounts for scattering of both particles in diametrically opposite directions.

$d\sigma$ is, as before, defined by the ratio of the particle flux into $d\Omega$ and the incident particle stream for one of two planewaves:

$$\frac{d\sigma}{d\Omega} = |f(\theta) \pm f(\pi-\theta)|^2 . \qquad (*)$$

It makes sense physically that the scattering of both particles must be taken into account when they are identical, because we cannot distinguish between the following two scenarios:



and

(*) is consistent with the typical QM treatment: add "wavefunctions", then take absolute value squared to compute e.g. probabilities.

Note that this is different from how we would classically allow for the two possibilities: $\frac{d\sigma}{d\Omega} = |f(\theta)|^2 + |f(\pi-\theta)|^2$.

There is no interference term here, unlike the QM formula where we get $\frac{d\sigma}{d\Omega} = |f(\theta)|^2 + |f(\pi-\theta)|^2 \pm 2\mathrm{Re}\{f(\theta)f^*(\pi-\theta)\}$.

Whether or not to use sym. or antisym. states ψ depends on the spin configuration. We now proceed to illustrate this.

Scattering of spin-0 particles

Spin-0 particles: bosons $\Rightarrow$ spatially symmetric wavefunction.

We thus (use) the upper sign $\frac{d\sigma}{d\Omega} = |f(\theta) + f(\pi-\theta)|^2$.

Assume for concreteness that the bosons interact via the Coulomb-potential, for which case we have:

$$f_c(\theta) = \frac{n}{2k\sin^2\frac{\theta}{2}} e^{-2i\ln\sin\frac{\theta}{2} + i\delta}$$

where $n = \frac{Z^2}{k a_0}\frac{m}{m_e}$. Inserting this into $\frac{d\sigma}{d\Omega}$:

$$\frac{d\sigma}{d\Omega} = \left(\frac{Z^2e^2}{4\pi\varepsilon E_T}\right)^2 \left[\frac{1}{\sin^4\frac{\theta}{2}} + \frac{1}{\cos^4\frac{\theta}{2}} + \frac{2\cos(n\ln\tan^2\frac{\theta}{2})}{\sin^2\frac{\theta}{2}\cos^2\frac{\theta}{2}}\right]$$

where $E_T = \frac{\hbar^2 k^2}{2m}$. The last term is a purely QM effect stemming from the interference between $f(\theta)$ and $f(\pi-\theta)$.

This effect due to identical particles in QM has been verified experimentally [C^{12} scattering on carbon, PRL 4, 365 (1960)].

Scattering of particles with spin

Even if the interaction between two spinful particles does not depend on the spin itself, we must consider the fact that the particles have spin to obtain the correct $\frac{d\sigma}{d\Omega}$.

To see this, consider e-e scattering (spin 1/2).

Now, two spin 1/2 states may be combined into one singlet $(\uparrow\downarrow - \downarrow\uparrow)$ or three triplet $(\uparrow\uparrow, \downarrow\downarrow, \uparrow\downarrow + \downarrow\uparrow)$ states.

If the particles are randomly polarized: probability $\frac{1}{4}$ for singlet (symmetric spatial wavefunction) and probability $\frac{3}{4}$ for triplet (antisym. $\rightarrow$). This yields:

$$\frac{d\sigma}{d\Omega} = \frac{3}{4}|f(\theta) - f(\pi-\theta)|^2 + \frac{1}{4}|f(\theta) + f(\pi-\theta)|^2.$$

From this, we can infer that:

- Particles scattered into $\theta = \frac{\pi}{2}$ must be singlets, since the triplet-contribution is zero for this angle.

- If the spins are not initially random, but fully polarized in the same direction (i.e. triplets), there can be no scattering into $\theta = \frac{\pi}{2}$.

CHAPTER 14

MAGNETIC FIELDS

We shall consider here the influence of magnetic fields on physical systems. This is extremely important because it is one of the simplest and most common experimental ways to manipulate eigenfunctions and energy levels.

14.1 The Zeeman effect

Normal Zeeman effect

To incorporate a $\vec{B}$-field into the S.E., we know from

earlier treatment that we should include a gauge field $\vec{A}$.

For $\vec{B} = B\vec{z}$, we may use e.g. $\vec{A} = \frac{1}{2} B(-y, x, 0)$.

The difference between Hamiltonians with and w.o. magnetic field becomes:

$$\hat{H} - \hat{H}_0 = \frac{(\vec{\hat{p}} - q\vec{A})^2}{2m} - \frac{\vec{\hat{p}}^2}{2m} = -\frac{q}{m}\vec{A}\cdot\vec{\hat{p}} + \frac{q^2}{2m}\vec{A}^2$$

$$= -\frac{qB}{2m}(x\hat{p}_y - y\hat{p}_x) + \frac{q^2B^2}{8m}(x^2+y^2)$$

Since $x p_y - y p_x = L_z$ is the ang. mom. component in the z-direction, we may write:

$$\hat{H}' = \hat{H} - \hat{H}_0 = -\frac{q}{2m} B\hat{L}_z + \frac{q^2B^2}{8m}(x^2+y^2) = \hat{H}_1' + \hat{H}_2'.$$

Focus now on the perturbation term $\hat{H}_1' \equiv -\vec{\mu}_L \cdot \vec{B}$ where $\vec{\mu}_L = \frac{q\vec{L}}{2m}$, since $\hat{H}_2'$ is quadratic and negligible for small B.

$\hat{H}_1'$ describes the coupling between external field and the induced field of a charged particle with orbital ang. mom.

For a spherically symmetric potential, $R_{n\ell}(r) Y_{\ell m}(\theta, \varphi)$ are eigenfunctions for $\hat{L}_z$ with eigenvalue $\hbar m$. Considering an electron ($q = -e$ and $m = m_e$), the added energy due to $\hat{H}_1'$

becomes $\Delta E = \frac{e\hbar B}{2m_e} \cdot m = \mu_B B \cdot m \quad (m = -l, \dots l)$.

Bohr-magneton $\mu_B = \frac{e\hbar}{2m_e}$. Every energy level is thus splitted into $2l+1$ levels with a spacing depending on B and not on the quantum numbers n or l. This is the normal Zeeman effect, but when we take into account spin we obtain the experimentally observed anomalous Zeeman effect.

Anomalous Zeeman effect

A particle with spin has an additional internal ang. mom. $\vec{m}_s$ which also couples to the magnetic field. The total perturbation then becomes $\hat{H}_1' = \frac{eB}{2m_e}(\hat{L}_z + 2\hat{S}_z)$ where we used $g_S = 2$ (Lande g-factor).

However, we must also consider how spin influences $\hat{H}_0$, i.e. the B-independent part. This part gains a spin-orbit interaction (see chapter 9):

$$\hat{H}_{SO} = f(r)\, \vec{L} \cdot \vec{S}$$

so that the eigenfunctions now depend on $\vec{J}^2$ and J_z ($\vec{J} = \vec{L} + \vec{S}$) since $\vec{L}$ and $\vec{S}$ are no longer conserved separately.

We proceed to distinguish between weak and strong magnetic fields.

Strong fields: In this case, we may disregard $\hat{H}_{sb}$ relative the magnetic term $\vec{A}$. The resulting splitting is then simply:

$$\Delta E = \frac{e\hbar}{2m_e}(m + 2m_s)B = \mu_B B(m + 2m_s).$$

A given energy level is then split into $2l+3$ levels for $l>0$ since $m+2m_s$ takes values between $-l-1$ and $l+1$. For $l=0$, the splitting is into two levels.

Weak fields: This is a more complicated situation since we cannot disregard $\hat{H}_{sb}$ any more. Thus, the eigenstates of the unperturbed Hamiltonian are $|j, m_j, l\rangle$. This is because $\hat{H}_0 + \hat{H}_{sb}$ commutes with both $\vec{J}^2$, J_z and $\vec{L}^2$ (see 9.1). Thus, the perturbation energy becomes:

$$\Delta E = \mu_B B \langle j, m_j, l | L_z + 2S_z | j, m_j, l\rangle = \mu_B B \langle j\, m_j\, l | J_z + S_z | j\, m_j\, l\rangle$$

$$= \mu_B B \left(\hbar m_j + \langle j m_j l | S_z | j m_j l\rangle\right)$$

For $s = \frac{1}{2}$, there are two possible values of j: $j = l \pm \frac{1}{2}$.

To compute the expectation value of S_z, we want to express $|j\, m_j\, l\rangle$ in terms of eigenspinors for S_z. This is done

via equations 8.63 - 8.64 (chapter 8):

$$|j = l+\tfrac{1}{2}, m_j, l\rangle = \sqrt{\frac{l+\frac{1}{2}-m_j}{2l+1}}\,|l, m_j+\tfrac{1}{2}\rangle\chi(-) + \sqrt{\frac{l+\frac{1}{2}+m_j}{2l+1}}\,|l, m_j-\tfrac{1}{2}\rangle\chi(+)$$

and

$$|j = l-\tfrac{1}{2}, m_j, l\rangle = \sqrt{\frac{l+\frac{1}{2}+m_j}{2l+1}}\,|l, m_j+\tfrac{1}{2}\rangle\chi(-) - \sqrt{\frac{l+\frac{1}{2}-m_j}{2l+1}}\,|l, m_j-\tfrac{1}{2}\rangle\chi(+).$$

We have here expressed the eigenstates of $\vec{J}^2$, J_z, and $\vec{L}^2$ via eigenstates of the orbital angular momentum, $|l\,m\rangle$, and the eigenstates $\chi(\pm)$ of S_z:

$$S_z\,\chi(\pm) = \pm\frac{\hbar}{2}\,\chi(\pm).$$

One then obtains the sought expectation value for S_z:

$$\langle j = l\pm\tfrac{1}{2}, m_j, l \,|\, S_z \,|\, j = l\pm\tfrac{1}{2}, m_j, l\rangle = -\frac{\hbar}{2}\frac{l+\frac{1}{2}\mp m_j}{2l+1} + \frac{\hbar}{2}\frac{l+\frac{1}{2}\pm m_j}{2l+1}$$

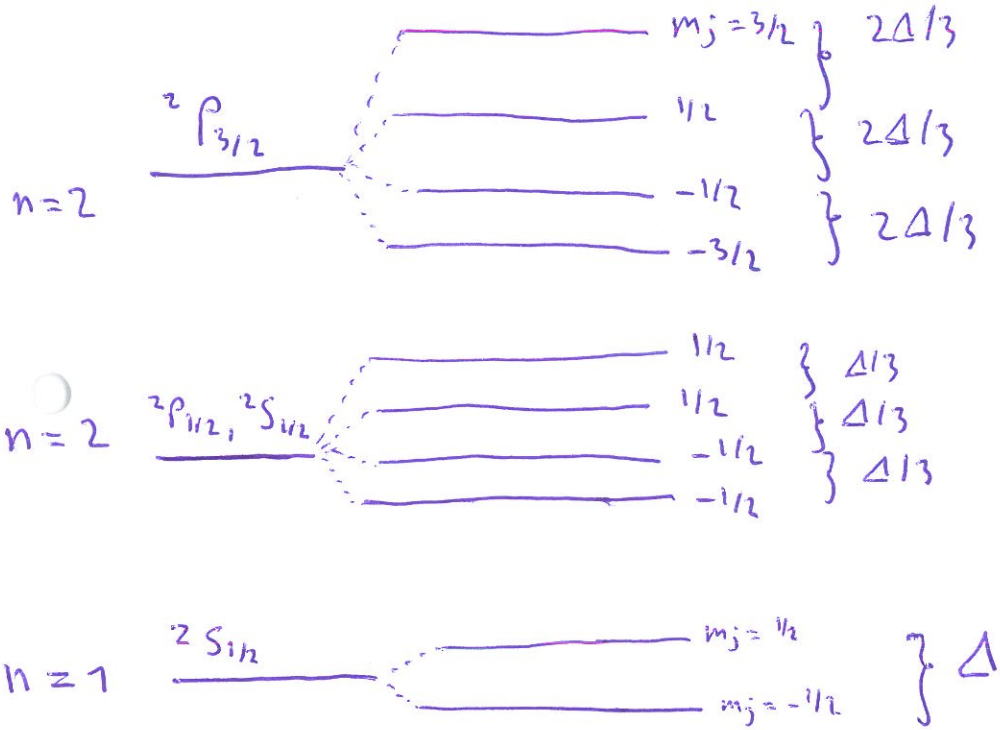
$$= \pm\frac{\hbar m_j}{2l+1}.$$

Inserted into ΔE, we obtain:

$$\Delta E = \mu_B B\,\frac{2j+1}{2l+1}\,m_j \quad \left(j = l\pm\tfrac{1}{2},\ m_j = -j, \dots j\right).$$

This gives rise to a different energy splitting with a spacing that is no longer independent on the quantum numbers.

We show the magnetic field splitting for the hydrogen $n=1$ and $n=2$ levels below



We have introduced the notation $^{2S+1}L_J$ to characterize the levels, where S is the q.n. for total spin ($S=\frac{1}{2}$ in our case), L is the q.n. for total orbital ang. mom. ($S: l=0$, $P: l=1$, $D: l=2, \ldots$) while J is the q.n. for total ang. mom. $\vec{J}$. Moreover,

$$\Delta \equiv 2\mu_B B.$$

For instance, $^2P_{1/2}$ means $s=\frac{1}{2}$, $l=1$, $j=\frac{1}{2}$.

14.2 Landau levels

The Zeeman effect is concerned with the effect of $\vec{B}$ on bound electrons, such as the coupling between spin $\vec{S}$ and field $\vec{B}$. We now consider free electrons and show that for a constant $\vec{B}$, the S.E. can be solved exactly.

We use a Landau-gauge* $\vec{A} = (-By, 0, 0)$ so that the Hamiltonian for $q = -e$ becomes:

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \frac{ie\hbar B}{m} y \frac{\partial}{\partial x} + \frac{e^2B^2}{2m} y^2 .$$

This $\hat{H}$ commutes with $\hat{p}_x$ and $\hat{p}_z$ and thus admits common eigenstates with these operators. The general solution should then have the form:

$$\psi(\vec{r}) = e^{ik_x x + ik_z z} \cdot \varphi(y) ,$$

Inserted into $\hat{H}\psi = E\psi$, we get this equation for φ:

$$-\frac{\hbar^2}{2m}\varphi'' + \left[\frac{\hbar^2 k_x^2}{2m} - \frac{e\hbar B k_x}{m} y + \frac{e^2B^2}{2m} y^2\right]\varphi + \frac{\hbar^2 k_z^2}{2m}\varphi = E\varphi$$

---

* Lev Landau (1908-1968), Soviet physicist. Known for phenomenological theory of phase transitions, theory of quantum liquids, Landau-damping, and more. Nobel prize in 1962.

This can be written more compactly:

$$-\frac{\hbar^2}{2m}\varphi'' + \frac{1}{2}m\omega_c^2(y-y_0)^2\varphi = \hat{E}\varphi \qquad (*)$$

where $E = \hat{E} + \frac{\hbar^2 k_z^2}{2m}$, $y_0 = \frac{\hbar k_x}{eB}$, and $\omega_c = \frac{eB}{m}$.

ω_c is seen to be the cyclotron frequency: classical angular frequency for the circular motion of an electron in a $\vec{B}$ field.

Now, (*) has a familiar form: a harmonic oscillator centered around y_0. We immediately know that the eigenvalues are:

$$\hat{E} = (n+\tfrac{1}{2})\hbar\omega_c \Rightarrow E = (n+\tfrac{1}{2})\hbar\omega_c + \frac{\hbar^2 k_z^2}{2m} \quad (n=0,1,2,\dots)$$

and the belonging eigenfunctions are:

$$\psi(\vec{r}) = e^{ik_x x + ik_z z}\varphi_n(y-y_0) \quad (\varphi_n \text{ is the } n\text{-th harm. osc. function})$$

The energy E for our particle thus has two parts:
free-particle motion along the $\vec{B}$ field (z-axis) and quantized motion perpendicularly to $\vec{B}$ (xy-plane).

Quantized levels for fixed k_z (vary n): Landau-levels.

Continuous energy bands for fixed n (vary k_z): Landau-Bands

Degeneracy

Since the energy does not depend on the quantity $y_0 \propto k_x$, the Landau levels are massively degenerate.

To see this, consider a large but finite volume $V = L_x L_y L_z$. Using periodic boundary conditions, e.g. $\psi(x+L_x) = \psi(x)$ (see section 5.2.3), the allowed values of the momenta are

$$k_x = \frac{2\pi n_x}{L_x} \quad \text{and} \quad k_z = \frac{2\pi n_z}{L_z}, \quad n_i \in \text{integers}.$$

In turn, this means that the allowed values for $y_0 = \frac{\hbar k_x}{eB}$ are separated by $\Delta y_0 = \frac{h}{eBL_x}$. The number of available positions for y_0 then becomes:

$$\frac{L_y}{\Delta y_0} = L_x L_y \frac{eB}{h} = \frac{\Phi_{tot}}{h/e}.$$

Here, $\Phi_{tot} = L_x L_y B$ is the total magnetic flux through $L_x \times L_y$. We may conclude that each Landau-level contains the same number of states: $\frac{\Phi_{tot}}{h/e}$. Each state then carries a flux quantum $\Phi_0 = h/e$. We will soon see a different example of flux quantization.

Using periodic b.c. allows us to use free-particle $\psi \propto e^{ikx}$ in contrast to hard-wall b.c. where $\psi = 0$ at the edges, while still obtaining the same density of states, see section 5.2.3 for more details

Oscillation of Fermi level

We saw above that the degree of degeneracy of Landau-levels was $L_x L_y B e/h$ per level. Taking spin into account, the degeneracy is doubled.

Thus, if the 2D electron density of the system is n_2, meaning there are in total $n_2 L_x L_y$ electrons, they can all reside in the same Landau level if the field is so strong that:

$$B > B_0 = \frac{1}{2} n_2 \frac{h}{e}.$$

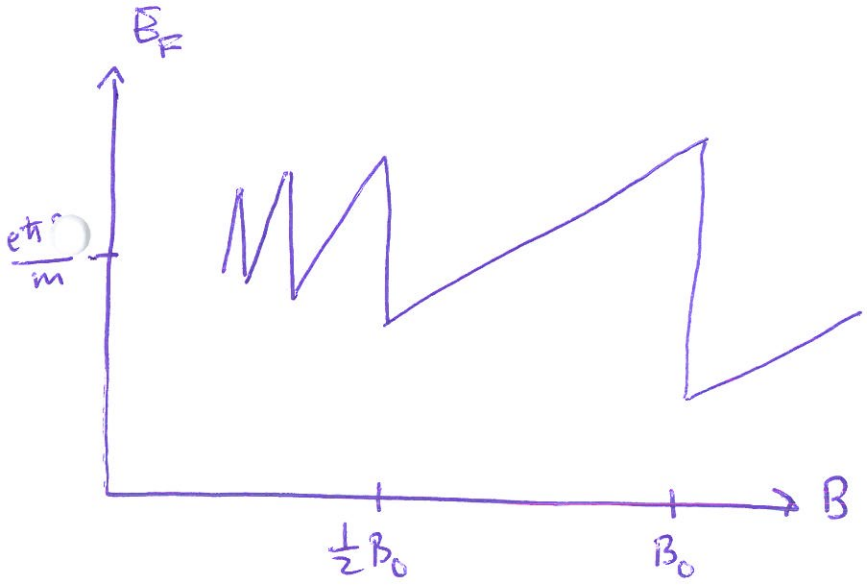
Consider in fact a 2D electron gas, which is typically studied experimentally in the context of Landau levels. We thus disregard excitations in the z-direction. Let us compute the Fermi energy E_F as a function of B. Note that: both the degeneracy of LL and the Landau level energy itself $\left[E_n = (n+\frac{1}{2})\hbar\frac{eB}{m}\right]$ are proportional to B.

- For $B > B_0$, all electrons are in the lowest LL so that $E_F = \frac{1}{2} e\hbar B/m$

- If $\frac{1}{2} B_0 < B < B_0$, the electrons that can't fit into the lowest LL have room to be in the second lowest LL: $E_F = \frac{3}{2} e\hbar B/m$.

This argument is repeated as B decreases. At $B = B_0$, E_F jumps from $\frac{1}{2}e\hbar B_0/m$ to $\frac{3}{2}e\hbar B_0/m$. At $B = \frac{1}{2}B_0$, E_F jumps from $\frac{3}{4}e\hbar B_0/m$ to $5/4\, e\hbar B_0/m$, etc.

In general: discontinuities at $B = \frac{B_0}{k}$ where E_F jumps between $(1 - \frac{1}{2k})e\hbar B_0/m$ and $(1 + \frac{1}{2k})e\hbar B_0/m$



For a 3D system, this picture is slightly modified. When $B < B_0$, the electrons that don't fit into the 0'th LL will not directly go into the 1'st LL, but instead populate states $k_z \neq 0$ with energy

$$E = \frac{1}{2}\hbar\omega_c + \frac{\hbar^2 2m}{k_z^2}$$

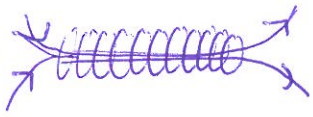
This energy will increase until it equals the energy of the 1'st LL, and then this level is starting to fill up.

We still get a sharp peak in E_F vs. B every time a new LL is activated.

Since the transport properties of metals are determined by the electrons at the Fermi level, the strong variation of E_F vs. B is manifested e.g. in the conductivity ρ which oscillates with B : Shubnikov-de Haas effect.

14.3 | Aharonov-Bohm effect

Wavefunction in space with $\vec{B}=0$

Assume $\vec{B}(\vec{r}) \neq 0$ is present in some places, but that other places have $\vec{B}=0$. Example: very long coil with current running through it only has $\vec{B} \neq 0$ inside  .

In the regions where $\vec{B}=0$, we have $\vec{A}=\nabla\lambda$ since $\nabla\times\vec{A}=0$ there. This means that (up to a constant):

$$\lambda(\vec{r}) = \int_{\vec{r}_0}^{\vec{r}} \vec{A}(\vec{s})\cdot d\vec{s}$$

($\vec{r}_0$ arbitrary point in the region where $\vec{B}=0$)

The integration path is arbitrary, as long as we stay inside the $\vec{B}=0$ region.

The wavefunction ψ is obtained from the S.E.

$$i\hbar\frac{\partial\psi}{\partial t} = \frac{1}{2m}\left(\frac{\hbar}{i}\nabla - q\vec{A}\right)^2\psi + V(\vec{r})\psi$$

where $V(\vec{r})$ is potential energy stemming from other effects than the field.

The physics must be gauge-invariant. Thus, let us do a gauge-transformation:

$$\vec{A}' = \vec{A} + \nabla\chi \quad , \quad \Phi' = \Phi - \frac{\partial\chi}{\partial t} \quad , \quad \psi' = \psi e^{iq\chi/\hbar}$$

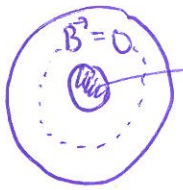
and use $\chi = -\lambda$. This gives:

$$i\hbar \frac{\partial \tilde{\psi}}{\partial t} = \frac{1}{2m}\left(\frac{\hbar}{i}\nabla\right)^2 \tilde{\psi} + V(\vec{r})\tilde{\psi}$$

This is the same equation as if $\vec{A} = 0$ in the first place.

<u>However</u>: we cannot in general just set $\vec{A} = 0$ in a region where $\vec{B} = 0$ <u>if</u> the field-free area encloses a region where $\vec{B} \neq 0$.

Consider a geometry:



If we integrate along the --- line, we get:

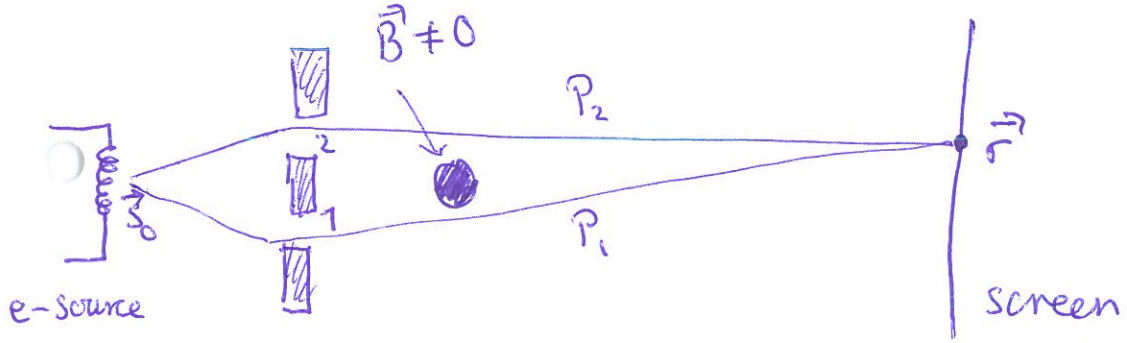
$$\oint \vec{A}(\vec{s})\cdot d\vec{s} = \iint_S \nabla\times\vec{A}\, dS = \Phi_S$$

where S is the shaded region and Φ_S is the flux through it. This equation shows that $\vec{A}$ <u>cannot</u> be zero everywhere in the white region where $\vec{B} = 0$.

Interference experiment

Does this mean that an electron moving only in an area with $\vec{B}=0$ can still be affected by the presence of $\vec{B}\neq 0$ in the inaccessible region?

Aharonov & Bohm suggested the following interference experiment to clarify this:



An electron source emits e^- from the point $\vec{s}_0$. The electrons pass through the slits 1 and 2 and hit the screen at $\vec{r}$, having taken the paths P_1 and P_2, respectively.

Assume the ● region is completely inaccessible to the electrons. The total wavefunction is a superposition of the contribution from paths P_1 and P_2: $\psi_{tot} = \psi_{P_1}(\vec{r},t) + \psi_{P_2}(\vec{r},t)$.

According to our previous treatment, we have:

$$\psi_{P_1}(\vec{r},t) = \psi_0(\vec{r},t)\, e^{i\left(\frac{e}{\hbar}\right)\int_{P_1}\vec{A}(\vec{s})\cdot d\vec{s}}$$

$$\psi_{P_2}(\vec{r},t) = \psi_0(\vec{r},t)\, e^{i\left(\frac{e}{\hbar}\right)\int_{P_2}\vec{A}(\vec{s})\cdot d\vec{s}}$$

$\psi_0(\vec{r},t)$ is as before the wave function for $\Phi = 0$. Note that the relative phase between ψ_{P_1} and ψ_{P_2} is:

$$\int_{P_1} \vec{A}(\vec{s}).d\vec{s} - \int_{P_2} \vec{A}(\vec{s}).d\vec{s} = \oint \vec{A}(\vec{s}).d\vec{s} = \Phi$$

where Φ is the flux through ●. We may then rewrite:

$$\psi_{tot}(\vec{r},t) = \left(\psi_0 e^{ie\Phi/\hbar} + \psi_0\right) e^{i\left(\frac{e}{\hbar}\right)\int_{P_2} \vec{A}(\vec{s}).d\vec{s}},$$

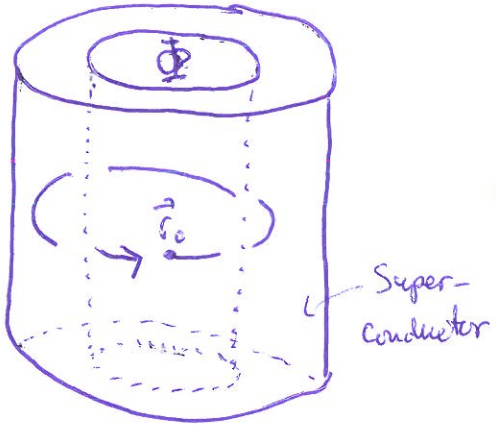
so that the probability density of electrons hitting the screen becomes $|\psi_{tot}|^2 = |\psi_0 e^{ie\Phi/\hbar} + \psi_0|^2$: the interference pattern changes with Φ even if the electrons never move in ●!

This is the Aharonov-Bohm effect, measured in 1960 by Chambers. We learn that $\vec{A}$ plays a fundamental role : however, note that the physically measurable quantity $|\psi_{tot}|^2$ is gauge-independent (only depends on Φ and not $\vec{A}$).

14.4 Flux quantization in superconductors

An interesting case where electrons move in field-free space is in a superconductor, which besides having zero electrical resistance also expels $\vec{B}$ from its interior.

For a SC cylinder, a flux Φ can pass through the hollow middle, meaning again that $\vec{A}$ cannot be zero in the superconductor despite $\vec{B}=0$ there.



The wave function ψ inside the superconductor can again be expressed as $\Phi=0$ wavefunction times a phase factor:

$$\psi(\vec{r}) = \psi_0(\vec{r})\, e^{-i\left(\frac{q}{\hbar}\right)\int_{\vec{r}_0}^{\vec{r}} \vec{A}(\vec{s})\cdot d\vec{s}}$$

If the integral path now is taken to form a closed loop inside the SC (as shown in the figure above), the wave function is multiplied with $e^{-iq\Phi/\hbar}$. Since the wavefunction has to be singled-valued, it follows that:

$$e^{-iq\Phi/\hbar} = e^{2in\pi} \qquad (n = 0, \pm 1, \pm 2, \ldots)$$

$$\Rightarrow \boxed{\Phi = \frac{2n\pi\hbar}{q}\cdot n}$$

The flux has to be quantized! This has been experimentally observed, and one found the flux to be quantized in units of $\pi\hbar/e$. This corresponds to $q=-2e$, suggesting that in superconductors the fundamental entity is an electron <u>pair</u> (in accordance with BCS theory).

CHAPTER 16

QUANTIZED RADIATION THEORY

We have treated the EM field classically so far. However, the EM field is also governed by QM and we now want to treat both the atomic system and the field quantum mechanically.

16.1 Quantization of the radiation field

The starting point to determine the QM Hamilton-operator for a system is to know the classical Hamiltonian. That is hence where our investigation begins.

Classical Hamiltonian for the field

Consider the existence of an EM field without any source terms (charges and currents) in a cubic volume $V = L^3$ with periodic boundary conditions. V is introduced for convenience so that we can quantify the number of modes in the system.

It is $\vec{A}$ that couples the atomic system with the EM field. In a Coulomb gauge with $\nabla \cdot \vec{A} = 0$, we may write $\vec{A}$ as a superposition of plane-waves: (see section 12.2.2)

$$\vec{A}(\vec{r},t) = \sum_{\vec{k},\lambda} \vec{e}_{k\lambda} \sqrt{\frac{\hbar}{2\varepsilon_0 V c k}} \left[\tilde{a}_{\vec{k}\lambda}\, e^{i\vec{k}\cdot\vec{r} - i\omega_k t} + \tilde{a}^{*}_{\vec{k}\lambda}\, e^{-i\vec{k}\cdot\vec{r} + i\omega_k t} \right]$$

where $\omega_k = kc$ and $\tilde{a}_{\vec{k}\lambda}$ are amplitude factors. Note that the photon $\vec{A}$ is transversely polarized since $\vec{e}_{k\lambda} \perp \vec{k}$, guaranteeing $\nabla \cdot \vec{A} = 0$.

The sum $\sum_{\vec{k},\lambda}$ goes over discrete wavevectors $\vec{k} = \frac{2\pi}{L}(n_x, n_y, n_z)$ and over the two polarization vectors $\vec{e}_{\vec{k}1}$ and $\vec{e}_{\vec{k}2}$ (both $\perp \vec{k}$).

Let $a_{\vec{k}\lambda} \equiv \hat{a}_{\vec{k}\lambda} e^{-i\omega_k t}$ for brevity of notation. Now, the energy of the field itself is:

$$\mathcal{H} = \frac{1}{2}\int_V \left[\varepsilon_0 \vec{E}^2 + \frac{1}{\mu_0}\vec{B}^2\right] d^3r = \frac{\varepsilon_0}{2}\int_V \left[\left(\frac{\partial \vec{A}}{\partial t}\right)^2 + c^2 (\nabla \times \vec{A})^2\right] d^3r$$

Inserting our expression for $\vec{A}$ gives:

$$\mathcal{H} = -\frac{\hbar}{4V} \sum_{k\lambda} \sum_{k'\lambda'} \sqrt{\omega_k \omega_{k'}} \left[\vec{\varepsilon}_{k\lambda} \cdot \vec{\varepsilon}_{k'\lambda'} + (\hat{k} \times \vec{e}_{k\lambda}) \cdot (\hat{k}' \times \vec{e}_{k'\lambda'})\right]$$

$$\cdot \int_V \left(a_{k\lambda} e^{i\vec{k}\cdot\vec{r}} - a^{*}_{k\lambda} e^{-i\vec{k}\cdot\vec{r}}\right)\left(a_{k'\lambda'} e^{i\vec{k}'\cdot\vec{r}} - a^{*}_{k'\lambda'} e^{-i\vec{k}'\cdot\vec{r}}\right) d^3r$$

where $\hat{k} = \vec{k}/|\vec{k}|$. We use the vector identity

$(\vec{A} \times \vec{B})(\vec{C} \times \vec{D}) = (\vec{A}\cdot\vec{C})(\vec{B}\cdot\vec{D}) - (\vec{A}\cdot\vec{D})(\vec{B}\cdot\vec{C})$ to rewrite:

$$(\hat{k} \times \vec{e}_{k\lambda})(\hat{k}' \times \vec{e}_{k'\lambda'}) = (\hat{k}\cdot\hat{k}')(\vec{e}_{k\lambda}\cdot\vec{e}_{k'\lambda'}) - (\hat{k}\cdot\vec{e}_{k'\lambda'})(\hat{k}'\cdot\vec{e}_{k\lambda})$$

If we additionally use that $\frac{1}{V} = \int_e i(\vec{k}_1 - \vec{k}_2)\cdot\vec{r}\, d^3r = \begin{cases} 1 & \text{if } \vec{k}_1 = \vec{k}_2 \\ 0 & \text{if } \vec{k}_1 \neq \vec{k}_2 \end{cases}$,

since the allowed $\vec{k}$-values are such that an integer number of wavelengths fit into each side L of the volume, we see that there is only a contribution to the sum $\sum_{kk'}$ from $\vec{k}' = \pm\vec{k}$.

Moreover, since $\vec{e}_{k\lambda} \perp \vec{k}$, we have $\vec{k}'\cdot\vec{e}_{k\lambda} = \pm\vec{k}\cdot\vec{e}_{k\lambda} = 0$ and $1 + \hat{k}\cdot\hat{k}' = \begin{cases} 2 & \text{if } \vec{k}' = \vec{k} \\ 0 & \text{if } \vec{k}' = -\vec{k} \end{cases}$, so that only $\vec{k}' = \vec{k}$ contributes.

Finally, since $\vec{e}_{k\lambda'}\cdot\vec{e}_{k\lambda} = \delta_{\lambda'\lambda}$ (orthogonal polarization vectors), we obtain in total:

$$\boxed{\mathcal{H} = \frac{1}{2}\sum_{k\lambda} \hbar\omega_k \left(a_{k\lambda}a^*_{k\lambda} + a^*_{k\lambda}a_{k\lambda}\right)}$$

Note that $a^*_{k\lambda}$ is a scalar amplitude, it commutes with $a_{k\lambda}$

$$\Rightarrow \mathcal{H} = \sum_{k\lambda} \hbar\omega_k\, a_{k\lambda}a^*_{k\lambda}.$$

It is now useful to introduce the real and canonical variables

$$q_{k\lambda} = \sqrt{\frac{\hbar}{2\omega_k}}\left(a_{k\lambda} + a^*_{k\lambda}\right) \quad \text{and} \quad p_{k\lambda} = \frac{1}{i}\sqrt{\frac{\hbar\omega_k}{2}}\left(a_{k\lambda} - a^*_{k\lambda}\right).$$

To prove that these are indeed canonical, recall that $a_{k\lambda} \sim e^{-i\omega_k t}$,

which provides:

$$\dot{q}_{k\lambda} = \sqrt{\frac{\hbar}{2\omega_k}}\left(\dot{a}_{k\lambda} + \dot{a}^*_{k\lambda}\right) = -i\sqrt{\frac{\hbar\omega_k}{2}}\left(a_{k\lambda} - a^*_{k\lambda}\right) = p_{k\lambda} = \frac{\partial\mathcal{H}}{\partial p_{k\lambda}}$$

$$\dot{p}_{k\lambda} = -i\sqrt{\frac{\hbar\omega_k}{2}}\left(\dot{a}_{k\lambda} - \dot{a}^*_{k\lambda}\right) = -\sqrt{\frac{\hbar\omega_k}{2}}\,\omega_k\left(a_{k\lambda} + a^*_{k\lambda}\right) = -\omega_k^2 q_{k\lambda} = -\frac{\partial\mathcal{H}}{\partial q_{k\lambda}}$$

which are precisely Hamilton's equations for canonical variables.
To show the last equality in each equation, note that:

$$a_{k\lambda} = \frac{1}{\sqrt{2\hbar\omega_k}} \left(\omega_k q_{k\lambda} + i p_{k\lambda}\right) \quad \text{and} \quad a^*_{k\lambda} = \frac{1}{\sqrt{2\hbar\omega_k}} \left(\omega_k q_{k\lambda} - i p_{k\lambda}\right)$$

$$\Rightarrow \boxed{\mathcal{H} = \frac{1}{2} \sum_{k\lambda} \left(p^2_{k\lambda} + \omega^2_k q^2_{k\lambda}\right)}$$

This is a key result: the classical radiation field is formally equivalent to a set of independent harm. osc. with mass 1 in our variables.

Quantization

Having established the equivalence to harm. osc., the procedure to go Q/M is clear: we replace the classical oscillators with quantum mechanical oscillators. The energy of the system then becomes $E = \sum_{k\lambda} \left(n_{k\lambda} + \frac{1}{2}\right) \hbar\omega_k$ where $n_{k\lambda} = 0, 1, 2, \ldots$ is the number of photons in the mode $(\vec{k}, \lambda)$. The corresponding state of the system is the product:

$$|n_{k_1\lambda_1}, n_{k_2\lambda_2}, \ldots\rangle = |n_{k_1\lambda_1}\rangle \cdot |n_{k_2\lambda_2}\rangle \cdots = \prod_{k\lambda} |n_{k\lambda}\rangle .$$

Moreover, we introduce (as for the standard Q/M harm. osc.) creation and annihilation operators (a^+, a) via:

$$q_{k\lambda} = \sqrt{\frac{\hbar}{2\omega_k}}\left(a_{k\lambda} + a_{k\lambda}^\dagger\right) \quad \text{and} \quad p_{k\lambda} = \frac{1}{i}\sqrt{\frac{\hbar\omega_k}{2}}\left(a_{k\lambda} - a_{k\lambda}^\dagger\right)$$

From the commutator $[p_{k\lambda}, q_{k\lambda}] = \hbar/i$, it follows that $[a_{k\lambda}, a_{k\lambda}^\dagger] = 1$. The operators for two different modes commute, as they are independent on each other.

The operators have the known properties: (omitting indices for brevity)

$$a^\dagger|n\rangle = \sqrt{n+1}\, e^{i\omega t}|n+1\rangle \quad \text{and} \quad a|n\rangle = \sqrt{n}\, e^{-i\omega t}|n-1\rangle,$$

so that $a_{k\lambda}^\dagger$ creates a photon in the mode $(\vec{k}, \lambda)$ while $a_{k\lambda}$ removes one such photon. The number operator $N_{k\lambda} = a_{k\lambda}^\dagger a_{k\lambda}$ counts the number of photons in mode $(\vec{k}, \lambda)$:

$$N_{k\lambda}\,|\ldots n_{k\lambda}, \ldots\rangle = n_{k\lambda}\,|\ldots, n_{k\lambda}, \ldots\rangle.$$

The QM operator for the vector potential can now be expressed via creation and annihilation operators:

$$\vec{A} = \sum_{k\lambda} \vec{e}_{k\lambda}\sqrt{\frac{\hbar}{2\varepsilon_0 V\omega_k}}\left[a_{k\lambda}e^{i\vec{k}\cdot\vec{r}} + a_{k\lambda}^\dagger e^{-i\vec{k}\cdot\vec{r}}\right]$$

Calculating the Hamilton-operator in the same way as the classical procedure then yields:

$$\mathcal{H} = \frac{1}{2}\sum_{k\lambda}\left(a_{k\lambda}a_{k\lambda}^\dagger + a_{k\lambda}^\dagger a_{k\lambda}\right)$$

Note that we cannot any longer freely exchange the order of $a_{k\lambda}$ and $a_{k\lambda}^\dagger$ because they do not commute. Instead, we get:

$$\mathcal{H} = E_0 + \sum_{k\lambda} \hbar\omega_k a_{k\lambda}^\dagger a_{k\lambda}$$

$$\text{where } E_0 = \frac{1}{2}\sum_{k\lambda} \hbar\omega_k$$

E_0 is the ground-state energy (sometimes referred to as the zero-point energy) of the radiation field. Note that the operator for the electric field $\vec{E}$ is obtained via:

$$\vec{E} = -\frac{\partial \vec{A}}{\partial t} = i\sum_{k\lambda} \vec{e}_{k\lambda}\sqrt{\frac{\hbar\omega_k}{2\varepsilon_0 V}}\left[a_{k\lambda} e^{i\vec{k}\cdot\vec{r}} - a_{k\lambda}^\dagger e^{-i\vec{k}\cdot\vec{r}}\right]$$

The constant E_0 can usually simply be removed since we can choose the reference level for energy where we like. However, there are interesting exceptions such as the Casimir effect: the essence there is that altering the geometry of a system (such as two metallic plates) changes the allowed frequency spectrum $\{\omega_{k\lambda}\}$ and thus changes E_0. If E_0 is reduced, it causes the system to spontaneously try to alter its geometry, leading e.g. to an attraction of the metallic plates.

16.2 Coherent states

If we compute the expectation value of $\vec{E}$ in a state $|n_{k\lambda}\rangle$ for a mode of the radiation field, we obtain:

$$\langle n_{k\lambda}|\vec{E}|n_{k\lambda}\rangle = 0$$

since $\langle n|a|n\rangle = \langle n|a^\dagger|n\rangle = 0$. That does not seem very encouraging in terms of correctly describing an EM wave.

The question becomes: what kind of QM state for the radiation field gives a description which seems more reconcilable with the classical picture?

Our previous treatment of a harm. osc. again provides the resolution: coherent states $|\alpha\rangle = \sum_{n=0}^{\infty} c_n|n\rangle$ corresponded to a classical oscillation.

Due to our established analogy between the QM treatment of the $\vec{A}$ field and a harm. osc., we can in the same way construct coherent photon states for each mode $(\vec{k},\lambda)$.

Using our previously derived result (see chapter 6):

$$\langle\alpha|a|\alpha\rangle = \alpha e^{-i\omega t} \quad \text{and} \quad \langle\alpha|a^\dagger|\alpha\rangle = \alpha^* e^{i\omega t}$$

it follows that the expectation value of the electric field operator $\vec{E}$ in a coherent state for the mode $(\vec{k}, \lambda)$ becomes:

$$\langle \alpha | \vec{E} | \alpha \rangle = i \vec{e}_{k\lambda} \sqrt{\frac{\hbar \omega_k}{2 \varepsilon_0 V}} \left[\alpha e^{i\vec{k}\cdot\vec{r} - i\omega_k t} - \alpha^* e^{-i\vec{k}\cdot\vec{r} + i\omega_k t} \right]$$

The correspondence to a classical harmonic wave becomes more clear if we write $\alpha = |\alpha| e^{i\theta}$:

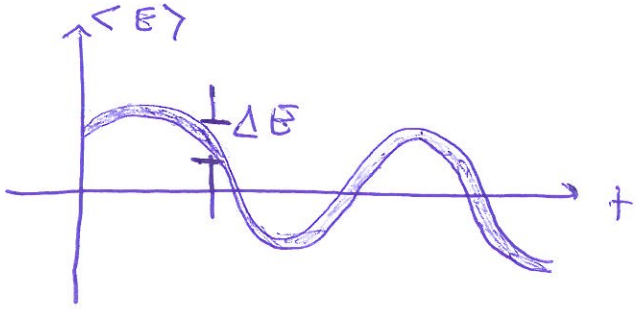
$$\boxed{\langle \alpha | \vec{E} | \alpha \rangle = -\vec{e}_{k\lambda} \sqrt{\frac{2\hbar\omega_k}{\varepsilon_0 V}} |\alpha| \operatorname{sen} (\vec{k}\cdot\vec{r} - \omega_k t + \theta)}$$

The importance of coherent states lies not only in the fact that it provides a clear formal similarity between the expectation value of $\vec{E}$ in the QM treatment and a classical wave, but also because a monochromatic (fixed wavelength) laser can generate such coherent excitations. Thus: direct experimental relevance.

An interesting observation is that the standard deviation $\Delta E = \sqrt{\langle \vec{E}^2 \rangle - \langle \vec{E} \rangle^2}$ from the expectation value is <u>independent</u> of the field amplitude α. One finds:

$$\Delta E = \sqrt{\frac{\hbar \omega_k}{2 \varepsilon_0 V}}$$

which thus becomes less and less relevant as $\vec{E}$ increases.



We can also compute the average number of photons in a coherent state $|\alpha\rangle$ for the mode $(\vec{k}, \lambda)$:

$$\langle n \rangle = \langle \alpha | N_{\vec{k}\lambda} | \alpha \rangle = \langle \alpha | a^{+}_{\vec{k}\lambda} a_{\vec{k}\lambda} | \alpha \rangle = |\alpha|^2$$

The entire distribution of photons [the probability $P(n)$ to find the mode excited with n photons] is found in the usual way: projecting the total state $|\alpha\rangle$ on the state $|n\rangle$ with n photons,

$$P(n) = |\langle n | \alpha \rangle|^2 = e^{-|\alpha|^2} \frac{|\alpha|^{2n}}{n!}$$

The photon-number in a monochromatic coherent state is thus Poisson-distributed:

$$\boxed{P(n) = e^{-\langle n \rangle} \cdot \frac{\langle n \rangle^n}{n!}}$$

16.3 Fully quantized radiation theory

We are now in a position to treat both subsystems which are part of radiation theory (atoms and photons) quantum mechanically.

We do so using perturbation theory.

The unperturbed Hamiltonian H_0 contains no interaction between the two subsystems. We may then write the total state as the product of indep. states for each part. It is natural to use the energy-states as basis-vectors:

$$|\text{atomic + photon system}\rangle = |\text{atomic system}\rangle \cdot |\text{radiation field}\rangle$$

$$\in \{ |4_i\rangle \cdot |n_{k_1\lambda_1}, n_{k_2\lambda_2} \cdots\rangle \}$$

The two subsystems are coupled via interaction terms such as

$$H_1' = -\frac{q}{m} \vec{A} \cdot \hat{\vec{p}} \quad \text{and} \quad H_3' = -\frac{q}{m} \vec{S} \cdot \underbrace{(\nabla \times \vec{A})}_{\vec{B}}$$

causing transitions between the unperturbed states. The transition rates can be computed via time-dep. pert. theory. We now consider some examples.

Spontaneous and stimulated emission

Spontaneous (stimulated) emission is the emission of light from an excited atom in the absence (presence) of photons in the initial state.

Let $(\vec{k}, \lambda)$ be [redacted] wavevector and polarization for the emitted photon. Excited state is $|4_2, t\rangle$ with energy E_2; final-state is $|4_1, t\rangle$ with energy E_1.

Thus, we can write:

$|i\rangle = |\psi_2\rangle\,|\dots, n_{k\lambda}, \dots\rangle$ and $|f\rangle = |\psi_1\rangle\,|\dots, n_{k\lambda}+1, \dots\rangle$

Assume that the dominant perturbation term is:

$$H_1' = \frac{e}{m}\vec{A}\cdot\vec{p} = \frac{e}{m}\sum_{k\lambda}\sqrt{\frac{\hbar}{2V\varepsilon_0\omega_k}}\left[a_{k\lambda}e^{i\vec{k}\cdot\vec{r}} + a_{k\lambda}^{\dagger}e^{-i\vec{k}\cdot\vec{r}}\right]\vec{e}_{k\lambda}\,\vec{p}$$

Matrix elements involving the photon states are simple since only the term with $a_{k\lambda}^{\dagger}$ contributes:

$$\langle \dots, n_{k\lambda}+1, \dots | H_1' | \dots, n_{k\lambda}, \dots\rangle = \frac{e}{m}\sqrt{\frac{\hbar}{2V\varepsilon_0\omega_k}}\, e^{-i\vec{k}\cdot\vec{r}+i\omega_k t}\sqrt{n_{k\lambda}+1}\;\vec{e}_{k\lambda}\cdot\vec{p},$$

meaning that ((and now including the time-dep. from $|\psi_i\rangle$))

$$\langle f|H_1'|i\rangle = \frac{e}{m}\sqrt{\frac{\hbar}{2V\varepsilon_0\omega_k}\,(n_{k\lambda}+1)}\cdot\vec{e}_{k\lambda}\cdot\vec{M}\;e^{-i(E_2-E_1-\hbar\omega_k)t/\hbar}$$

where $\vec{M} = \langle\psi_1|e^{-i\vec{k}\cdot\vec{r}}\vec{p}\,|\psi_2\rangle$

Using our results derived in chapter 11.2 for the transition rate:

$$W_{2\to 1} = \frac{2\pi}{\hbar}\cdot\frac{e^2}{m^2}\,\frac{\hbar}{2V\varepsilon_0\omega_k}\,(n_{k\lambda}+1)\,|\vec{e}_{k\lambda}\cdot\vec{M}|^2\,\delta(E_2-E_1-\hbar\omega_k)$$

The δ-function ensures energy conservation.

We can also obtain the total transition rate from atomic state 2 to state 1, regardless of the mode of the emitted photon, by performing over all possible modes. We use that there are $\frac{V}{(2\pi)^3} d^3k$ modes with wavevector $\vec{k}$ in the element d^3k for a given polarization, which yields:

$$w_{2\to 1} = \sum_{\lambda} \int W_{2\to 1} \, V \cdot \frac{d^3k}{(2\pi)^3}$$

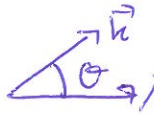
$$= \frac{e^2}{m^2} \sum_{\lambda} \int \frac{d^3k}{(2\pi)^3} \frac{\pi}{\varepsilon_0 \omega_k} (n_{k\lambda} + 1) \, \delta(E_2 - E_1 - \hbar\omega_k) \, |\vec{e}_{k\lambda} \cdot \vec{M}|^2$$

Using that $d^3k = 2\pi \sin\theta \, d\theta \, k^2 dk$ and

$$\delta(E_2 - E_1 - \hbar\omega_k) = \delta(\hbar\omega_{21} - \hbar k c) = \frac{1}{\hbar c} \delta(c^{-1}\omega_{21} - k),$$

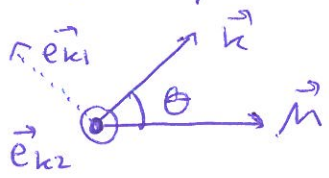
the integral over $\vec{k}$ becomes trivial due to the δ-function:

$$w_{2\to 1} = \sum_{\lambda} \frac{e^2 \omega_{21}}{4\pi\varepsilon_0 m^2 \hbar c^3} \int_0^{\pi} \sin\theta \, d\theta \, |\vec{e}_{k\lambda} \cdot \vec{M}|^2 (n_{k\lambda} + 1)$$

with $k = \frac{\omega_{21}}{c}$. The angle θ specifies the direction of $\vec{k}$ relative $\vec{M}$:  . Let us for now focus on spontaneous emission $n_{k\lambda} = 0$.

Spontaneous emission

The summation over the polarization directions is easy if we assume that $\vec{e}_{k1}$ lies in the plane spanned by $\vec{k}$ and $\vec{M}$, so that $\vec{e}_{k2}$ is $\perp$ this plane:



Since $\vec{e}_{k2} \perp \vec{M}$, we obtain $\sum_{\lambda} |\vec{e}_{k2} \cdot \vec{M}|^2 = |\vec{e}_{k1} \cdot \vec{M}|^2 = \sin^2\theta \cdot |\vec{M}|^2$

Performing the resulting angular integration $\int_0^{\pi} \sin^3\theta \, d\theta = \frac{4}{3}$

yields:

$$w_{2\to 1} = \frac{e^2 \omega_{21}}{3\pi\varepsilon_0 m^2 \hbar c^3} \left| \langle \psi_1 | e^{-i\vec{k}\cdot\vec{r}} \vec{p} | \psi_2 \rangle \right|^2$$

The name "spontaneous emission" was given during a time when one believed that it truly was not caused by any interaction. We now see that this point of view is incorrect: the emission occurs as a result of stimulation by the EM field in vacuum.

Stimulated emission

By setting $n_{k\lambda} = 0$ in the factor $(n_{k\lambda}+1)$, we omitted the possibility of stimulated emission: the presence of photons.

A key difference from spontaneous emission is that stimulated

photons will have the same direction and polarization as the stimulation, rather than being arbitrary. This is a crucial principle behind how a laser works.

The opposite process, stimulated absorption, has a transition rate proportional to $n_{k\lambda}$ since

$$|\langle n_{k\lambda}-1|a_{k\lambda}|n_{k\lambda}\rangle|^2 = n_{k\lambda}.$$

CHAPTER 14

QUANTUM STATISTICS

So far, we have considered quantum systems described by a single wave function (or state vector): such systems are said to be in a pure state.

These have been assumed prepared in a specific way so that the state vector is completely known.

We will now study quantum systems that have states which are incompletely known: mixed states. Instead of a single wavefunction, one must use a statistical mixture of wavefunctions to describe such systems.

Thus: quantum statistics dealing with such quantum systems as mixed states is the quantum analogue of classical statistical mechanics.

A crucial fact that must be strongly emphasized is:

> Mixed states are not the same as superposition of states

Let us illustrate this with a concrete example. Two identical boxes A and B contain a large number of spin-1/2 particles.

100% of the part. are in state $\frac{1}{\sqrt{2}}(|+\rangle_z + |-\rangle_z)$

50% of the part. are in state $|+\rangle_z$.
50% -"- state $|-\rangle_z$.

Which statement is true:

i) The boxes are the same: the difference is just semantics
ii) The boxes are technically different, but experimentally indistinguishable
iii) The boxes are experimentally different

The correct answer is iii), as A is in a pure state (superposition of states) while B is in a mixed state. We can prove this as follows.

Consider a so-called Stern-Gerlach device which effectively measures spin in a given direction. If we use a S-G device oriented in the z-direction, A and B give identical results.

But! If the S-G device is oriented in the x-direction, all particles in box A is measured to be spin-up, while approximately half of the particles in box B are measured to be spin-up while the other half is measured to be spin-down.

This can be understood by noting that $|+\rangle_z + |-\rangle_z$ is the $+\hbar/2$ eigenstate of $\hat{S}_x$, while $|+\rangle_z$ and $|-\rangle_z$ individually may be written as 50-50 linear combinations of the $\pm\hbar/2$ eigenstates of $\hat{S}_x$, e.g.

$$|+\rangle_z = \frac{(|+\rangle_z + |-\rangle_z) + (|+\rangle_z - |-\rangle_z)}{2}.$$

In order to be able to distinguish mathematically clearly between pure states (which can be superpositions) and mixed states, we will begin by introducing the density matrix formalism. As a concrete application, we shall analyze spin-1/2 particles.

14.1 The density matrix

Consider a system consisting of an ensemble (collection) of N sub-systems $\alpha = 1, 2, \ldots N$. Suppose each sub-system is described by a pure state $\psi^{(\alpha)}$. Using Dirac notation, we denote this pure state by $|\alpha\rangle$. All state vectors are assumed normalized to unity, but need not be orthogonal to each other.

Next, select a complete set of basis vectors $|n\rangle$, i.e. orthonormal eigenvectors of some complete set of operators. We then know that $\langle n'|n\rangle = \delta_{n'n}$ and $\sum_n |n\rangle\langle n| = 1$.

We expand the pure state $|\alpha\rangle$ in these basis states $|n\rangle$:

$$|\alpha\rangle = \sum_n c_n^{(\alpha)} |n\rangle \quad \Rightarrow \quad c_n^{(\alpha)} = \langle n|\alpha\rangle .$$

Moreover, since $\langle\alpha|\alpha\rangle = 1 \quad \Rightarrow \quad \sum_n |c_n^{(\alpha)}|^2 = 1$.

Consider an observable represented by an operator A.
Expectation value in state $|\alpha\rangle$:

$$\langle A\rangle_\alpha = \langle\alpha|A|\alpha\rangle = \sum_{nn'} c_{n'}^{(\alpha)*} c_n^{(\alpha)} \langle n'|A|n\rangle$$

$$= \sum_{nn'} \langle n|\alpha\rangle\langle\alpha|n'\rangle\langle n'|A|n\rangle .$$

Now, the average value of A in the ensemble of pure states is called the <u>ensemble (or statistical) average</u> of A is given by:

$$\langle A\rangle = \sum_{\alpha=1}^{N} W_\alpha \langle A\rangle_\alpha$$ where W_α is the statistical weight of each pure state $|\alpha\rangle$, i.e. the probability of finding the system in this state. $(0 \le W_\alpha \le 1)$.

Clearly, $\sum_{\alpha=1}^{N} W_\alpha = 1$. We then have:

$$\langle A\rangle = \sum_{\alpha=1}^{N} \sum_{nn'} W_\alpha c_{n'}^{(\alpha)*} c_n^{(\alpha)} \langle n'|A|n\rangle$$

$$= \sum_{\alpha=1}^{N} \sum_{nn'} \langle n|\alpha\rangle W_\alpha \langle\alpha|n'\rangle\langle n'|A|n\rangle$$

Let us introduce the density operator $\hat{\rho}$:

$$\hat{\rho} = \sum_{\alpha=1}^{N} |\alpha\rangle W_\alpha \langle\alpha|$$

Taking matrix elements of the density operator between basis states $|n\rangle$, we obtain the density matrix ρ in the $\{n\}$ representation whose elements are:

$$\rho_{nn'} \equiv \langle n|\hat{\rho}|n'\rangle = \sum_{\alpha=1}^{N} \langle n|\alpha\rangle W_\alpha \langle\alpha|n'\rangle \qquad (*)$$

$$= \sum_{\alpha=1}^{N} W_\alpha c_{n'}^{(\alpha)*} c_n^{(\alpha)}.$$

Note: the density operator is independent of the choice of the representation, but the density matrix has a different form in different representations.

We can thus express $\langle A\rangle$ as follows:

$$\langle A\rangle = \sum_{\alpha=1}^{N} \sum_{nn'} W_\alpha c_{n'}^{(\alpha)*} c_n^{(\alpha)} \langle n'|A|n\rangle$$

$$= \sum_{nn'} \langle n|\hat{\rho}|n'\rangle \langle n'|A|n\rangle$$

$$= \sum_{n} \langle n|\hat{\rho}A|n\rangle = \mathrm{Tr}(\rho A)$$

according to our definition of the matrix elements $(*)$.
We have then found that:

> Knowing the density matrix enables us to obtain the ensemble average of A

We see that a normalization condition $\mathrm{Tr}\rho = 1$ is obtained by setting $A = 1$ (identity operator).

If we had pure states $|\alpha\rangle$ that were not normalized to unity, then the calculation would have given:

$$\langle A \rangle = \frac{\mathrm{Tr}(\rho A)}{\mathrm{Tr}(\rho)}.$$

The density matrix is Hermitian, as seen from its definition (*): $\langle n|\hat{\rho}|n'\rangle = \langle n'|\hat{\rho}|n\rangle^*$.

A consequence of this is that we can always diagonalize it by means of a unitary transformation. Its diagonal elements $\rho_{nn} = \langle n|\hat{\rho}|n\rangle = \sum_{\alpha=1}^{N} W_\alpha |c_n^{(\alpha)}|^2$ have a simple physical interpretation: it is the probability of finding a member of the ensemble in the pure state $|n\rangle$. We also see from the equations that $\rho_{nn} \geq 0$: $\hat{\rho}$ is a so-called positive semi-definite operator.

Since $\mathrm{Tr}\rho = 1$ and $\rho_{nn} \geq 0$, it follows that $0 \leq \rho_{nn} \leq 1$. Moreover, $\mathrm{Tr}(\rho^2) \leq \mathrm{Tr}(\rho) = 1$ because of this. This relation holds regardless of which representation we write the density

matrix in, since Tr is invariant under a unitary transformation due to its cyclic property: $\mathrm{Tr}(U\rho U^\dagger) = \mathrm{Tr}(UU^\dagger\rho) = \mathrm{Tr}(\rho)$.

Consider the special case such that the system is in a particular pure state $|\lambda\rangle$. Then, $W_\alpha = \delta_{\alpha\lambda}$ and from our definition $\hat{\rho} = \sum_{\alpha=1}^{N} |\alpha\rangle W_\alpha \langle\alpha|$, we have $\hat{\rho}^\lambda \equiv \hat{\rho} = |\lambda\rangle\langle\lambda|$.

This is called a projection operator onto the state $|\lambda\rangle$ which satisfies $(\rho^\lambda)^2 = \rho^\lambda \Rightarrow \mathrm{Tr}[(\rho^\lambda)^2] = \mathrm{Tr}(\rho^\lambda) = 1$.

The equation $\mathrm{Tr}[(\rho^\lambda)^2] = 1$ in fact gives us a criterion for deciding whether a state is pure or not that is invariant under all unitary transformations (since Tr is invariant).

It also follows that $\mathrm{Tr}(\rho^\lambda A) = \sum_{nn'} \langle n|\hat{\rho}^\lambda|n'\rangle\langle n'|A|n\rangle = \langle\lambda|A|\lambda\rangle$.

Suppose that we use a rep. $\{k\}$ in which ρ^λ is diagonal. Then, the above equation is satisfied if

$$\rho^\lambda_{kk'} = \delta_{k\lambda}\delta_{k'\lambda}.$$

ρ^λ then only has one non-vanishing matrix element which is equal to 1 in the λth row and column.

⟹ All eigenvalues of the pure state density ~~operator~~ matrix ρ are equal to zero in any rep. except one eigenvalue which is equal to unity. (since eigenvalues don't change under unitary transformations). This is an equivalent way of characterizing a pure state via the density matrix.

In labelling the rows and columns of ρ with indices n and n', both n and n' in general refer to a set of indices (such as quantum numbers). Often times, however, we are only interested in a particular property of the system, e.g. spin. We then omit the dependence of ρ on all other variables, keeping only the relevant spin variables and in this manner define a reduced density matrix.

14.2 The density matrix for a spin-1/2 system. Polarization.

We shall now apply the general methods presented in 14.1 on the case of spin-1/2 particles, e.g. beam of electrons.

The pure states of a spin-1/2 particle are labelled by momentum eigenvalues (p_x, p_y, p_z) and the spin projection eigenvalues $m_s \hbar$ $(m_s = \pm \frac{1}{2})$. Let $\hat{z}$ be the quantization axis.

The states are then $|p_x, p_y, p_z, m_s\rangle$ and the density matrix elements are $\langle n|\hat{\rho}|n'\rangle = \langle p_x, p_y, p_z, m_s|\hat{\rho}|p_x', p_y', p_z', m_s'\rangle$.

Momentum indices : continuous. Spin indices : discrete.

We focus here on the spin properties - disregard momentum labels and look at the reduced density matrix $\langle m_s|\hat{\rho}|m_s'\rangle$ (2×2 matrix in spin space).

Consider two beams of electrons : ·····> N_a electrons in the pure state $|\chi^{(a)}\rangle$

– – – –> N_b electrons in the pure state $|\chi^{(b)}\rangle$.

The density operator describing the joint beam:

$$\hat{\rho} = W_a |\chi^{(a)}\rangle\langle\chi^{(a)}| + W_b |\chi^{(b)}\rangle\langle\chi^{(b)}|$$

where the statistical weights are: $W_a = \frac{N_a}{N_a+N_b}$, $W_b = \frac{N_b}{N_a+N_b}$.

We now choose a basis set of two states $|\chi_1\rangle$ and $|\chi_2\rangle$, e.g. the two basic spinors $|\alpha\rangle = \begin{pmatrix}1\\0\end{pmatrix}$ and $|\beta\rangle = \begin{pmatrix}0\\1\end{pmatrix}$ (spin-up and spin-down) and expand our pure states in terms of these:

$$|\chi^{(a)}\rangle = c_1^{(a)}|\chi_1\rangle + c_2^{(a)}|\chi_2\rangle, \quad |\chi^{(b)}\rangle = c_1^{(b)}|\chi_1\rangle + c_2^{(b)}|\chi_2\rangle$$

It follows that the density matrix in the $\{|x_i\rangle\}$ representation is given by:

$$\rho = \begin{pmatrix} W_a |c_1^{(a)}|^2 + W_b |c_1^{(b)}|^2 & W_a c_1^{(a)} c_2^{(a)*} + W_b c_1^{(b)} c_2^{(b)*} \\ W_a c_1^{(a)*} c_2^{(a)} + W_b c_1^{(b)*} c_2^{(b)} & W_a |c_1^{(a)}|^2 + W_b |c_2^{(b)}|^2 \end{pmatrix}$$

If our mixture consists of N_1 electrons in $|x_1\rangle \equiv |\alpha\rangle$ state and N_2 electrons in the $|x_2\rangle \equiv |\beta\rangle$ state, the joint beam is represented by the density operator:

$$\hat{\rho} = W_1 |x_1\rangle\langle x_1| + W_2 |x_2\rangle\langle x_2| \quad \text{with } W_1 = \frac{N_1}{N_1+N_2}, \; W_2 = \frac{N_2}{N_1+N_2}.$$

Since now $c_1^{(a)} = c_2^{(b)} = 1$ and $c_1^{(b)} = c_2^{(a)} = 0$, the density matrix becomes diagonal in the $\{|x_i\rangle\}$ rep.: $\rho = \begin{pmatrix} W_1 & 0 \\ 0 & W_2 \end{pmatrix}$.

Polarization

Let ρ be a general 2×2 density matrix describing a spin-$1/2$ system. The unit matrix and three Pauli matrices form a complete set of 2×2 matrices, so we may write:

$$\rho = a_0 I + a_x \sigma_x + a_y \sigma_y + a_z \sigma_z = a_0 I + \vec{a}\cdot\vec{\sigma}.$$

$\{a_0, a_x, a_y, a_z\}$ are in general complex parameters.

Since we know that $\mathrm{Tr}(\rho) = 1$ must be satisfied, it follows that $a_0 = \frac{1}{2}$ by using $\mathrm{Tr}\, I = 2$ and $\mathrm{Tr}\,\sigma_i = 0$.

The coefficients a_i, $i = x,y,z$ give information about the polarization of the mixture of states described by ρ. To see this, first note that $\langle \sigma_i \rangle = \mathrm{Tr}(\rho\sigma_i)$ as we have derived previously. Inserting our general expression for ρ and using $\mathrm{Tr}(\sigma_i\sigma_j) = 2\sigma_{ij}$, we find $\langle \sigma_i \rangle = 2a_i$. We can then write:

$$\rho = \frac{1}{2}\left(I + \vec{\sigma}\cdot\vec{P}\right) \quad \text{where} \quad \vec{P} = \langle \vec{\sigma} \rangle \text{ is the polarization vector.}$$

Since ρ is Hermitian, we may always diagonalize it by choosing an appropriate set of basis states. We have

$$\rho = \frac{1}{2}(I + \vec{\sigma}\cdot\vec{P}) = \frac{1}{2}\begin{pmatrix} 1+P_z & P_x - iP_y \\ P_x + iP_y & 1-P_z \end{pmatrix} \Rightarrow \rho_{\text{diag}} = \frac{1}{2}\begin{pmatrix} 1+P & 0 \\ 0 & 1-P \end{pmatrix},$$

where $P \equiv \pm|\vec{P}| = \pm\sqrt{P_x^2 + P_y^2 + P_z^2}$.

We see that in the representation where ρ is diagonal, one has $P_x = P_y = 0$ and $P = P_z$.

Thus, if we let $|\uparrow\rangle$ and $|\downarrow\rangle$ correspond to the kets for spin up and spin down with $\vec{P}$ along the z-axis, we obtain:

$\vec{\sigma}\cdot\vec{p}\,|\uparrow\rangle = p\,|\uparrow\rangle$ and $\vec{\sigma}\cdot\vec{p}\,|\downarrow\rangle = -p\,|\downarrow\rangle$. We previously established the physical interpretation of the elements ρ_{nn}: the prob. of finding a member of the ensemble in the pure state $|n\rangle$. It follows in our case that $(1+P)/2$ is the prob. of finding in our mixture the pure states with spin-up along $\vec{p}$.

This prob. may also be expressed as $\frac{N_+}{N_+ + N_-}$ where $N_\pm$ is the number of spin measurements giving the value $\pm\hbar/2$ in the $\vec{p}$-direction. It follows that:

$$\frac{1}{2}(1 \pm P) = \frac{N_\pm}{N_+ + N_-} \quad \Rightarrow \quad P = \frac{N_+ - N_-}{N_+ + N_-}.$$

In effect, we have proven that the polarization P is, quite naturally, the probability of finding the system in the state $|\uparrow\rangle$ minus the $-\,''\,-$ $|\downarrow\rangle$.

If $P=0$, $\rho = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & \frac{1}{2} \end{pmatrix}$, and the system is in a completely unpolarized and random state.

In contrast, when the system is in a pure state we have previously shown that $\rho^2 = \rho$. When is this the case?

We see that:

$$\rho^2 = \left[\frac{1}{2}(I + \vec{\sigma}\cdot\vec{P})\right]^2 = \frac{1}{4}(I + 2\vec{\sigma}\cdot\vec{P} + P^2)$$

This is equal to $\frac{1}{2}(I + \vec{\sigma}\cdot\vec{P})$ if $P^2 = 1 \Rightarrow$ there are two pure states, corresponding to $P = +1$ and $P = -1$. The physical interpretation is clear: the system is then totally polarized in the direction of $\vec{P}$ ($P = +1$) or oppositely to $\vec{P}$ ($P = -1$). The corresponding density matrices for pure states with spin projection $\pm \hbar/2$ along $\hat{z}$ is:

$$\rho = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \text{ for } P = +1 \quad \text{and} \quad \rho = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \text{ for } P = -1.$$

For intermediate values, $0 < |P| < 1$, the system is partially polarized.

We conclude this analysis of spin-1/2 systems by commenting on the number of parameters required to determine the density matrix. From our parametrization $\rho = \frac{1}{2}\begin{pmatrix} 1+P_z & P_x - iP_y \\ P_x + iP_y & 1-P_z \end{pmatrix}$, it is clear that the 2×2 density matrix for a spin-1/2 mixed state is entirely specified by three real independent parameters (P_x, P_y, P_z).

In effect, three indep. measurements are required to determine ρ for a spin-1/2 system.

In the special case of pure states, our previous discussion showed that $P^2 = 1$ is satisfied, meaning that only two real indep. parameters are required in that case.

The curriculum ends here: the example below is not part of the curriculum.

EXAMPLE Scattering of particles of spin-1/2 by particles of spin-0.

We will now illustrate the use of ρ and $\vec{P}$ by considering elastic scatt. of spin-1/2 part. by spin-0 part. (for instance, scattering of nucleons by pions).

Let the quantization axis be parallel with the direction of incidence $\hat{z}$. Let the initial spin state have $S_z = m\hbar$ and final state $S_z = m'\hbar$. The scattering amplitude is denoted $f_{m'm}(\theta, \varphi)$ where (θ, φ) are the angles determining the relative momentum of the particles in the final state, $\hbar\vec{k}'$. The initial relative momentum $\hbar\vec{k} \parallel \hat{z}$, so that for elastic scattering:

$$k = |\vec{k}| = |\vec{k}'| \quad \text{and} \quad \vec{k} \cdot \vec{k}' = k^2 \cos\theta .$$

$f_{m'm}(\theta, \varphi)$ forms a 2D spin space matrix ($m, m' = \pm 1/2$), and need not be diagonal since the interaction between spin-0 and spin-1/2 part. may in general be spin-dependent.

If the spin-1/2 particles are initially unpolarized and no spin measurement is made in the final state, then:

$$\left(\frac{d\sigma}{d\Omega}\right)_{unp} = \frac{1}{2}\sum_{mm'} |f_{m'm}(\theta,\varphi)|^2$$

(summing over final spin states and averaging over initial).

If the scattering has rotational invariance (which it should), we can say something about the form of $f_{m'm}(\theta,\varphi)$.

The only vectors in the problem are $\vec{k}, \vec{k}', \vec{\sigma}$ where $\vec{S} = \frac{\hbar}{2}\vec{\sigma}$ is the spin-1/2 operator. We may construct five independent quantities which are invariant under rotations:

$\vec{k}\cdot\vec{k}$, $\vec{k}\cdot\vec{k}'$, $\vec{\sigma}\cdot(\vec{k}\times\vec{k}')$, $\vec{\sigma}\cdot\vec{k}$, $\vec{\sigma}\cdot\vec{k}'$. If we restrict our attention to parity-conserving interactions (such as EM and strong interactions), then we should keep only the terms unaltered by a parity transformation $\vec{k}\to(-\vec{k})$, $\vec{k}'\to(-\vec{k}')$, $\vec{S}\to\vec{S}$.

$$\Rightarrow f_{m'm}(\theta,\varphi) = f(\theta)\,\delta_{m'm} + i g(\theta)\langle m'|\vec{\sigma}|m\rangle\cdot\hat{n}$$

where we defined $\hat{n} = \dfrac{\vec{k}\times\vec{k}'}{|\vec{k}\times\vec{k}'|}$. The amplitudes $f(\theta), g(\theta)$ are thus functions of k^2 and $\vec{k}\cdot\vec{k}'$ only.

A convenient observation is that $f_{m'm}(\theta,\varphi)$ is the matrix element in spin space of the operator $\hat{f}$:

$$\hat{f} = f(\theta)\, I + i g(\theta)\, \vec{\sigma}\cdot\hat{n} \quad \text{such that} \quad \langle m'|\hat{f}|m\rangle = f_{mm'}.$$

Consider scattering from an arbitrary initial spin state $|\chi\rangle$ to a final spin state $|\chi'\rangle$ where these states have the form $|\chi\rangle = a|\uparrow\rangle + b|\downarrow\rangle$ and $|\chi'\rangle = a'|\uparrow\rangle + b'|\downarrow\rangle$. The differential scatt. cross section is then given by:

$$\frac{d\sigma}{d\Omega} = |\langle\chi'|\hat{f}|\chi\rangle|^2.$$

Suppose now instead that the initial beam is not in a pure state, but that it is partially polarized and described by $\hat{\rho}$ or by $\vec{P}$ [recall that $\rho = \frac{1}{2}(I + \vec{\sigma}\cdot\vec{P})$]. If $\vec{P} \parallel \hat{z}$, we know that

$$P = \frac{N_+ - N_-}{N_+ + N_-} \quad \text{where } N_\pm \text{ is the number of measurements}$$

of S_z in the incident beam that gives the results $\pm\hbar/2$.

The density operator $\hat{\rho}'$ describing the scattered beam in the direction (θ,φ) can be found from the operator $\hat{f}$ as follows.

$|x'\rangle$ is obtained from $|x\rangle$ via $|x'\rangle = C\hat{f}|x\rangle$ where C is a normalization factor (analogously to our treatment of the scattering amplitude in the Born approximation).

The density operator is then per definition:

$$\hat{\rho}' = \sum_i W_i |C|^2 |\hat{f}x^i\rangle\langle\hat{f}x^i|$$

where W_i is the statistical weight of the pure state $|x^i\rangle$ in the initial beam. We can rewrite this as:

$$\hat{\rho}' = |C|^2 \hat{f}\left(\sum_i W_i |x^i\rangle\langle x^i|\right)\hat{f}^+ = |C|^2 \hat{f}\hat{\rho}\hat{f}^+.$$

To find $|C|^2$, we use $\mathrm{Tr}\,\rho' = 1 \Rightarrow \hat{\rho}' = \dfrac{\hat{f}\hat{\rho}\hat{f}^+}{\mathrm{Tr}(f\rho f^+)}$. (*)

~~Note that $\hat{f}$ is both an operator and matrix, we have $\hat{f} = f$ in this case.~~ Note that we're distinguishing between operators ($\hat{\cdot}$) and matrices.

Eq. (*) is the relation between initial and final density operators. In the present example, we obtain:

$$\vec{P}' = \mathrm{Tr}\{\rho'\vec{\sigma}\} = \frac{\mathrm{Tr}\{ff^+\vec{\sigma}\} + \mathrm{Tr}\{f(\vec{\sigma}\cdot\vec{P})f^+\vec{\sigma}\}}{\mathrm{Tr}\{ff^+\} + \mathrm{Tr}\{f(\vec{\sigma}\cdot\vec{P})f^+\}}$$

where we used that $\rho = \frac{1}{2}(I + \vec{\sigma}\cdot\vec{P})$.

This gives a relation between final and initial polarization.

If the initial beam is unpolarized ($\vec{P}=0$) and no spin measurement is made in the final state, we have to go back to the expression:

$$\left(\frac{d\sigma}{d\Omega}\right)_{unp} = \frac{1}{2}\sum_{mm'} |f_{m'm}(\theta,\varphi)|^2 .$$

One may verify directly that this is equivalent to:

$$\left(\frac{d\sigma}{d\Omega}\right)_{unp} = \frac{1}{2}\,Tr\{f f^{+}\} = |f(\theta)|^2 + |g(\theta)|^2$$

since $f = f(\theta)I + i g(\theta)\,\vec{\sigma}\cdot\hat{n}$. According to our derived expression for $\vec{P}'$, we obtain:

$$\vec{P}' = \frac{Tr\{f f^{+}\vec{\sigma}\}}{2\left(\frac{d\sigma}{d\Omega}\right)_{unp}} \equiv S(\theta)\hat{n} \quad \text{where} \quad S(\theta) = \frac{2\,Im\{f(\theta)\cdot g^{*}(\theta)\}}{\left(\frac{d\sigma}{d\Omega}\right)_{unp}} .$$

for the polarization produced in the scattered beam in the direction (θ,φ).