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Lecture notes for QMII (661)

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ABSTRACT: These are the notes for the lectures. They contain what is explained in class and can be used to refresh your memory or to stay up to date if you miss a class. They do *not* replace the book since they have much less information. Also take into account that the actual lectures might run a little behind schedule.

KEYWORDS: Quantum Mechanics.

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1. Lecture 1

1.1 Approximate methods

In quantum mechanics, once the Hamiltonian that describes a physical system is known, there are two important class of problems that need to be solved. One is to find the **energy eigenstates**, another is to determine the **time evolution** of an initial state. In general those problems cannot be solved exactly and approximate methods are required.

An approximation can be made once an (adimensional) small parameter λ, $(0 < \lambda \ll 1)$ is identified.

From a mathematical point of view, relevant quantities are expanded in a Taylor series:

$$f(\lambda) = f(0) + \lambda f'(0) + \ldots + \frac{1}{n!}\lambda^n f^{(n)}(0) + \ldots \tag{1.1}$$

In practical calculations we have to be able to compute $f(0)$ plus at least the first correction exactly. A simple check that always needs to be done is that the corrections are indeed small compared to the term being corrected. Another thing to take into account is that, since the perturbation expansion is truncated, it is not possible to balance the corrections and the main term, for example to find minima, etc. Summarizing, one has to be careful not taking the results away from their region of validity.

It is interesting to note that even if we compute all orders in perturbation theory and resume the series, that does not imply that we know the exact function $f(\lambda)$ since non-perturbative corrections are possible. Indeed, consider the function

$$f(\lambda) = e^{-\frac{1}{\lambda}} \tag{1.2}$$

It turns out that

$$\left.\frac{d^n f(\lambda)}{d\lambda^n}\right|_{\lambda=0} = 0, \qquad n = 0, 1, 2, \ldots \tag{1.3}$$

That means that the perturbation expansion of such function (around $\lambda = 0$) vanishes. This seems as an exceptional case but it turns out to appear a lot in practice. Corrections of this type are often called “non-perturbative effects”.

From a physical point of view, the idea of an approximation method is to isolate the main physics and leave smaller effects as corrections. In many cases we only need to compute $f(0)$ and check that the first correction is within experimental uncertainty. Often, it is only necessary to determine the parameter λ and find that it is indeed small. Only afterwards, when the experiment becomes more precise, further corrections might be needed. In other cases, however, the term $f(0)$ vanishes and the existence of corrections, even if very small, indicate the existence of new physical phenomena. For example, radioactive decay is a very tiny effect but can be noticed since it is the only physical process that can change one chemical element into another.

For that reason, it is important to be able to isolate and estimate the perturbative corrections before doing a concrete calculation. Consider the familiar case of the hydrogen atom. The Hamiltonian and bound state energy levels of a particle of mass m and charge $q = -e$ in the Coulomb potential of a much heavier particle of charge $q = +e$ are

$$H = \frac{p^2}{2m} - \frac{e^2}{r} \tag{1.4}$$

$$E_n = -\frac{e^2}{2a_0 n^2}, \quad a_0 = \frac{\hbar^2}{me^2} \tag{1.5}$$

In particular the ground state energy is

$$E_{gs} = \frac{me^4}{2\hbar^2} = -13.6 \text{ eV} \simeq -10 \text{ eV} \tag{1.6}$$

What are, and how do we estimate the corrections?. Before going into that, let us remind ourselves the value of some constants and set the units we use to measure them. Generically, we give two values, one that is good enough for our calculations and then one used for a rough order of magnitude estimate. For precision calculations the currently recommended values can be found from NIST (http://physics.nist.gov/cuu/Constants) The energy will be measured in eV which is the energy gained by an electron when moving across a potential difference of 1V.

$$1\,\text{eV} = e \times 1\text{V} = 1.6 \times 10^{-19}\text{C.V} = 1.6 \times 10^{-19}\text{J}, \quad (\text{J=Joules, C=Coulomb, V=Volt}) \tag{1.7}$$

The charge of the electron is $q = -e$ where $e = 1.6 \times 10^{-19}C$. However, since energy is $U \sim e^2/r$ it is more convenient to use the following units

$$e^2 = 1.44 \text{ MeV fm} \tag{1.8}$$

where 1 fm $= 10^{-15}$m. For Planck's constant we use the same units to get

$$\hbar c \simeq 197 \text{ MeV fm} \approx 200 \text{ MeV fm} \tag{1.9}$$

The value $\hbar c \simeq 197\text{MeV fm}$ is good enough for our calculations, a rough order of magnitude estimate can be done using $\hbar c \approx 200$ MeV fm. For precise values see http://physics.nist.gov/cuu/Constants. From here, the fine structure constant α_e is:

$$\alpha_e = \frac{e^2}{\hbar c} \simeq \frac{1}{137} \tag{1.10}$$

The mass m_e of the electron has an energy equivalent of

$$m_e c^2 \simeq 0.511 \text{ MeV} \approx 0.5 \text{ MeV} \tag{1.11}$$

Electric fields are measured (from $E \sim e/r^2$) in units

$$|\vec{E}| \sim \frac{\sqrt{\text{MeV fm}}}{\text{fm}} = \sqrt{\frac{\text{MeV}}{\text{fm}^3}} \tag{1.12}$$

and therefore $|\vec{E}|^2$ is an energy density. Magnetic fields can be measured in the same units as electric field

$$B \sim \sqrt{\frac{\mathrm{MeV}}{\mathrm{fm}^3}} \tag{1.13}$$

in which case the Lorentz force has the form

$$\vec{F} = q\vec{E} + \frac{q}{c}\vec{v} \times \vec{B} \tag{1.14}$$

However in experimental physics it is more common to use Tesla ($1\mathrm{T} = \frac{\mathrm{V.s}}{\mathrm{m}^2} = \frac{\mathrm{Kg}}{\mathrm{C.s}}$) as the unit of magnetic field, in which case the Lorentz force reads

$$\vec{F} = q\vec{E} + q\vec{v} \times \vec{B} \tag{1.15}$$

The energy of a magnetic dipole $\vec{\mu}$ in a magnetic field $\vec{B}$ is given by

$$U = -\vec{\mu}.\vec{B} \tag{1.16}$$

The magnetic moment of an electron is

$$\vec{\mu} = -g_s \mu_B \frac{\vec{S}}{\hbar} \tag{1.17}$$

where $\vec{S}$ is the spin of the electron, $g_s \simeq 2$ and μ_B is Bohr's magneton. The expression for Bohr's magneton depends on the units we use to measure magnetic field. If we measure the magnetic field in Tesla then

$$\mu_B = \frac{e\hbar}{2m_e} \tag{1.18}$$

If we measure the magnetic field in the same units as electric field (q/r^2) then

$$\mu_B = \frac{e\hbar}{2m_e c} \tag{1.19}$$

1.2 Making estimates

In many cases it is enough to make a rough estimate of the size of the corrections to know if they will invalidate the results we already have and thus decide if we need to compute them in full or not. As an example consider the energy levels of the hydrogen atom and identify the different physical effects that correct their energies and estimate the values of such corrections. Let us list some of them in no particular order:

- Relativistic corrections. We can estimate them from the ratio between the energy involved and the mass of the electron:

$$\frac{E_0}{mc^2} \sim \frac{10 \text{ eV}}{0.5 \text{ MeV}} = 2 \times 10^{-5} \tag{1.20}$$

This is the same, in order of magnitude as $(v/c)^2$. Notice that relativistic corrections to the energy are quadratic in v/c. The correction to the energy can be estimated to be

$$\delta E \sim 2 \times 10^{-5} E_0 \sim 2 \times 10^{-4} \text{ eV} \tag{1.21}$$

Notice the small parameter can be written as

$$\frac{E_0}{mc^2} \sim \frac{me^4}{\hbar^2}\frac{1}{mc^2} = \left(\frac{e^2}{\hbar c}\right)^2 = \alpha_e^2 \tag{1.22}$$

- Spin orbit. An electron is not only a charge but also a tiny magnet. A magnet moving inside an electric field feels an interaction as if in a magnetic field $B \sim \frac{v}{c}E$ (relativistic effect). Therefore

$$\delta E \sim \mu_B \frac{v}{c} E \sim \mu_B \frac{v}{c}\frac{e}{a_0^2} \tag{1.23}$$

Since, from the previous case we found $v/c \sim \alpha_e$ we find

$$\frac{\delta E}{E_{gs}} \sim \frac{e^2 m^2 e^4}{\hbar^4}\frac{\hbar c}{mc^2}\, \alpha_e \sim \alpha_e^2 \tag{1.24}$$

namely of the same order than the relativistic correction.

- Spin-spin. The proton is also a magnetic dipole and therefore there is a dipole-dipole interaction between electron and proton. The magnetic field of the proton behaves as

$$|\vec{B}| \sim \frac{|\vec{\mu_P}|}{r^3} \tag{1.25}$$

with

$$|\vec{\mu_P}| = g_P \frac{m_e}{m_P}\mu_B, \quad g_P = 5.586, \quad m_P c^2 = 938 \text{ MeV} \tag{1.26}$$

so we estimate

$$\delta E \sim \frac{\mu_P \mu_e}{a_0^3} \sim g_P \frac{m_e}{m_P}\left(\frac{e\hbar}{m_e c}\right)^2 \left(\frac{m_e e^2}{\hbar}\right)^3 \sim \frac{m_e}{m_P}\frac{m_e e^8}{\hbar^4 c^2} \tag{1.27}$$

Thus,

$$\frac{\delta E}{E_{gs}} \sim g_P \frac{m_e}{m_P}\alpha_e^2 \tag{1.28}$$

suppressed by the factor $g_P \frac{m_e}{m_P} \sim \frac{5.6}{2000} \sim 0.003$ respect to the spin-orbit and relativistic corrections.

- Finite size of the proton. The proton can be approximated by a charged sphere of radius $r_P \sim 1\,\mathrm{fm}$. The small parameter should be the ratio

  $$\frac{r_P}{a_0} \sim 10^{-5} \tag{1.29}$$

  In fact we can do better by computing the average energy of the electron when it is inside the proton

  $$\delta E \sim \int_0^{r_P} |\psi(0)|^2 \frac{e^2}{r} r^2 dr \sim e^2 \frac{r_P^2}{a_0^3} = \frac{e^2}{a_0} \frac{r_P^2}{a_0^2} \tag{1.30}$$

  We find

  $$\frac{\delta E}{E_{gs}} \sim \frac{r_P^2}{a_0^2} \sim 10^{-10} \tag{1.31}$$

  Notice that the idea is that the first correction is quadratic in the small parameter and therefore smaller than expected.

You can consider other corrections and see how they behave. In general it is important to do this analysis to discard those corrections that are not relevant for the experimental precision we want to achieve. Also, it does not make sense to start computing a certain correction to higher orders in perturbation theory if those higher orders are of the same order of another phenomenon that we are ignoring. This estimates are useful as a starting point after which you can start doing actual computations. It is important also to make a hierarchy of perturbations, namely which are the most important etc.

2. Lecture 2

2.1 A calculable example

In a two state system, it is possible to compute the eigenvalues exactly. In fact with the help of a computer and a good numerical subroutine (*e.g.* from the linear algebra package Lapack) one can compute eigenvalues in systems of several thousand states. If only the ground state is required, one can look at systems of several million states. In any case, the simple two by two system can be solved both analytically and in perturbation theory to understand the problem one is facing. In fact this is a general procedure, when studying a new method or technique it is always good to reproduce some results one already knows to bridge the gap.

Consider the Hamiltonian

$$H = \begin{pmatrix} a & b \\ c & d \end{pmatrix} \tag{2.1}$$

with eigenvalues

$$\epsilon_\pm = \frac{1}{2}\left((a+d) \pm \sqrt{(a-d)^2 + 4bc}\right) \tag{2.2}$$

In perturbation theory we have a Hamiltonian that can be diagonalized exactly plus a correction. We simulate that by taking

$$H = \begin{pmatrix} \epsilon_1 & 0 \\ 0 & \epsilon_2 \end{pmatrix} + \lambda \begin{pmatrix} v_{11} & v_{12} \\ v_{21} & v_{22} \end{pmatrix} \tag{2.3}$$

where all quantities are real except v_{12} and v_{21} which satisfy $v_{12} = v_{21}^*$. We also assume that we order the eigenvalues so that $\epsilon_1 > \epsilon_2$. We now find, for example

$$\epsilon_+ = \frac{\epsilon_1 + \epsilon_2 + \lambda(v_{11} + v_{22})}{2} + \sqrt{\left(\frac{\epsilon_1 - \epsilon_2 + \lambda(v_{11} - v_{22})}{2}\right)^2 + \lambda^2\, v_{12} v_{21}} \tag{2.4}$$

Expanding in a Taylor series we find

$$\epsilon_+ = \epsilon_1 + \lambda v_{11} + \lambda^2 \frac{|v_{12}|^2}{\epsilon_1 - \epsilon_2} + \dots \tag{2.5}$$

The result is simple but illustrates perfectly the general result we are going to find later. The first correction to the energy is simply the corresponding diagonal element of the perturbation. Quite often this is the only correction needed. The second order shows a problem. For the perturbative expansion to make sense we need $\lambda \frac{|v_{12}|}{\epsilon_1 - \epsilon_2} \ll 1$, namely that the correction in energy is much smaller that the energy difference $|\epsilon_1 - \epsilon_2|$. This will be more evident when we compute the correction to the eigenstate. The extreme case is that of degenerate states $\epsilon_1 = \epsilon_2$, but notice that it is not necessary that they are exactly equal to ruin the expansion, only within the "error" $|v_{12}|$. In that case we need to diagonalize the perturbation exactly but the good news is that this has to be done only within the (approximately) degenerate subspace.

We can also compute the corresponding eigenvector.

$$\begin{pmatrix} a-\epsilon & b \\ c & d-\epsilon \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{2.6}$$

or equivalently

$$|\psi\rangle = \alpha|1\rangle + \beta|2\rangle \tag{2.7}$$

If we do not normalize the state a simple solution is

$$|\psi\rangle = |1\rangle - \frac{(a-\epsilon)}{b}|2\rangle \tag{2.8}$$

which has the clear meaning of the initial eigenstate plus a small correction. Replacing the previous values we find

$$|\psi\rangle = |1\rangle + \lambda\frac{v_{21}}{(\epsilon_1-\epsilon_2)}|2\rangle + \mathcal{O}(\lambda^2) \tag{2.9}$$

Now it is evident that the correction to the state will be small, namely its norm will be small compared to one, if

$$\lambda\left|\frac{v_{21}}{(\epsilon_1-\epsilon_2)}\right| \ll 1 \tag{2.10}$$

and not simply $\lambda \ll 1$. In that sense λ is useful to organize the perturbative expansion but more care is needed to check its validity.

2.2 Perturbation theory to a non-degenerate level

Consider a Hamiltonian H_0 of which we can compute its exact eigenvalues $E_n^{(0)}$ and eigenvectors $|E_n^{(0)}\rangle$, that is

$$H_0|E_n^{(0)}\rangle = E_n^{(0)}|E_n^{(0)}\rangle, \quad n = 0, 1, \ldots \tag{2.11}$$

We assume a discrete spectrum but similar formulas are valid if there is a continuum. Now consider what happens if we add a small perturbation

$$H = H_0 + \lambda V \tag{2.12}$$

Take a non-degenerate eigenstate of H_0, $|E_n^{(0)}\rangle$ and expand the new eigenstate and eigenvalue around it:

$$E = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots \tag{2.13}$$

$$|E\rangle = |\psi_0\rangle + \lambda|\psi_1\rangle + \lambda^2|\psi_2\rangle + \ldots \tag{2.14}$$

We assume that the corrections to the state are orthogonal to the initial state since any parallel correction can be absorbed by redefining the first coefficient. The eigenstate equation now reads:

$$(H_0+\lambda V)(|\psi_0\rangle+\lambda|\psi_1\rangle+\lambda^2|\psi_2\rangle+\ldots) = (E_n^{(0)}+\lambda E_n^{(1)}+\lambda^2 E_n^{(2)}+\ldots)(|\psi_0\rangle+\lambda|\psi_1\rangle+\lambda^2|\psi_2\rangle+\ldots) \tag{2.15}$$

Equating terms of the same order we find

$$H_0|\psi_0\rangle = E_n^{(0)}|\psi_0\rangle \tag{2.16}$$

$$H_0|\psi_1\rangle + V|\psi_0\rangle = E_n^{(0)}|\psi_1\rangle + E_n^{(1)}|\psi_0\rangle \tag{2.17}$$

$$H_0|\psi_2\rangle + V|\psi_1\rangle = E_n^{(0)}|\psi_2\rangle + E_n^{(1)}|\psi_1\rangle + E_n^{(2)}|\psi_0\rangle \tag{2.18}$$

The first equation simply establishes that

$$|\psi_0\rangle = |E_n^{(0)}\rangle \tag{2.19}$$

The second one can be projected over $|E_n^{(0)}\rangle$ giving

$$E_n^{(1)} = \langle E^{(0)}|V|E_n^{(0)}\rangle \tag{2.20}$$

Projecting over all the other states we find that the correction to the eigenstate is

$$|\psi_1\rangle = -\sum_{m\neq n} \frac{|E_m^{(0)}\rangle\langle E_m^{(0)}|V|E_n^{(0)}\rangle}{E_m^{(0)} - E_n^{(0)}} \tag{2.21}$$

As a bonus we can project the third equation onto the vector $|E_n^{(0)}\rangle$ obtaining

$$E_n^{(2)} = \langle\psi_0|V|\psi_1\rangle \tag{2.22}$$

therefore the second order correction to the energy is given by

$$E_n^{(2)} = -\sum_{m\neq n} \frac{|\langle E_m^{(0)}|V|E_n^{(0)}\rangle|^2}{E_m^{(0)} - E_n^{(0)}} \tag{2.23}$$

Notice that if we are correcting the ground state then $E_m^{(0)} > E_n^{(0)}$ and therefore the second order correction is always negative. In this case it is easy to put bounds to the correction:

$$-\sum_{m>0} \frac{|\langle E_m^{(0)}|V|E_{gs}^{(0)}\rangle|^2}{E_1^{(0)} - E_{gs}^{(0)}} \leq E_{gs}^{(2)} \leq -\sum_{m=1}^{p} \frac{|\langle E_m^{(0)}|V|E_{gs}^{(0)}\rangle|^2}{E_m^{(0)} - E_{gs}^{(0)}} \tag{2.24}$$

where in the second inequality the sum is only over a few states instead of all of them (perhaps even one state can give a good bound). In the first inequality we can use the completeness of the eigenstate basis to write

$$\sum_{m>0} \frac{|\langle E_m^{(0)}|V|E_{gs}^{(0)}\rangle|^2}{E_1^{(0)} - E_{gs}^{(0)}} = \frac{1}{E_1^{(0)} - E_{gs}^{(0)}} \left(\langle E_{gs}^{(0)}|V^2|E_{gs}^{(0)}\rangle - \langle E_{gs}^{(0)}|V|E_{gs}^{(0)}\rangle^2 \right) \tag{2.25}$$

Thus, the bounds read

$$-\frac{\langle E_{gs}^{(0)}|(\Delta V)^2|E_{gs}^{(0)}\rangle}{E_1^{(0)} - E_{gs}^{(0)}} \le E_{gs}^{(2)} \le -\sum_{m=1}^{p} \frac{|\langle E_m^{(0)}|V|E_{gs}^{(0)}\rangle|^2}{E_m^{(0)} - E_{gs}^{(0)}} \tag{2.26}$$

which can be a useful formula if we are not able to compute $E_{gs}^{(2)}$ exactly. In the last formula we introduced $\Delta V = V - \langle V\rangle = V - \langle E_{gs}^{(0)}|V|E_{gs}^{(0)}\rangle$.

2.2.1 Sum rules

The expression for the second order correction to the energy is hard to evaluate since it involves a sum over all states

$$E_n^{(2)} = -\sum_{m\neq n} \frac{|\langle E_m^{(0)}|V|E_n^{(0)}\rangle|^2}{E_m^{(0)} - E_n^{(0)}} \tag{2.27}$$

We just saw how we can put bounds on this contribution. There is a technique that, when applicable, allows such sums to be evaluated exactly. It consists in finding an operator F such that

$$[F, H]|E_n^{(0)}\rangle = V|E_n^{(0)}\rangle \tag{2.28}$$

where $|E_n^{(0)}\rangle$ is the state that we want to correct (for example the ground state). Notice that it is not necessary that $[F, H] = V$ in general, they only have to give the same result when applied to the state $|E_n^{(0)}\rangle$. If such operator F exists then we have

$$\langle E_m^{(0)}|V|E_n^{(0)}\rangle = \langle E_m^{(0)}|[F, H]|E_n^{(0)}\rangle = (E_n^{(0)} - E_m^{(0)})\langle E_m^{(0)}|V|E_n^{(0)}\rangle \tag{2.29}$$

and then

$$E_n^{(2)} = \sum_{m\neq n} \langle E_n^{(0)}|V|E_m^{(0)}\rangle\langle E_m^{(0)}|F|E_n^{(0)}\rangle \tag{2.30}$$

$$= \langle E_n^{(0)}|VF|E_n^{(0)}\rangle - \langle E_n^{(0)}|V|E_n^{(0)}\rangle\langle E_n^{(0)}|F|E_n^{(0)}\rangle \tag{2.31}$$

which is much easier to evaluate since it does not require any sums over states. Such results that allow the computation of sum over all states have the generic name of *sum rules* and, whenever applicable, greatly simplify calculations.

3. Lecture 3

3.1 An example: 2s-1s transition frequency

We mention that the atomic levels of the hydrogen atom are corrected. An interesting case is the level $2s$. It cannot decay to $1s$ by emitting one photon since that would violate angular momentum conservation. Recall that there are no spherically symmetric waves in electromagnetism. Therefore the decays happens by two photon emission which is less likely. Thus, the $2s$ state is long lived and the $2s-1s$ line is very sharp. The frequency of such transition is measured to be

$$\nu_{2s-1s} = \frac{E_{2s}-E_{1s}}{h} = 2466061413187074(46)\text{Hz} \tag{3.1}$$

Let us compute the first corrections that give rise to such a result. Before starting let us recall the values of some constants

$$\begin{aligned} \alpha_e &= \frac{1}{137.035999074} && (3.2)\\ m_e c^2 &= 0.510998910 \text{ MeV} && (3.3)\\ h &= 4.135667516 \times 10^{-15} \text{ eV s} && (3.4)\\ c &= 299792458 \frac{\text{m}}{\text{s}} && (3.5)\\ m_P c^2 &= 938.272046 \text{ MeV} && (3.6)\\ & && (3.7) \end{aligned}$$

Consider now the successive contributions to the result:

- Coulomb potential We start with the value from the non-relativistic Schroedinger equation:

  $$E^{(0)}_{2s} - E^{(0)}_{1s} = \frac{3}{4}E_{gs} = \frac{3}{4}\frac{\alpha^2}{2}\, m_e c^2 \tag{3.8}$$

  This gives

  $$\nu^{(0)}_{2s-1s} = 2.4673813840 \times 10^{15} \text{ Hz} \tag{3.9}$$

  already a good approximation with a discrepancy $\sim 10^{12}$ Hz with respect to the experimental value.

- Proton recoil Since the proton has a finite mass it is also moving. From Newtonian mechanics we know we can replace the electron mass by the reduced mass

  $$m_r = \frac{m_e m_P}{m_e + m_P} = \frac{m_e}{1+\frac{m_e}{m_P}} \tag{3.10}$$

This can be considered in perturbation theory but it can be done exactly by replacing $m_e \to m_r$ in the formula for the energy difference:

$$E_{2s}^{(0)} - E_{1s}^{(0)} = \frac{3}{4}\frac{\alpha^2}{2}\, m_r c^2 \tag{3.11}$$

This gives, as the zeroth order approximation

$$\nu_{2s-1s}^{(0)} = 2.4660383380 \times 10^{15} \text{ Hz} \tag{3.12}$$

with a discrepancy $\sim 2 \times 10^{10}$ Hz.

- Relativistic correction

  The energy of a relativistic particle is given by

$$E = \sqrt{m^2c^4 + p^2c^2} = mc^2 + \frac{p^2}{2m^2} - \frac{p^4}{8m^3c^2} + \dots \tag{3.13}$$

The appropriate way to compute the relativistic corrections is to use the Dirac equation. In that case one obtains an extra term called the Darwin term and the spin orbit interaction. The last one can be ignored since we are dealing with states of zero angular momentum. The perturbation reads:

$$V = -\frac{p^4}{8m^3c^2} + \frac{e^2\pi\hbar^2}{2m^2c^2}\delta^{(3)}(\vec{r}) \tag{3.14}$$

The second term is the Darwin term. We cannot derive it here but can argue heuristically for its existence as follows. In the relativistic theory one cannot localize the electron at distances smaller that the Compton wave-length $\lambda_C \sim \frac{h}{mc}$ 10^{-12}m. Therefore the electron feels an effective potential

$$\langle V(\vec{r} + \delta\vec{r})\rangle = V(r) + \frac{1}{2}\frac{\partial^2 V(\vec{r})}{\partial r_i \partial r_j}\langle \delta r_i \delta r_j\rangle + \dots \tag{3.15}$$

where the angled brackets represent average over rapid fluctuation of the electron inside the Compton wave-length. Since such fluctuations should be isotropic we find

$$\langle \delta r_i \delta r_j\rangle \sim \lambda_C^2 \delta^{ij} \tag{3.16}$$

Thus the effective potential is

$$V_{eff}(r) \simeq V(r) + \frac{1}{2}c_1 \lambda_C^2 \nabla^2 V(r) \tag{3.17}$$

up to an unknown constant c_1. For the Coulomb potential we have (from Maxwell's equations)

$$\nabla^2 V = -4\pi\rho = -4\pi e \delta^{(3)}(\vec{r}) \tag{3.18}$$

where ρ is the charge density of the proton (here considered point-like). The constant c_1 should be determined from Dirac's equation and turns out to be as discussed before (notice also that this potential should be multiplied by $-e$ the electron charge). The relativistic correction can now be easily computed as the mean value of the perturbation in the unperturbed state:

$$\delta E = -\frac{1}{8m^3c^2}\langle E^{(0)}|p^4|E^0\rangle + \frac{e^2\pi\hbar^2}{2m^2c^2}|\psi(0)|^2 \tag{3.19}$$

The relevant wave-functions are

$$\psi_{1s} = \frac{1}{\sqrt{\pi}a_0^{\frac{3}{2}}}\ e^{-\frac{r}{a_0}} \tag{3.20}$$

$$\psi_{2s} = \frac{1}{\sqrt{4\pi}}\frac{1}{(2a_0)^{\frac{3}{2}}}\left(2-\frac{r}{a_0}\right)\ e^{-\frac{r}{2a_0}} \tag{3.21}$$

To compute the mean value of p^4 we can notice that

$$\langle E^{(0)}|p^4|E^0\rangle = \parallel p^2|E^0\rangle \parallel^2 \tag{3.22}$$

Acting on a wave function that depends only on r (and not on ϕ, θ), the operator p^2 acts as

$$p^2\psi(r) = -\hbar^2\nabla^2\psi(r) = -\hbar^2\left(\partial_r^2\psi + \frac{2}{r}\partial_r\psi\right) \tag{3.23}$$

For the ground state we find

$$-\hbar^2\left(\partial_r^2\psi + \frac{2}{r}\partial_r\psi\right) = -\hbar^2\frac{1}{\sqrt{\pi}a_0^{\frac{7}{2}}}\left(1-2\frac{a_0}{r}\right)\ e^{-\frac{r}{a_0}} \tag{3.24}$$

and therefore

$$\langle E_{1s}^{(0)}|p^4|E_{1s}^0\rangle = \hbar^4\int d^3r\frac{1}{\pi a_0^7}\left(1-2\frac{a_0}{r}\right)^2\ e^{-\frac{2r}{a_0}} \tag{3.25}$$

$$= \hbar^4\frac{4}{a_0^7}\int_0^\infty drr^2\left(1-2\frac{a_0}{r}\right)^2\ e^{-\frac{2r}{a_0}} = 5\frac{\hbar^4}{a_0^4} \tag{3.26}$$

Similarly

$$\langle E_{2s}^{(0)}|p^4|E_{2s}^{(0)}\rangle = \frac{13}{16}\frac{\hbar^4}{a_0^4} \tag{3.27}$$

Together with the Darwin term we find

$$\langle E_{1s}^{(0)}|V|E_{1s}^{(0)}\rangle = -\frac{5}{8m^3c^2}\frac{\hbar^4}{a_0^4} + \frac{e^2\pi\hbar^2}{2m^2c^2}\frac{1}{\pi a_0^3} = -\frac{mc^2\alpha^2}{2}\frac{\alpha^2}{4} \tag{3.28}$$

$$\langle E_{2s}^{(0)}|V|E_{2s}^{(0)}\rangle = -\frac{13}{128m^3c^2}\frac{\hbar^4}{a_0^4} + \frac{e^2\pi\hbar^2}{2m^2c^2}\frac{1}{4\pi}\frac{4}{(2a_0)^3} = -\frac{mc^2\alpha^2}{2}\frac{5\alpha^2}{64} \tag{3.29}$$

The difference contributes

$$\delta E_{2s} - \delta E_{1s} = \frac{mc^2\alpha^2}{2}\alpha^2\left(-\frac{5}{64}+\frac{1}{4}\right) = \frac{mc^2\alpha^2}{2}\frac{11}{64}\alpha^2 \tag{3.30}$$

Therefore, up to now we have

$$\nu_{2s-1s} = \frac{1}{h}\left(\frac{3}{4}\frac{\alpha^2}{2}\,m_r c^2 + \frac{mc^2\alpha^2}{2}\frac{11}{64}\alpha^2\right) = 2.4660684490 \times 10^{15}\ \text{Hz} \tag{3.31}$$

with a discrepancy $\sim 7 \times 10^9$ Hz.

- Lamb shift There is a correction that comes from quantizing the electromagnetic field, known as the Lamb shift. We are not going to compute it here but, for s states, it turns out to be:

$$\delta E_{ns} = \frac{4}{3}\frac{\alpha^5}{\pi n^3}mc^2\left(\ln\frac{n^2}{\alpha^2}+\frac{19}{30}\right) \tag{3.32}$$

This contributes

$$\frac{\delta E_{2s} - \delta E_{1s}}{h} = -9.7569180990 \times 10^9\ \text{Hz} \tag{3.33}$$

Adding it to the previous result the discrepancy is reduced to $\sim 3 \times 10^9$ Hz. It is clear that the improvements are more and more difficult to compute so we finish here. On the other hand there is an interesting contribution to compute coming from the finite size of the proton. We compute that now.

3.2 Proton finite size contribution to the hydrogen energy levels

We compute this contribution separately since it should only be considered after more important contribution are included. Nevertheless it contributes to the experimental value and has been a recent source of interest since some discrepancies were found in a similar calculation for muonic hydrogen.

Imagine the proton is a sphere of radius R with uniform charge density

$$\rho = \frac{e}{V}, \qquad V = \frac{4}{3}\pi R^3 \tag{3.34}$$

It is usual to define the so called charge proton radius through the equation

$$r_P^2 = \langle r^2 \rangle = \frac{\int r^2 \rho(r)\, d^3r}{\int \rho(r)\, d^3r} = \frac{3}{5}R^2 \tag{3.35}$$

Using Gauss law we find the electric field to be

$$\vec{E} = \begin{cases} \frac{e}{r^2}\hat{r} & r > R \\ \\ \frac{e\,r}{R^3}\hat{r} & r < R \end{cases} \tag{3.36}$$

and from here the potential is

$$\phi = \begin{cases} \frac{e}{r} & r > R \\ \frac{e}{2R}\left(3 - \frac{r^2}{R^2}\right) & r < R \end{cases} \tag{3.37}$$

where we chose the constants so that $\phi \to 0$ for $r \to \infty$ and so that $\phi(r)$ is continuous at $r = R$. The potential energy is $V(r) = -e\phi(r)$ and therefore

$$V(r) = \begin{cases} -\frac{e^2}{r} & r > R \\ -\frac{e^2}{2R}\left(3 - \frac{r^2}{R^2}\right) & r < R \end{cases} \tag{3.38}$$

For $r > R$ the potential is evidently the same as for a point-like proton. We can identify the perturbation

$$H = H_0 + \mathcal{V} = \frac{p^2}{2m} - \frac{e^2}{r} + \mathcal{V}(r) \tag{3.39}$$

with

$$\mathcal{V}(r) = \begin{cases} 0 & r > R \\ \frac{e^2}{r} - \frac{e^2}{2R}\left(3 - \frac{r^2}{R^2}\right) & r < R \end{cases} \tag{3.40}$$

The correction to the energy of the ground state is simply the mean value of the perturbation

$$\langle 1s|\mathcal{V}|1s\rangle = \frac{4\pi}{\pi a_0^3}\int_0^R r^2\, dr\ \left(\frac{e^2}{r} - \frac{e^2}{2R}\left(3 - \frac{r^2}{R^2}\right)\right) e^{-\frac{2r}{a_0}} \tag{3.41}$$

$$\simeq \frac{4\pi}{\pi a_0^3}\int_0^R r^2\, dr\ \left(\frac{e^2}{r} - \frac{e^2}{2R}\left(3 - \frac{r^2}{R^2}\right)\right) \tag{3.42}$$

$$= \frac{4e^2}{10a_0^3}R^2 \tag{3.43}$$

It is legitimate to ignore the exponential factor since it introduces powers of $\frac{R}{a_0}$ which is the small parameter. The correction to the ground state energy is therefore

$$\langle 1s|\mathcal{V}|1s\rangle = \frac{2e^2}{5a_0^3}R^2 = \frac{4}{5}|E_{gs}|\left(\frac{R}{a_0}\right)^2 = \frac{4}{3}|E_{gs}|\left(\frac{r_P}{a_0}\right)^2 \tag{3.44}$$

Since $r_P \sim 1\text{fm} = 10^{-15}\text{m}$ and $a_0 \sim 10^{-10}\text{m}$ the correction is $\langle 1s|\mathcal{V}|1s\rangle \sim 10^{-10}|E_{gs}|$ and too small to enter in our calculation of the $2s-1s$ transition. However, a more precise computation of the electromagnetic and relativistic effects is enough to determine the charge proton radius from the $2s-1s$ frequency and compare it with results from scattering for example. Nevertheless, since the proton radius is not known as precisely, this effect puts a limit on the theoretical computations. As mentioned at the beginning the same calculation can be done for muonic hydrogen and compared to experiment..

3.3 Variational method

Perturbation theory is not always an option since it requires the system to be well approximated by a system that can be solved exactly. If you only want to compute the ground state another method you can use is the so called variational approach. It is based on the simple premise that the ground state is the state with minimal energy, namely

$$E_{gs} = \min_{|\psi\rangle} \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \tag{3.45}$$

where the minimum is attained when $|\psi\rangle = |\psi_{gs}\rangle$. What one does is to propose a ground state depending on certain parameters and then minimizing the expectation value of the Hamiltonian with respect to those parameters. It is an approximation because we are minimizing in a subset of all states so we don't expect to find the real minimum. How close we get depends on how well we can guess the wave-function of the ground state.

3.4 Example: Yukawa potential

Consider a particle in a Yukawa potential with Hamiltonian given by:

$$H = \frac{p^2}{2m} - \frac{Ze^2}{r}e^{-\frac{r}{R}} \tag{3.46}$$

Such potential arise in nuclear physics from the interchange of pions. In the present case it is thought as a model for a screened Coulomb interaction in an atom with multiple electrons. In that case Z is the number of protons and R is the atomic radius. The effective charge that the particle sees is Ze for $r \ll R$ and 0 for $r \gg R$. Our analysis is independent of this physical interpretation and just aims at finding the ground state of such potential.

We expect the ground state to be spherically symmetric $\psi = \psi(r)$. The corresponding Schroedinger equation reads

$$-\frac{\hbar^2}{2m}\left(\partial_r^2\psi + \frac{2}{r}\partial_r\psi\right) - \frac{Ze^2}{r}e^{-\frac{r}{R}}\psi = E\psi(r) \tag{3.47}$$

As always it is convenient to define adimensional quantities so we introduce the variables:

$$u = \frac{r}{R}, \qquad \epsilon = E\,\frac{mR^2}{\hbar^2}, \qquad \beta_0 = \frac{Zme^2R}{\hbar^2} \tag{3.48}$$

The equation reduces to

$$-\frac{1}{2}\left(\partial_u^2\psi + \frac{2}{u}\partial_u\psi\right) - \beta_0\frac{e^{-u}}{u}\psi = \epsilon\psi \tag{3.49}$$

This equation cannot be solved exactly. For each β_0 we can find a spectrum of values ϵ_n such that the wave function goes to zero at infinity and is well behaved at $u = 0$. Later we are going to show how to find a numerical solution to such problem by integrating the differential equation. Presently, we are going to look for an approximate ground state using the variational method. Although approximate, the result is analytic and can be used to understand the behavior of the solutions as the parameter β_0 changes. The same analysis done numerically would be more involved since we need to solve for several values of β_0 and interpolate.

As a guess, for the ground state we consider the usual $1s$ wave function of the hydrogen atom:

$$\psi(r) = \frac{1}{\sqrt{\pi}}\frac{1}{\rho^{\frac{3}{2}}}e^{-\frac{r}{\rho}} \tag{3.50}$$

where ρ is a variational parameter. Here we should note that the more variables we incorporate into the wave-function the more likely we are to approximate the ground state. On the other hand, if the wave-function is so complicated that we cannot do the computation of $\langle\psi|H|\psi\rangle$ analytically, we would need to resort to a numerical analysis defeating the simplicity of the method. For that reason we chose a simple function with only one variational parameter.

It is straight-forward to compute

$$\langle\psi|\frac{p^2}{2m}|\psi\rangle = -\frac{2\hbar^2}{m\rho^3}\int_0^\infty r^2\,dre^{-\frac{r}{\rho}}\left(\partial_r^2 + \frac{2}{r}\partial_r\right)e^{-\frac{r}{\rho}} = \frac{\hbar^2}{2m\rho^2} \tag{3.51}$$

and

$$\langle\psi| - \frac{Ze^2}{r}e^{-\frac{r}{R}}|\psi\rangle = -\frac{4Ze^2}{\rho^3}\int_0^\infty rdre^{-\left(\frac{2}{\rho}+\frac{1}{R}\right)r} = -\frac{Ze^2}{\rho}\frac{4}{\left(2+\frac{\rho}{R}\right)^2} \tag{3.52}$$

All together

$$\langle\psi|H|\psi\rangle = \frac{\hbar^2}{2m\rho^2} - \frac{4Ze^2}{\rho}\frac{1}{\left(2+\frac{\rho}{R}\right)^2} \tag{3.53}$$

Notice that we took the state $|\psi\rangle$ to be normalized, $\langle\psi|\psi\rangle = 1$ and therefore we do not need to divide by the norm. Again, we introduce adimensional quantities:

$$\beta = \frac{\rho}{R} \tag{3.54}$$

and find

$$\langle\psi|H|\psi\rangle = \frac{\hbar^2}{mR^2}\left(\frac{1}{2\beta^2} - \frac{4\beta_0}{\beta}\frac{1}{(\beta+2)^2}\right) \tag{3.55}$$

Taking derivatives and doing some simple algebra we find that

$$\frac{\partial}{\partial\beta}\langle\psi|H|\psi\rangle = 0 \iff (\beta+2)^3 = 8\beta\beta_0\left(1+\frac{3}{2}\beta\right) \tag{3.56}$$

The last equation is a cubic equation that can be solved in terms of cubic and square roots. Replacing in the expression for the energy we find the ground state energy. More illuminating is to take some limits. Here we consider the case

$$\beta_0 \to \infty \tag{3.57}$$

In that case there is a solution such that $\beta \to 0$. There are two other possible solutions of the cubic equation ($\beta \simeq -\frac{2}{3}$, $\beta \simeq 12\beta_0$) but they do not lead to bound states since the corresponding energy is positive. In that limit, that in fact correponds to the Coulomb potential, we find simply from the equation for β andusing the value of β_0 from eq.(3.48)

$$\beta \simeq \frac{1}{\beta_0} \tag{3.58}$$

and

$$\frac{E_{gs}}{\hbar^2/(mR^2)} = \epsilon_{gs} \simeq -\frac{\beta_0^2}{2} \quad \Rightarrow \quad E_{gs} = -\frac{Z^2me^4}{2\hbar^2} \tag{3.59}$$

namely the exact result for the Coulomb potential but only because we used the Hydrogen atom ground state wave function as a variational guess. It is interesting to solve the Schroedinger equation exactly for some values of β_0 and compare with the variational approach. For example for $\beta_0 = 10$ we find that the variational result, after solving the cubic equation is $\epsilon_{gs} = -40.705144$ whereas the numerical value is $\epsilon_{gs} = -40.705803$. This exact value we can found using numerical integration of the differential equation. In the next subsection we present a simple Maple program that gives the result. The same solutions can be found with Mathematica, Matlab, etc.

3.5 Yukawa potential: Numerical integration

We transcribe now a maple program that solves the problem numerically. **Notice:** If you input this program take into account that latex broke some input lines into multiple lines. They should be entered as a single line. Otherwise download the program from the course website.

```
> ## Consider the Yukawa potential and try to find the ground state.
```

```
> ## As we saw, the minimal energy is
> Emin:=(beta0,beta)->(1/2/beta^2-4*beta0/beta/(beta+2)^2);
```

$$Emin := (\beta 0,\, \beta) \to \frac{1}{2}\,\frac{1}{\beta^2} - \frac{4\,\beta 0}{\beta\,(\beta+2)^2}$$

```
> # where beta is determined from minimizing Emin which gives
> betaeq:=beta->(beta+2)^3-8*beta*beta0*(1+3/2*beta);
```

$$betaeq := \beta \to (\beta+2)^3 - 8\,\beta\,\beta 0\,(1 + \frac{3}{2}\,\beta)$$

```
> # for example consider  beta0=10
```

$$S1 := 8 + \beta^3 + (6 - 12\,\beta 0)\,\beta^2 + (-8\,\beta 0 + 12)\,\beta$$

```
> res:=[evalf(solve(subs(beta0=10,betaeq(beta)),beta))];
```

$$res := [114.5927963 - 0.2\,10^{-9}\,I,\, -0.6934677818 - 0.3464101616\,10^{-7}\,I, 0.1006714618 + 0.3464101616\,10^{-7}\,I]$$

```
> [Emin(10,res[1]),Emin(10,res[2]),Emin(10,res[3])];
```

$$[0.00001239847096 + 0.1\,10^{-24}\,I,\, 34.83013199 + 0.66\,10^{-14}\,I,\, -40.70514436 - 0.56\,10^{-12}\,I]$$

```
> # the third one is negative indicating a bound state with
> E=-40.70514436 (at least from variational method)
> # Let's compare with numerical solution of the Schroedinger
> equation
> Eq1:=(beta0,E)->-1/2*(diff(psi(u),u$2)+2/u*diff(psi(u),u))
> -beta0*exp(-u)/u*psi(u)-E*psi(u);
```

$$Eq1 := (\beta 0,\, E) \to -\frac{1}{2}\,(\tfrac{d^2}{du^2}\,\psi(u)) - \frac{\frac{d}{du}\,\psi(u)}{u} - \frac{\beta 0\,e^{(-u)}\,\psi(u)}{u} - E\,\psi(u)$$

```
> dsolve({Eq1(10,-0.1),psi(0)=1,D(psi)(0)=0},numeric,output=listprocedure);

Error, (in dsolve/numeric/checking) ode system has a removable
singularity at u=0. Initial data is restricted to {psi(u) =
-.10000000000000*diff(psi(u),u)}
```

```
> # OK, we need to redefine the differential equation
> exp(beta0*u)*subs(psi(u)=exp(-beta0*u)*chi(u),Eq1(beta0,E));
```

$$e^{(\beta 0\,u)}\left(-\frac{1}{2}\,(\tfrac{\partial^2}{\partial u^2}\,(e^{(-\beta 0\,u)}\,\chi(u))) - \frac{\frac{\partial}{\partial u}\,(e^{(-\beta 0\,u)}\,\chi(u))}{u} - \frac{\beta 0\,e^{(-u)}\,e^{(-\beta 0\,u)}\,\chi(u)}{u} - E\,e^{(-\beta 0\,u)}\,\chi(u)\right)$$

```
> expand(%);
```

$$-\frac{1}{2}\,\beta 0^2\,\chi(u) + \beta 0\,(\tfrac{d}{du}\,\chi(u)) - \frac{1}{2}\,(\tfrac{d^2}{du^2}\,\chi(u)) + \frac{\beta 0\,\chi(u)}{u} - \frac{\frac{d}{du}\,\chi(u)}{u} - \frac{\beta 0\,\chi(u)}{e^u\,u} - E\,\chi(u)$$

```
> Eq2:=(beta0,E)->-1/2*beta0^2*chi(u)+beta0*diff(chi(u),u)
> -1/2*diff(chi(u),`$`(u,2))+1/u*beta0*chi(u)-1/u*diff(chi(u),u)
> -beta0/exp(u)/u*chi(u)-E*chi(u);
```

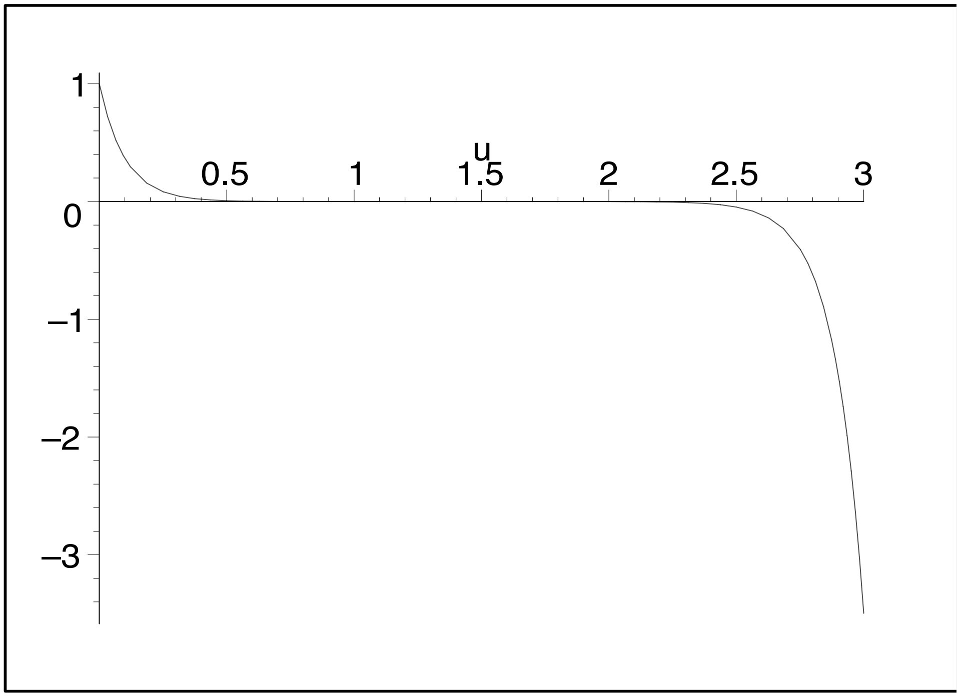
$$Eq2 := (\beta 0,\, E) \to$$

$$-\frac{1}{2}\,\beta 0^2\,\chi(u) + \beta 0\,(\tfrac{d}{du}\,\chi(u)) - \frac{1}{2}\,(\tfrac{d^2}{du^2}\,\chi(u)) + \frac{\beta 0\,\chi(u)}{u} - \frac{\frac{d}{du}\,\chi(u)}{u} - \frac{\beta 0\,\chi(u)}{e^u\,u} - E\,\chi(u)$$

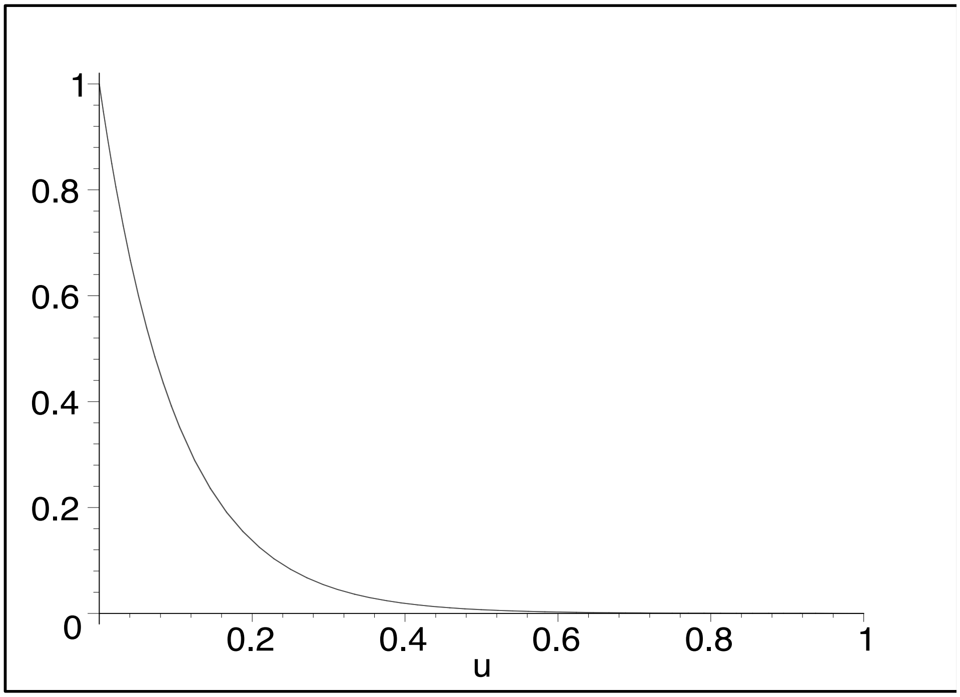
```
>  # OK now it's working
>  sol1:=dsolve({Eq2(10,-40.705803),chi(0)=1,D(chi)(0)=0},numeric,
>  output=listprocedure):
>  chi1s:=subs(sol1,chi(u));
```

$$chi1s := \mathbf{proc}(u)\ \ldots\ \mathbf{end\ proc}$$

```
>  # Here we need to explore the values of E and see where the sign of
>  the aymptotic function changes.
>  # We look for a function with no zeros (nodes) since we want the
>  ground state.
>  plot([exp(-10*u)*chi1s(u)],u=0..3);
```



```
>  #If the value of E is changed in the last decimal place the function
goes to plus infinity.
>  #We find  E=-40.705803  showing that the variational procedure
>  gave a quite accurate result.
>  #To see why let's plot the wave functions
>  plot([exp(-u/.1006714618),exp(-10*u)*chi1s(u)],u=0..1
```



```
>  # They cannot be distinguished within the precision of the plot.
>  It was a good guess.
```

3.6 WKB approximation

The variational method is adequate to find the ground state. For highly excited states there is another method known as WKB. It applies to the case where the eigenstates are determined from a one dimensional Schroedinger equation:

$$-\frac{\hbar^2}{2m}\partial_x^2\psi(x) + V(x)\psi(x) = E\psi(x) \tag{3.60}$$

The idea is to approximate the wave function $\psi(x)$ in the region where $|E - V(x)|$ is very large. Naturally we need to say very large compared to what. The main point is that when $(E - V(x))$ is large and positive the wave-function oscillates rapidly with a wave-length λ of order $\lambda^2 \sim \frac{\hbar^2}{2m}\frac{1}{|E-V(x)|}$. The WKB approximation is valid if, in a region of size λ the potential can be considered approximately constant. To be more precise consider rewriting the wave-function in terms of a function $S(x)$ as

$$\psi(x) = e^{S(x)} \tag{3.61}$$

The Schroedinger equation becomes

$$-\frac{\hbar^2}{2m}\left[\partial_x^2 S + (\partial_x S)^2\right] = E - V(x) \tag{3.62}$$

The approximation is

$$(\partial_x S)^2 \gg \partial_x^2 S \tag{3.63}$$

which reduces the equation to

$$(\partial_x S)^2 \simeq -\frac{2m}{\hbar^2}(E - V(x)) = -k(x)^2 \qquad \Rightarrow \qquad S(x) \simeq i\int^x k(x')dx' \tag{3.64}$$

where we defined

$$k(x) = \sqrt{\frac{2m}{\hbar^2}(E - V(x))} \tag{3.65}$$

Equivalently the approximation is valid when

$$k(x)^2 \ll |\partial_x k(x)|, \quad \Rightarrow \quad |\partial_x \lambda(x)| \ll 1 \;\text{ with }\; \lambda(x) = \frac{2\pi}{k(x)} \tag{3.66}$$

Physically this means that the wave-function can be thought of as a sinusoidal wave with slowly changing wave-length $\lambda(x)$. To perform a systematic expansion we write

$$S(x) = S_0(x) + S_1(x) + \dots \tag{3.67}$$

with

$$S_0(x) = \int^x k(x')dx' \tag{3.68}$$

The next order is determined by replacing eq.(3.67) in (3.62):

$$(\partial_x S_0 + \partial_x S_1)^2 + \partial_x^2 S_0 + \partial_x^2 S_1 = -k(x)^2 \tag{3.69}$$

$$(\partial_x S_0)^2 + 2\partial_x S_0 \partial_x S_1 + (\partial_x S_1)^2 + \partial_x^2 S_0 + \partial_x^2 S_1 = -k(x)^2 \tag{3.70}$$

Since $(\partial_x S_0)^2 = -k(x)^2$ and we assume S_1 to be small we obtain

$$2\partial_x S_0 \partial_x S_1 = -\partial_x^2 S_0 \qquad \Rightarrow \qquad S_1 = -\frac{1}{2}\ln \partial_x S_0 = -\frac{1}{2}\ln k(x) \tag{3.71}$$

Putting everything together we find that the wave-function, at this order can be written as

$$\psi = \frac{A}{\sqrt{k(x)}}\; e^{i\int^x k(x')\,dx'} + \frac{B}{\sqrt{k(x)}}\; e^{-i\int^x k(x')\,dx'} \tag{3.72}$$

In the regions where $V(x) \gg E$ is is convenient to write this functions as a sum of increasing and decreasing exponentials

$$\psi = \frac{A}{\sqrt{\kappa(x)}}\; e^{+\int^x \kappa(x')\,dx'} + \frac{B}{\sqrt{\kappa(x)}}\; e^{-\int^x \kappa(x')\,dx'} \tag{3.73}$$

where

$$\kappa(x) = \sqrt{\frac{2m}{\hbar^2}(V(x)-E)} \tag{3.74}$$

Now we go back to the initial assumption

$$(\partial_x S)^2 \gg \partial_x^2 S \tag{3.75}$$

Suing $S \simeq S_0$ we get

$$|\partial_x k(x)| \ll k(x)^2, \quad \text{or} \quad |\partial_x \lambda(x)| \ll 1 \tag{3.76}$$

where we defined the position dependent wave-length as $\lambda(x) = \frac{2\pi}{k(x)}$. Physically this means that the wave-length changes slowly with the position and the wave function can be described as a sinusoidal wave whose wave-length and amplitude change little across a distance of a wave-length. A strong point of this approximation is that it can be systematically pursued to higher orders. This is particularly useful when using the WKB method to study properties of differential equations near singular points. In the context of quantum mechanics this is not used very often so we stop here and look for some applications. The main two are the computation of approximate bound states and the computation of tunneling probability through a barrier.

3.7 WKB approximation for a bound state

Consider a situation a such as in figure 1 where we expect a bound state for some energy E. Such energy is determined by requiring the wave-function to decay exponentially at $x \to \pm\infty$. This can only happen for very precise values of E, namely the energy eigenvalues. In general one can choose a wave function that decays, say at $x \to -\infty$ but then it will diverge at $x \to +\infty$. The WKB cannot be used directly since it is not applicable around the points $x_{1,2}$ where $V(x_{1,2}) = E$. For that reason we divide the x-axis in three regions and write the wave-function as

$$\psi_I = \frac{A}{\sqrt{\kappa(x)}}\; e^{+\int^x \kappa(x')\,dx'} \tag{3.77}$$

$$\psi_{II} = \frac{B}{\sqrt{k(x)}}\; e^{i\int^x k(x')\,dx'} + \frac{C}{\sqrt{k(x)}}\; e^{-i\int^x k(x')\,dx'} \tag{3.78}$$

$$\psi_{III} = \frac{D}{\sqrt{\kappa(x)}}\; e^{-\int^x \kappa(x')\,dx'} + \frac{F}{\sqrt{\kappa(x)}}\; e^{+\int^x \kappa(x')\,dx'} \tag{3.79}$$

We would like to find the value of the energy E such that the coefficient F vanishes, $F = 0$. Although the WKB method gives us approximate expressions for the wavefunction in the different regions, it is not enough since we need to match the functions to obtain the coefficients. Namely, given the coefficient A we should be able to find B, C, D and F. Or, if we require $F = 0$ then we should be able to find the energy E for which that happens. For that purpose we introduce two more regions, around the points $x_{1,2}$, namely the regions excluded from the WKB approximation and expand the potential as

$$V(x) \simeq V(x_1) + V'(x_1)(x - x_1) + \ldots = E + V'(x_1)(x - x_1) + ldots \tag{3.80}$$

$$V(x) \simeq V(x_2) + V'(x_2)(x - x_2) + \ldots = E + V'(x_2)(x - x_2) + \ldots \tag{3.81}$$

where we used $V(x_1) = V(x_2) = E$. Also, $V'(x_1) < 0$ and $V'(x_2) > 0$. In the region near x_1 the Schroedinger equation reads

$$-\frac{\hbar^2}{2m}\partial_x^2\psi + (E + V'(x_1)(x - x_1))\psi = E\psi \tag{3.82}$$

Introducing the new variable

$$u = \frac{x - x_1}{a}, \qquad a^3 = \frac{\hbar^2}{2m|V'(x_1)|} \tag{3.83}$$

the equation reads

$$\partial_u^2\psi + u\psi = 0 \tag{3.84}$$

This is known as the Airy equation. The solution that vanishes at $u \to -\infty$ is

$$\psi(u) = -\mathbf{Ai}(-u) \tag{3.85}$$

where **Ai** is the Airy function, a special function with the property

$$\mathbf{Ai}(-u) = \begin{cases} \frac{1}{2\sqrt{\pi}|u|^{\frac{1}{4}}} e^{-\frac{2}{3}|u|^3} & u \to -\infty \\ \frac{1}{\sqrt{\pi}|u|^{\frac{1}{4}}} \cos\left(\frac{2}{3}|u|^{\frac{3}{2}} - \frac{\pi}{4}\right) & u \to +\infty \end{cases} \tag{3.86}$$

On the other hand, the WKB approximation, near x_1 has a phase given by

$$\int_{x_1}^{x} \sqrt{\frac{2m}{\hbar^2}(E - V(x))}dx \simeq \sqrt{\frac{2m|V'(x_1)|}{\hbar^2}} \int_{x_1}^{x} \sqrt{x - x_1}\, dx \tag{3.87}$$

$$= \frac{2}{3}\sqrt{\frac{2m|V'(x_1)|}{\hbar^2}}(x - x_1)^{\frac{3}{2}} = \frac{2}{3}|u|^{\frac{3}{2}} \tag{3.88}$$

Therefore, the right linear combination of WKB waves that match a decreasing function on the region I is

$$\psi_{II} = \cos\left(\frac{1}{\hbar}\int_{x_1}^{x} p(x)dx - \frac{\pi}{4}\right) \tag{3.89}$$

with

$$p(x) = \sqrt{2m(E - V(x))} \tag{3.90}$$

If we consider this function near $x = x_2$ we find

$$\psi_{II} = \cos\left(\frac{1}{\hbar}\int_{x_1}^{x_2} p(x)dx + \frac{1}{\hbar}\int_{x_2}^{x} p(x)dx - \frac{\pi}{4}\right) \tag{3.91}$$

On the other hand, repeating the same argument as before, one can see that the function that matches a decreasing function on the region III is given by

$$\psi_{II} = \cos(\frac{1}{\hbar}\int_{x_2}^{x} p(x)dx + \frac{\pi}{4}) \tag{3.92}$$

The only way that both expressions are compatible is if

$$\int_{x_1}^{x_2} p(x)dx = \left(n + \frac{1}{2}\right)\hbar\pi \tag{3.93}$$

which is the Bohr-Sommerfeld quantization condition and should be thought as an equation for E appearing inside $p(x)$. Different values of the integer n correspond to different energy eigenstates.

3.8 WKB approximation: tunneling through a barrier.

Another case where the WKB approximation is very useful is in the computation of the tunneling probability through a barrier. An important example that we are going to use to illustrate this idea is Gamow's theory of α decay. When proposed it played an important role in establishing the validity of quantum mechanics in the realm of nuclear physics. An α particle is a very stable configuration of two protons and two neutrons (nucleus of ${}^{4}_{2}\mathbf{He}$). Certain heavy nuclei can be described as a bound state of a lighter nucleus and an α particle in a quasi-bound state, namely in an unstable but long-lived state. A simple potential that describes this system is a sum of an attractive potential due to the strong interactions and the Coulomb repulsion:

$$V(r) = \begin{cases} -V_0 & \text{if } 0 < r < r_1 \\ \frac{2(Z-2)e^2}{r} & \text{if } r > r_1 \end{cases} \tag{3.94}$$

where r_1 is the range of the attractive potential. This is illustrated in figure 2 where we plotted the radial potential assuming the angular momentum is $\ell = 0$ (no centrifugal

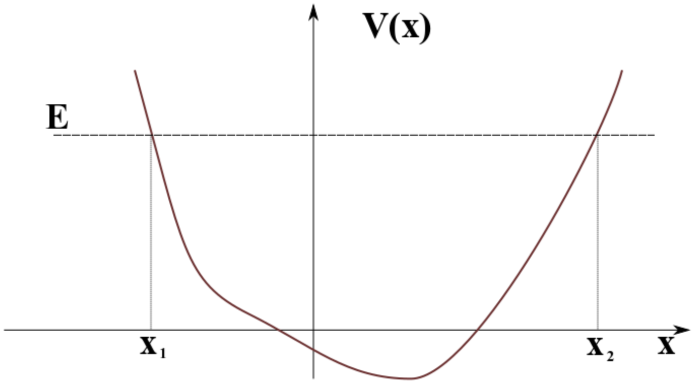


Figure 1: Bound state computation using WKB approximation

barrier). If this potential has a bound state (E¡0) then the nucleus is stable, however, we assume here that no such stable state exists. Instead, there is a metastable state for an energy $E > 0$. In the figure we plot (in blue) an eigenstate localized inside the nucleus. Inside the barrier the wave-functions is a sum of an increasing and decreasing exponentials whose coefficients follow form matching with the wave-function inside. If the energy is such that we only have a decreasing exponential, as in the figure, outside the barrier, the eigenstate will be a wave with exponentially small amplitude. By doing a linear combination of states with similar energy, we can localize the particle inside the nucleus and eliminate the waves outside. Such state will not be an eigenstate of the

Hamiltonian, it will be time dependent and, after some time, the alpha particle will be emitted with energy E. We can estimate the time it takes for the particle to leave by computing the probability current

$$j = \frac{\hbar k}{2M_\alpha}|B|^2 \tag{3.95}$$

where, far from the nucleus we considered the particle to be free with momentum $\hbar k$ and $|B|$ is the coefficient of the wave function that we estimate as

$$|B|^2 \sim \frac{1}{r_1} e^{-2\gamma}| \tag{3.96}$$

where $\sim \frac{1}{r_1}$ is the coefficient inside the nucleus (by normalization) and $e^{-2\gamma}$ is the exponential suppression inside the barrier. The total probability of being inside the nucleus will decrease as

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial t}\int_0^{r_1} |\chi(r)|^2 = -j \tag{3.97}$$

for the probability to go from $P = 1$ to $P \simeq 0$ it will take a time

$$\tau \sim \frac{1}{j} = \frac{2M_\alpha}{\hbar k} e^{2\gamma} \tag{3.98}$$

which is then our estimate for the mean-life of the nucleus. The main factor is $e^{-2\gamma}$, *i.e.* the tunneling probability that can be estimated using WKB. The potential barrier extends to a distance r_2 such that

$$E = \frac{2(Z-2)e^2}{r_2} \tag{3.99}$$

In the region $r_1 < r < r_2$ the WKB approximation gives the wave-function as the sum of an increasing and decreasing exponential. The ratio of the wave-function amplitudes outside and inside the barrier is smallest when only the decaying exponential contributes, we expect that the state will then be the most stable. Assuming that this is the case, the quantity γ can be computed as

$$\gamma = \int_{r_1}^{r_2} \sqrt{\frac{2M_\alpha}{\hbar^2}\left(\frac{2(Z-2)e^2}{r} - E\right)} = \int_{r_1}^{r_2} \sqrt{\frac{4M_\alpha(Z-2)e^2}{\hbar^2}\left(\frac{1}{r} - \frac{1}{r_2}\right)} \tag{3.100}$$

$$= 2(Z-2)\alpha_e\sqrt{\frac{2M_\alpha c^2}{E}}(\phi_1 - \sin\phi_1\cos\phi_1) \simeq \pi(Z-2)\alpha_e\sqrt{\frac{2M_\alpha c^2}{E}} \tag{3.101}$$

where

$$\phi_1 = \arccos\sqrt{\frac{r_1}{r_2}} \tag{3.102}$$

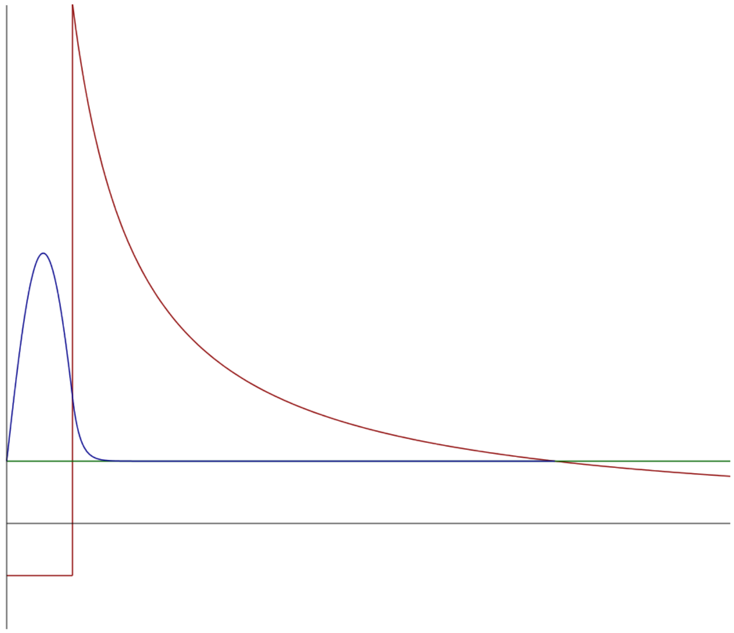


Figure 2: Simple model of alpha decay.

The inverse of the decay probability per unit time is the mean life $\tau_{\frac{1}{2}} = \frac{1}{w}$. This model is too crude to give a reliable estimate of the mean life, however it predicts correctly the dependence of the mean life with the energy of the alpha particle emitted:

$$\ln \frac{\tau_{\frac{1}{2}}}{1\,\mathrm{yr}} \simeq 2\pi(Z-2)\alpha_e \sqrt{\frac{2M_\alpha c^2}{E}} \tag{3.103}$$

Using as example Uranium or Thorium, it is simple to check this dependence and obtain a good estimate of the slope of the line $\tau_{\frac{1}{2}}$ vs. $1/\sqrt{E}$. In fact such law was discovered experimentally before it was explained by Gamow as a nice application of quantum mechanics to nuclear physics.

4. Symmetries

A symmetry is a transformation of a system that does not change the results of an experiment. For example the same experiment gives the same result independently of the position, this is translational symmetry. The same with the orientation, namely rotational symmetry. Such symmetries are basic laws of Nature. They can be broken only by external fields, e.g. gravity, electric and magnetic fields, etc. Of course, if an atom is in an electric field and we rotate the atom *and* the electric field then the results are invariant, the rotational symmetry that is broken is the one that rotates only the atom.

In quantum mechanics, the precise statement is that symmetries are generated by operators $\mathcal{O}$ that commute with the Hamiltonian:

$$[H, \mathcal{O}] = 0 \tag{4.1}$$

where $\mathcal{O}$ generates the infinitesimal transformation

$$|\psi\rangle \to |\psi\rangle - i\epsilon\mathcal{O}|\psi\rangle \simeq e^{-i\epsilon\mathcal{O}}|\psi\rangle \tag{4.2}$$

This immediately implies that, for any state $|\psi\rangle$

$$\frac{d}{dt}\langle\psi|\mathcal{O}|\psi\rangle = 0 \tag{4.3}$$

Moreover, the probabilities of measuring the different eigenvalues of $\mathcal{O}$ are independent of time, that is $\mathcal{O}$ is conserved. As in classical mechanics, symmetries are associated with conserved quantities. The most obvious is time translations generated by the Hamiltonian itself which is obviously conserved since $[H, H] = 0$.

It can also imply the existence of degeneracies in the spectrum. Suppose we have an energy eigenstate

$$H|E_n\rangle = E_n|E_n\rangle \tag{4.4}$$

If we apply $\mathcal{O}$ and use that $H\mathcal{O} = \mathcal{O}H$ we get

$$H\mathcal{O}|E_n\rangle = \mathcal{O}H|E_n\rangle = E_n\mathcal{O}|E_n\rangle \tag{4.5}$$

namely the state $\mathcal{O}|E_n\rangle$, if it does not vanish, is an eigenstate of H with the same eigenvalue E_n. Therefore, if $\mathcal{O}|E_n\rangle \neq 0$ and it is not equal (or proportional) to $|E_n\rangle$ then there are at least two states with the same energy and the spectrum is degenerate for that energy. If it is not degenerate we gain the valuable information that $|E_n\rangle$ is invariant under transformations generated by $\mathcal{O}$. Although it can happen that $\mathcal{O}$ commutes with the Hamiltonian but only generates trivial transformations, in general, such an operator $\mathcal{O}$ provides a way to classify the spectrum and find degeneracies.

4.1 Rotations

Rotations are generated by the angular momentum operator and is the most common symmetry used in quantum mechanics. The generators are

$$J_x, J_y, J_z \tag{4.6}$$

with commutation relations

$$[J_x, J_y] = i\hbar J_z \tag{4.7}$$

$$[J_z, J_y] = -i\hbar J_x \tag{4.8}$$

$$[J_z, J_x] = i\hbar J_y \tag{4.9}$$

or, equivalently,

$$J_\pm = J_x \pm iJ_y, J_z \tag{4.10}$$

with commutation rules

$$[J_z, J_\pm] = \pm\hbar\, J_\pm \tag{4.11}$$

$$[J_+, J_-] = 2\hbar J_z \tag{4.12}$$

In a basis of eigenstates of J_z they act as

$$J_z|jm\rangle = \hbar m|j\,m\rangle \tag{4.13}$$

$$J_+|jm\rangle = \hbar\sqrt{j(j+1)-m(m+1)}|j\,m+1\rangle \tag{4.14}$$

$$J_-|jm\rangle = \hbar\sqrt{j(j+1)-m(m-1)}|j\,m-1\rangle \tag{4.15}$$

If J_+ commutes with H then, the second equation shows that all the states $|jm\rangle$ in the same multiplet have the same energy. Of course there can be several multiplets with the same j but each with different energy.

4.2 Parity

Parity is the symmetry $\vec{r} \to -\vec{r}$. This symmetry can be thought of as if you were looking at an experiment through a mirror. A mirror actually reflects only one axis. However, reflecting two axis is equivalent to a rotation of angle π. Therefore inverting one axis or three is equivalent up to a rotation.

Denoting the parity operator as Π we define

$$\Pi|\vec{r}\rangle = |-\vec{r}\rangle \tag{4.16}$$

Having determined the action of parity on a basis we can determine its action on any state. For example

$$\Pi|\vec{p}\rangle = \Pi \int d^3\vec{r}|\vec{r}\rangle\langle\vec{r}|\vec{p}\rangle = \int d^3\vec{r}| - \vec{r}\rangle\langle\vec{r}|\vec{p}\rangle = \int d^3\vec{r}'|\vec{r}'\rangle\langle-\vec{r}'|\vec{p}\rangle \tag{4.17}$$

$$= \int d^3\vec{r}'|\vec{r}'\rangle\langle\vec{r}'| - \vec{p}\rangle = | - \vec{p}\rangle \tag{4.18}$$

where we used

$$\langle-\vec{r}|\vec{p}\rangle = e^{-\frac{i}{\hbar}\vec{p}\vec{r}} = \langle\vec{r}| - \vec{p}\rangle \tag{4.19}$$

We can then compute, for example, for the x component

$$\Pi\hat{x}|x\rangle = \Pi x|x\rangle = x\Pi|x\rangle = x| - x\rangle \tag{4.20}$$

$$\hat{x}\Pi|x\rangle = \hat{x}| - x\rangle = -x| - x\rangle \tag{4.21}$$

Since this is true for all vectors in the basis $\{|x\rangle\}$ we find

$$\Pi\hat{x} = -\hat{x}\Pi \tag{4.22}$$

We say that the operator $\hat{x}$ has negative parity. The same happens with $\hat{p}$. For the angular momentum we find instead

$$\Pi\hat{L}_z = \Pi(\hat{x}\hat{p}_y - \hat{y}\hat{p}_x) = -\hat{x}\Pi\hat{p}_y + \hat{y}\Pi\hat{p}_x \tag{4.23}$$

$$= (\hat{x}\hat{p}_y - \hat{y}\hat{p}_p)\,\Pi = \Pi\hat{L}_z \tag{4.24}$$

Simply put, interchanging Π with x or p gives a minus sign. Since $L = \vec{r} \times \vec{p}$ there is no minus sign in interchanging Π with L. We say that L has positive parity and is a pseudo-vector. It rotates as a vector but is parity even.

Since L commutes with Π all states in the same L multiplet have the same parity. To find the parity we need to resort to the properties of spherical harmonics

$$\langle x|\Pi|lm\rangle = \langle -x|lm\rangle = Y_{lm}(\pi - \theta, \phi + \pi) \tag{4.25}$$

For the case $m = 0$ we have

$$Y_{l0}(\pi - \theta) = P_l(-\cos\theta) = (-)^l P_l(\cos\theta) \tag{4.26}$$

Since all states in the multiplet have the same parity we conclude

$$\Pi|lm\rangle = (-)^l|lm\rangle \tag{4.27}$$

4.3 Selection rules

Selection rules are rules that allows to determine that certain matrix elements are zero without having to do any actual computations. It is an extremely important tool, not only computationally, but also as a way to understand the physical properties of the system,

In the case of parity, consider states with definite parity and an operator V also with definite parity.

$$\Pi|\alpha\rangle = \epsilon_\alpha|\alpha\rangle \tag{4.28}$$

$$\Pi|\beta\rangle = \epsilon_\beta|\beta\rangle \tag{4.29}$$

$$\Pi V = \epsilon_V V\Pi \tag{4.30}$$

where all ϵ factors are either 1 or -1. The matrix element $\langle\alpha|V|\beta\rangle$ satisfies

$$\langle\alpha|V|\beta\rangle = \langle\alpha|\Pi\Pi V\Pi\Pi|\beta\rangle = \epsilon_\alpha\epsilon_\beta\langle\alpha|\Pi V\Pi|\beta\rangle = \epsilon_\alpha\epsilon_\beta\epsilon_V\langle\alpha|V\Pi\Pi|\beta\rangle = \epsilon_\alpha\epsilon_\beta\epsilon_V\langle\alpha|V|\beta\rangle \tag{4.31}$$

If $\epsilon_\alpha\epsilon_\beta\epsilon_V = 1$ we don't learn anything new. If $\epsilon_\alpha\epsilon_\beta\epsilon_V = -1$ the matrix element is equal to minus itself, that is, it vanishes.

$$\epsilon_\alpha\epsilon_\beta\epsilon_V = -1 \quad \Rightarrow \quad \langle\alpha|V|\beta\rangle = 0 \tag{4.32}$$

Part of the power of the selection rule is its extreme simplicity. If the total parity is negative then the matrix element vanishes.

For example, consider the problem of computing the electric dipole moment of the neutron. The neutron is in a non degenerate ground state $|\alpha\rangle$ (except that the spin can be up or down) and we have

$$\vec{d}_n = \langle\alpha,\uparrow|\vec{d}|\alpha,\uparrow\rangle \tag{4.33}$$

where we assumed that the spin was up, for example. Under parity, the orientation of the spin does not change and the energy is invariant. That means that the state is invariant under parity

$$\Pi|\alpha,\uparrow\rangle = \epsilon_\alpha|\alpha,\uparrow\rangle \quad \Rightarrow \quad \langle\alpha,\uparrow|\Pi = \epsilon^*_\alpha\langle\alpha,\uparrow| \tag{4.34}$$

for some phase ϵ_α, $|\epsilon_\alpha| = 1$. Thus, using parity we find

$$\langle\alpha|\vec{d}|\alpha\rangle = \langle\alpha|\Pi\,\Pi\,\vec{d}\,\Pi\,\Pi|\alpha\rangle = -\epsilon^*_\alpha\epsilon_\alpha\,\langle\alpha|\vec{d}|\alpha\rangle \quad \Rightarrow \quad \langle\alpha|\vec{d}|\alpha\rangle = 0 \tag{4.35}$$

where we used $\Pi\vec{d}\Pi = -\vec{d}$. Any observation of a neutron dipole moment would imply a violation of parity. On the other hand the magnetic moment $\vec{\mu}$ obeys $\Pi\vec{\mu}\Pi = \vec{\mu}$ and therefore a neutron magnetic moment is possible and in fact it is not zero.

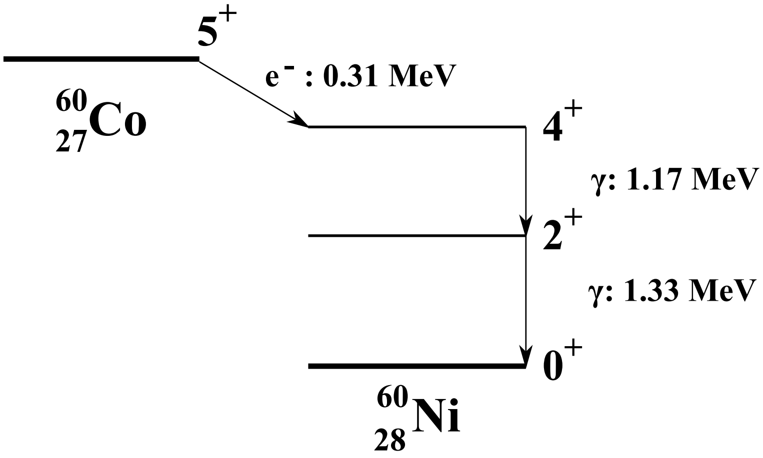


Figure 3: Main decay of Cobalt 60 which can be used to test violation of parity by the weak interactions.

4.4 Non-conservation of parity for weak interactions

Neutrons are unstable particles and decay into proton electron an anti-neutrino:

$$n^0 \to p^+ + e^- + \bar{\nu}_e \tag{4.36}$$

This decay is produced by the weak interaction and violates parity. The first test was done in the decay of Cobalt $^{60}_{28}$Co into Nickel: It turns out that when the nuclei are polarized, the electrons come out in direction opposite to the spin. If you consider a mirror on the xy plane, the reflected image shows the spin still in the same direction but the electron coming out parallel to the spin. An observer looking at the mirror experiment will realize that it is not possible, that is, one can distinguish between an experiment and its mirror image. One way to understand it is that the anti-neutrinos have only one possible helicity. In that case their mirror image does not exist breaking parity. However, if a particle is massive it has to have both helicities. Indeed, if its spin is aligned in the direction of the momentum, by moving faster than the particle, we will see the particle moving backwards but the spin still aligned in the same direction that is now opposite to the velocity. the only exception is if the particle is massless, then it moves at the speed of light and it may have only one helicity. Initially this was supposed to be the cse for the neutrino. Recent experiments indicate that neutrinos are massive and therefore there has to be another neutrino with the opposite helicity. One possibility is that it has not been detected and does not appear in the weak decays we described. This difference in coupling will break parity again. Another interesting possibility is that the anti-neutrino is the neutrino with opposite helicity, namely the neutrino is its own antiparticle. This is described as saying that the neutirno is a

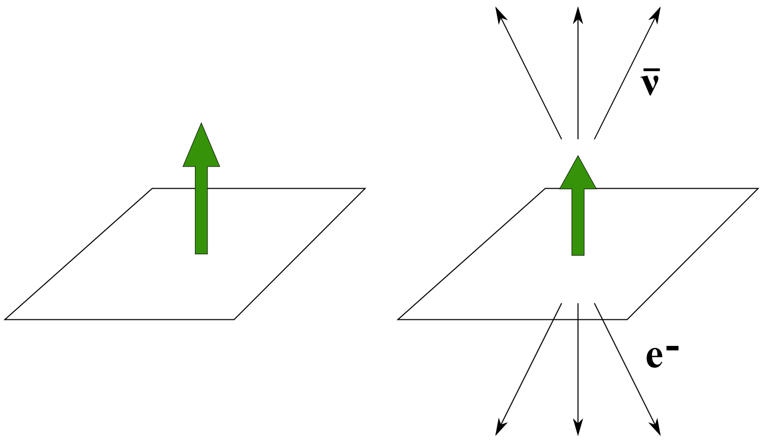


Figure 4: Schematics of Cobalt 60 experiment. The electrons are emitted mainly in a direction opposite to the nuclear spin. If seen though a mirror in the indicated plane, the spin would be the same but the electrons would be coming up. Such physical situation does not exist in violation of the parity symmetry.

Majorana particle. At the moment there is no experimental evidence of any of these two hypothesis. What is clear is that the radioactive decay we described emits electrons preferably in one direction and therefore breaks parity.

4.5 Selection rules for angular momentum

To apply the selection rules for rotations we need to assign angular momentum to operators. What one does is to group operators in multiplets of given total angular momentum. Consider for example a multiplet of angular momentum $l = 2$, that is a set of 5 states $\{|2m\rangle, m = -2, -1, 0, 1, 2\}$. If we apply the momentum operators p_x, p_y, p_z we get 15 states:

$$p_a|2m\rangle, \qquad a = x, y, z \quad m = -2, \ldots, 2 \tag{4.37}$$

The question we ask is what angular momentum those 15 states have. The answer is based on the commutators

$$[J_a, p_b] = i\hbar\epsilon_{abc}p_c \tag{4.38}$$

which can be easily derived from the definition

$$J_a = \epsilon_{abc}x_b p_c \tag{4.39}$$

We assume that all the angular momentum is orbital since the spin commutes with p_a anyway.

Now we consider the J_z component of the states in eq.(4.37). For example

$$J_z(p_z|2m\rangle) = [J_z, p_z]|2m\rangle + p_z J_z|2m\rangle = \hbar m p_z|2m\rangle \tag{4.40}$$

$$J_z(p_x|2m\rangle) = [J_z, p_x]|2m\rangle + p_x J_z|2m\rangle = i\hbar p_y|2m\rangle + \hbar m p_x|2m\rangle \tag{4.41}$$

$$J_z(p_y|2m\rangle) = [J_z, p_y]|2m\rangle + p_y J_z|2m\rangle = -i\hbar p_x|2m\rangle + \hbar m p_y|2m\rangle \tag{4.42}$$

Clearly, the state $p_z|2m\rangle$ has $J_z = \hbar m$ but the other two are not eigenstates of J_z. We can fix that by taking linear combinations:

$$J_z(p_x + ip_y)|2m\rangle = \hbar(m+1)(p_x + ip_y)|2m\rangle \tag{4.43}$$

$$J_z(p_x - ip_y)|2m\rangle = \hbar(m-1)(p_x + ip_y)|2m\rangle \tag{4.44}$$

We then conclude that $(p_x \pm ip_y)|2m\rangle$ is an eigenstate of J_z with eigenvalue $J_z = \hbar(m\pm1)$ Therefore, the eigenvalues of J_z for the 15 states are

$$J_z = 3, 2, 1, 2, 1, 0, 1, 0, -1, 0, -1, -2, -1, -2, -3 \tag{4.45}$$

We identify a multiplet with $J = 3$ ($J_z = -3, -2, -1, 0, 1, 2, 3$) one with $J = 2$ ($J_z = -2, -1, 0, 1, 2$) and one with $J = 1$ ($J_z = -1, 0, 1$). That this is indeed that case can be verified by applying $J_\pm$ and checking that they act as expected on these multiplets. In summary, we find that the 15 states have the same properties as the composition of angular momentum $J = 1$ with $J = 2$. For that reason we say that the operators p_a carry angular momentum $J = 1$. The key for these result is the commutation relations of the operators p_a with J_a.

This can be easily generalized. A set of $2k + 1$ operators labeled as T^k_q with $q = -k \dots k$ is in such a multiplet if it satisfies the commutation relations:

$$[J_z, T^k_q] = \hbar q T^k_q \tag{4.46}$$

$$[J_+, T^k_q] = \hbar\sqrt{k(k+1) - q(q+1)}\ T^k_{q+1} \tag{4.47}$$

$$[J_-, T^k_q] = \hbar\sqrt{k(k+1) - q(q-1)}\ T^k_{q-1} \tag{4.48}$$

If a multiplet $|lm\rangle$ is given we can construct the $(2k + 1) \times (2l + 1)$ states

$$T^k_q|lm\rangle \tag{4.49}$$

They are eigenstates of J_z as can be seen from

$$J_z T^k_q|lm\rangle = [J_z, T^k_q]|lm\rangle + T^k_q J_z|lm\rangle = \hbar(q + m)T^k_q|lm\rangle \tag{4.50}$$

We also have

$$\begin{aligned} J_+ T^k_q|lm\rangle &= [J_+, T^k_q]|lm\rangle + T^k_q J_+|lm\rangle \qquad (4.51) \\ &= \hbar\sqrt{k(k+1) - q(q+1)}\, T^k_{q+1}\,|lm\rangle + \sqrt{l(l+1) - m(m+1)}\, T^k_q\,|lm+1\rangle \end{aligned}$$

which is exactly the same result that we would obtain if we consider two particles, one with angular momentum k, the other l and try to apply the total angular momentum operator:

$$
\begin{aligned}
J_+|kq\rangle \otimes |lm\rangle &= J^{(1)}|kq\rangle \otimes |lm\rangle + |kq\rangle \otimes J_+^{(2)}|lm\rangle \\
&= \hbar\sqrt{k(k+1)-q(q+1)}\,|k\,q+1\rangle \otimes |lm\rangle + \sqrt{l(l+1)-m(m+1)}\,|lm\rangle \otimes |lm+1\rangle
\end{aligned}
\tag{4.52}
$$

Therefore all the rules of composition of angular momenta apply. We obtain that the total angular momentum J can have the values

$$J = |k-l| \ldots (k+l) \tag{4.53}$$

and the states are given by the Clebsch-Gordan coefficients:

$$|JM\rangle = \sum_{q=-k}^{k} \sum_{m=-l}^{l} C_{JM}^{kq,lm}\; T_q^k|lm\rangle \tag{4.54}$$

The Clebsch-Gordan coefficients can be obtained from a table, a computer program or by computing them using the commutation rules of the angular momentum.

Now it is easy to establish the selection rule for angular momentum. The matrix element $\langle l_1 m_1|T_q^k|l_2 m_2\rangle$ vanishes if any of these conditions is *not* satisfied

$$m_1 = q + m_2 \tag{4.55}$$

$$|l_2 - k| \leq l_1 \leq l_2 + k \tag{4.56}$$

To understand better the meaning of tensor operator let us consider two simle examples. First scalar operators: they have $k = q = 0$ and coomute with all components of angular momentum:

$$[J_z, T_0^0] = 0, \quad [J_+, T_0^0] = 0, \quad [J_-, T_0^0] = 0, \tag{4.57}$$

Examples of such operators are $\vec{p}^2$, $\vec{r}^2$, $\vec{L}^2$, $\vec{p}\vec{L}$, $\frac{\vec{L}\vec{r}}{r^3}$, namely any operator that is rotationally invariant. The second example is vector operators. We already discussed $\vec{p}$ at the beginning of this subsection, let us just finish the discussion. This operator is actually a set of three operators p_x, p_y, p_z and therefore should correspond to $k = 1$, $q = -1, 0, 1$. Writing the commutation rules for T_0^1 we find

$$[J_z, T_0^1] = 0 \tag{4.58}$$

$$[J_+, T_0^1] = \hbar\sqrt{2}\,T_{+1}^1 \tag{4.59}$$

$$[J_-, T_0^1] = \hbar\sqrt{2}\,T_{-1}^1 \tag{4.60}$$

Noticing that

$$[J_z, p_z] = 0 \tag{4.61}$$

$$[J_+, p_z] = -\hbar\,(p_x + ip_y) \tag{4.62}$$

$$[J_-, p_z] = \hbar\,(p_x - ip_y) \tag{4.63}$$

Thus, we identify (up to an overall constant)

$$T^1_0 = \sqrt{2}p_z, \quad T^1_{+1} = -(p_x + ip_y), \quad T^1_{-1} = p_x - ip_y \tag{4.64}$$

Since the commutation rules are the same for any vector, this identification works equally well for $\vec{r}$, $\vec{L}$, $\vec{p} \times \vec{L}$ or any other vector operator.

4.6 Wigner–Eckart Theorem

In the previous section we found out that the $(2k+1) \times (2j+1)$ states given by $T^k_q|\nu jm\rangle$ rotate as two particle states $|kj, qm\rangle$. Using the Clebsch-Gordan coefficients $\langle kjqm|kj; j'm'\rangle$ we can construct states that have definite angular momentum, namely that rotate as $|j'm'\rangle$:

$$\sum_{qm} T^k_q|\nu jm\rangle\langle kjqm|kj; j'm'\rangle = \sum_{\nu'} A^{jj'k}_{\nu\nu'}|\nu' j'm'\rangle \tag{4.65}$$

where, on the right hand side, we wrote the most general state of the system with total angular momentum j' and projection m' in terms of unknown coefficients $A^{jj'k}_{\nu\nu'}$. Here ν denotes any other quantum numbers, for example in the Hydrogen atom it represents the radial quantum number. Multiplying by the inverse Clebsch-Gordan and summing in the subspace we obtain

$$T^k_q|\nu jm\rangle = \sum_{\nu', j', m'} A^{jj'k}_{\nu\nu'}|\nu' j'm'\rangle\langle kj; j'm'|kj, qm\rangle \tag{4.66}$$

From here it follows that

$$\langle\nu' j'm'|T^k_q|\nu jm\rangle = \langle kj; j'm'|kj, qm\rangle\frac{\langle\nu' j'||T^k||\nu j\rangle}{\sqrt{2j+1}} \tag{4.67}$$

where we defined the so called reduced matrix elements

$$\frac{\langle\nu' j'||T^k||\nu j\rangle}{\sqrt{2j+1}} = A^{jj'k}_{\nu\nu'} \tag{4.68}$$

The practical interest of this theorem is that the reduced matrix element can be computed by evaluating just one matrix element of T^k_q. After that, all other matrix elements of T^k_q (for fixed j, j', ν, ν') follow from the Clebsch-Gordan coefficients. From a physical point of view, the different values of the quantum numbers q, m, m' are related by rotations and therefore we only need to know one value.

4.7 Time reversal

In the absence of time-dependent forces, time translation is a symmetry that results in conservation of Energy. Given that, there is a more subtle symmetry called time reversal and denoted as T. In classical mechanics such operation of time reversal (T) consists in flipping the velocities of all particles $\vec{v} \to -\vec{v}$. If the forces depend only on the position, the system will retrace its steps and come back to the time reversal of the initial state. That is, if the evolution is such that ($t > 0$):

$$(\vec{x}_1, \vec{v}_1, t = 0) \longrightarrow (\vec{x}_2, \vec{v}_2, t) \tag{4.69}$$

then the same forces produce the evolution

$$(\vec{x}_2, -\vec{v}_2, t = 0) \longrightarrow (\vec{x}_1, -\vec{v}_1, t) \tag{4.70}$$

This follows from Newton's equation

$$m\frac{d^2\vec{x}}{dt^2} = -\vec{\nabla}V(\vec{x}) \tag{4.71}$$

which is invariant under $t \to -t$. In macroscopic systems, an arrow of time is introduced by thermodynamics. Namely the entropy of an isolated system always increases when we go forward in time. Such law is not invariant under $t \to -t$. In the Newton equation it appears as dissipation. Friction forces are not time reversal since they depend on the velocity. In particular the direction of the friction force is always opposite to the velocity. Its magnitude can be constant or depend on the velocity depending for example if it is friction between two solid bodies or friction in air, a liquid etc. Therefore we have

$$m\frac{d^2\vec{x}}{dt^2} = -\vec{\nabla}V(\vec{x}) - f(|\vec{v}|)\,\vec{v}, \qquad \vec{v} = \frac{d\vec{x}}{dt} \tag{4.72}$$

where $f(|\vec{v}|) > 0$. This equation is clearly not invariant under $t \to -t$. In the case of electromagnetic forces we have

$$m\frac{d^2\vec{x}}{dt^2} = q(\vec{E} + \vec{v} \times \vec{B}) \tag{4.73}$$

Although this is not invariant under $t \to -t$, it can be made invariant if we do $\vec{B} \to -\vec{B}$ at the same time. This makes sense since magnetic field are produced by currents which should flip under time reversal. It is interesting to consider two other symmetries of these simple equation. One is parity (P) given by $\vec{x} \to -\vec{x}$, $\vec{E} \to -\vec{E}$, $\vec{B} \to \vec{B}$. The other is charge conjugation (C) given by $q \to -q$, $\vec{E} \to -\vec{E}$, $\vec{B} \to -\vec{B}$. Therefore we have separate invariance under C, P and T. This is not true for all other interactions, however it is expected that nature is invariant under a combined CPT transformation.

Going back to time reversal, in classical mechanics we map a state $(\vec{x}, \vec{v})$ to $(\vec{x}, -\vec{v})$. In quantum mechanics, the position and momentum are not defined simultaneously. If we define a time reversal operator Θ that satisfies $\Theta|x\rangle = |x\rangle$ then Θ is just the identity, we cannot ask that, at the same time $\Theta|p\rangle = |-p\rangle$.

To see what happens let's start by the very property that defines the time-reversal operator Θ:

$$e^{-\frac{i}{\hbar}Ht}\Theta|\psi(t)\rangle = \Theta|\psi(t=0)\rangle \tag{4.74}$$

where

$$|\psi(t)\rangle = e^{-\frac{i}{\hbar}Ht}|\psi(t=0)\rangle \tag{4.75}$$

In words, the time evolution of the time reversal state, birngs back the time reverse of the initial state. If we write $|\psi\rangle$ in terms of eigenstates of energy $|E_n\rangle$ the equation reads

$$e^{-\frac{i}{\hbar}Ht}\Theta\sum_n c_n e^{-\frac{i}{\hbar}E_n t}|E_n\rangle = \Theta\sum_n c_n|E_n\rangle \tag{4.76}$$

where we used:

$$|\psi\rangle = \sum_n c_n|E_n\rangle, \qquad \Rightarrow \qquad |\psi(t)\rangle = \sum_n c_n e^{-\frac{i}{\hbar}E_n t}|E_n\rangle \tag{4.77}$$

If Θ is a linear operator, since equation (4.76) has to be valid for any c_n the only possibility is that

$$\Theta|E_n\rangle = \eta_n|-E_n\rangle \tag{4.78}$$

so that the phases cancel. However this is impossible since generically there is not a state with energy $-E$ for each state with energy E. In fact, the energy is bounded from below (otherwise you could gain an infinite energy by interacting with such a system) and in general not from above.

The answer is to define Θ as an *anti-linear* operator which satisfies

$$\Theta(\alpha|1\rangle + \beta|2\rangle) = \alpha^*\Theta|1\rangle + \beta^*\Theta|2\rangle \tag{4.79}$$

That is, Θ is distributive with respect to the sum, but scalars are conjugated. This solves the problem if we also assume

$$\Theta|E_n\rangle = \eta_n|E_n\rangle \tag{4.80}$$

Indeed,

$$e^{-\frac{i}{\hbar}Ht}\Theta\sum_n c_n e^{-\frac{i}{\hbar}E_n t}|E_n\rangle = e^{-\frac{i}{\hbar}Ht}\sum_n c_n^* e^{\frac{i}{\hbar}E_n t}\eta_n|E_n\rangle \tag{4.81}$$

$$= \sum_n c_n^* e^{\frac{i}{\hbar}E_n t}\eta_n e^{-\frac{i}{\hbar}E_n t}|E_n\rangle \tag{4.82}$$

$$= \sum_n c_n^* \eta_n |E_n\rangle \tag{4.83}$$

$$= \Theta|\psi\rangle \tag{4.84}$$

Therefore it is just necessary to find an operator Θ that is anti-linear and that commutes with H, namely $[\Theta, H] = 0$. It also solves the problem that we mentioned before in relation to position and momentum. For a particle we define

$$\Theta|\vec{x}\rangle = |\vec{x}\rangle \tag{4.85}$$

It now implies

$$\Theta|p\rangle = \int d^3\vec{x}\,\Theta(|\vec{x}\rangle\langle\vec{x}|\vec{p}\rangle) = \int d^3\vec{x}\,\langle\vec{x}|\vec{p}\rangle^*\Theta|\vec{x}\rangle = \int d^3\vec{x}\,\langle\vec{x}|\vec{p}\rangle^*|\vec{x}\rangle \tag{4.86}$$

$$= \int d^3\vec{x}\,e^{-\frac{i}{\hbar}\vec{p}\vec{x}}|\vec{x}\rangle = |-\vec{p}\rangle \tag{4.87}$$

So, for and anti-linear operator we *can* have

$$\Theta|\vec{x}\rangle = |\vec{x}\rangle \tag{4.88}$$

$$\Theta|\vec{p}\rangle = |-\vec{p}\rangle \tag{4.89}$$

Equivalently

$$\Theta\hat{x} = \hat{x}\Theta \tag{4.90}$$

$$\Theta\hat{p} = -\hat{p}\Theta \tag{4.91}$$

From where we find

$$[\Theta, H] = [\Theta, \frac{\vec{p}^2}{2m} + V(\vec{x})] = 0 \tag{4.92}$$

that is, for a particle in a potential, such operator Θ acts as time reversal operator in a similar way as in classical mechanics.

A couple of interesting properties. On the wave function Θ acts as

$$(\Theta\psi)(x) = \langle x|\Theta|\psi\rangle = \int dx'\langle x|\Theta(|x\rangle\langle x|\psi\rangle) \tag{4.93}$$

$$= \int dx'\langle x|\psi\rangle^*\langle x|x'\rangle = \int dx'\delta(x-x')\psi(x')^* = \psi^*(x) \tag{4.94}$$

That is, it conjugates the wave-function. The probability of finding the particle at a given position is still the same since it is given by $|\psi^*(x)|^2 = |\psi(x)|^2$. For the momentum wave function, it turns out that the probability of measuring p in a state is the same as the probability of measuring $-p$ in the time reversed state

$$|\langle p|\Theta\psi\rangle|^2 = |\langle -p|\psi\rangle|^2 \tag{4.95}$$

Finally it is interesting to consider the operator Θ^2 which is a linear operator since

$$\begin{aligned}\Theta^2(\alpha|1\rangle + \beta|2\rangle) &= \Theta(\alpha^*\Theta|1\rangle + \beta^*\Theta|2\rangle) &(4.96)\\ &= \alpha\Theta^2|1\rangle + \beta\Theta^2|2\rangle &(4.97)\end{aligned}$$

Since in the $|\vec{x}\rangle$ basis

$$\Theta^2|\vec{x}\rangle = |\vec{x}\rangle \tag{4.98}$$

then, Θ^2 is the identity operator. There is subtlety however when we take into account the spin. We'll find that Θ^2 can be minus the identity.

4.8 Time reversal of angular momentum eigenstates and Kramers degeneracy

It is clear that under time reversal a state $|lm\rangle$ gets converted into $|l\ -m\rangle$, that is the particle rotates the other way. More formally

$$\Theta\hat{L}_z = \Theta(xp_y - yp_x) = -(xp_y - yp_x)\Theta = -L_z\Theta \tag{4.99}$$

The same with the other components:

$$\Theta\vec{L} = -\vec{L}\Theta \tag{4.100}$$

This implies

$$\Theta\ell_+ = -\ell_-\Theta, \qquad \Theta\ell_- = -\ell_+\Theta \tag{4.101}$$

Therefore we find

$$\Theta|lm\rangle = \eta_m|l\ -m\rangle \tag{4.102}$$

where η_m is a phase we need to determine. The easiest way to determine it is to consider the wave-function which is nothing else than the corresponding spherical harmonic which satisfies

$$Y^*(\theta,\phi) = (-)^m\, Y(\theta,\phi) \tag{4.103}$$

Thus

$$\Theta|lm\rangle = (-)^m|l\ -m\rangle \tag{4.104}$$

Another way to obtain this is to use that

$$\begin{aligned}\Theta\ell_-|\ell,m\rangle &= \sqrt{\ell(\ell+1)-m(m-1)}\Theta|\ell,m-1\rangle = \sqrt{\ell(\ell+1)-m(m-1)}\eta_{m-1}|\ell,-m+1\rangle\\ -\ell_+\Theta|\ell,m\rangle &= -\eta_m\ell_+|\ell,-m\rangle = -\eta_m\sqrt{\ell(\ell+1)-(-m)(-m+1)}|\ell,-m+1\rangle &(4.105)\end{aligned}$$

Both results should agree implying that $\eta_{m-1} = -\eta_m$, namely signs alternate. Using that the wave-function for $m = 0$ is real we get $\eta_m = (-)^m$ as before. In any case we again find

$$\Theta^2 |lm\rangle = |lm\rangle \tag{4.106}$$

It is interesting to consider what happens in the case of half-integer spin. The main result that we obtain is that $\Theta^2 = -1$ when acting on states of half-integer spin. In order to derive that result, let us consider

$$\Theta J_- = \Theta(J_x - iJ_y) = (-J_x - iJ_y)\Theta = -J_+\Theta \tag{4.107}$$

Notice that we get J_+ because we have to conjugate the imaginary coefficient i. Another result we need is

$$J_-^{2m} |jm\rangle = A_m |j-m\rangle \tag{4.108}$$

where A_m is a real and positive numerical constant that can be easily found from eq.(4.14). In fact, from there we also find

$$J_+^{2m} |j-m\rangle = A_m |jm\rangle \tag{4.109}$$

with the same constant A_m. Finally we have

$$\Theta |jm\rangle = \eta_m |j\ -m\rangle \tag{4.110}$$

for some unknown phase η_m (which is equal to $(-)^m$ for integer spin). Now we can compute

$$\begin{aligned}\Theta^2 |jm\rangle &= \Theta \eta_m |j-m\rangle = \eta_m^* \Theta \frac{1}{A_m} J_-^{2m} |jm\rangle = \frac{\eta_m^*}{A_m} (-)^{2m} J_+^{2m} \Theta |jm\rangle && (4.111)\\ &= \frac{\eta_m^* \eta_m}{A_m} (-)^{2m} J_+^{2m} |j-m\rangle = (-)^{2m} |jm\rangle && (4.112)\end{aligned}$$

where we used $\eta_m \eta_m^* = 1$. The result agrees with the expected result for integer j. However, for half-integer j, it is also true that m is half-integer and $(-)^{2m} = -1$. Summarizing

$$\Theta^2 |jm\rangle = (-)^{2j} |jm\rangle \tag{4.113}$$

This result is obviously reminiscent of the fact that a 2π rotation acting on a half-integer spin gives a minus sign (instead of being just the identity) To relate both facts it is useful to note that if we rotate the state $|jm\rangle$ by π around the y-axis (or x-axis) we get the state $|j-m\rangle$ since such rotation inverts the z-axis. There can be a phase therefore

$$e^{i\pi J_y} |jm\rangle = \tilde{\eta}_m |j\ -m\rangle \tag{4.114}$$

We can now compute

$$\begin{aligned}
\Theta^2|jm\rangle &= \Theta\eta_m|j-m\rangle = \eta_m^*\Theta\frac{1}{\tilde{\eta}_m}e^{i\pi J_y}|jm\rangle = \frac{\eta_m^*}{\tilde{\eta}_m^*}\Theta e^{i\pi J_y}|jm\rangle && (4.115)\\
&= \frac{\eta_m^*}{\tilde{\eta}_m^*}\Theta e^{i\pi J_y}\Theta^{-1}\Theta|jm\rangle = \frac{\eta_m^*}{\tilde{\eta}_m^*}e^{\Theta i\pi J_y\Theta^{-1}}\Theta|jm\rangle && (4.116)\\
&= \frac{\eta_m^*}{\tilde{\eta}_m^*}e^{i\pi J_y}\eta_m|j,\,-m\rangle = \frac{\eta_m^*\eta_m}{\tilde{\eta}_m^*\tilde{\eta}_m}e^{i\pi J_y}e^{i\pi J_y}|jm\rangle && (4.117)\\
&= e^{2\pi i J_y}|jm\rangle && (4.118)
\end{aligned}$$

where we used

$$Bf(A)B^{-1} = f(BAB^{-1}) \tag{4.119}$$

for any two operators A, B and function f as can be obtained by expanding in Taylor series both sides. Also

$$\Theta iJ_y = iJ_y\Theta \tag{4.120}$$

since we get a minus sign from conjugating i and another from commuting J_y with Θ. Summarizing, the result is straight-forward and very illuminating:

$$\Theta^2|jm\rangle = e^{2\pi iJ_y}|jm\rangle \tag{4.121}$$

so indeed Θ^2 is equivalent to a 2π rotation!. A very important consequence is that, in a system of total half-integer spin and symmetric under time reversal states of energy $|E\rangle$ have to come in pairs, this is called Kramers degeneracy. Indeed, we have

$$|E\rangle' = \Theta|E\rangle \tag{4.122}$$

Since Θ commutes with the Hamiltonian both states have the same energy. However they have to be different. If this were not the case, namely

$$|E\rangle' = \eta|E\rangle \tag{4.123}$$

for some phase η we would have

$$\Theta\Theta|E\rangle = \Theta\eta|E\rangle = \eta^*\Theta|E\rangle = \eta^*\eta|E\rangle = |E\rangle \tag{4.124}$$

contradicting what we just learned, namely $\Theta^2|E\rangle = -|E\rangle$ for states of half-integer spin. One important example is an external electric field. It can never lift completely the degeneracy for the case of total half-integer spin since an electric field does not break time-reversal. On hte contrary, a magnetic field breaks time-reversal and lifts the degeneracy between all values of S_z.

4.9 Selection rule for time reversal

To derive such a selection rule first observe that if

$$\Theta|1\rangle = |\tilde{1}\rangle \tag{4.125}$$

$$\Theta|2\rangle = |\tilde{2}\rangle \tag{4.126}$$

then

$$\langle 1|\Theta A\Theta|2\rangle = \langle\tilde{2}|A^\dagger|\tilde{1}\rangle \tag{4.127}$$

Indeed:

$$\langle 1|\Theta A\Theta|2\rangle = \int dxdx'\langle 1|\Theta|x'\rangle\langle x'|A\Theta|x\rangle\langle x|2\rangle = \int dxdx'\langle x|2\rangle\langle x'|A|x\rangle^*\langle 1|x'\rangle \tag{4.128}$$

$$= \int dxdx'\psi_2(x)\psi_1(x)^*\langle x'|A|x\rangle^* \tag{4.129}$$

where $\psi_1(x) = \langle x|1\rangle$ is the wave function of state $|1\rangle$ and the same for state $|2\rangle$. Also, the scalars should be conjugated every time they go over Θ, as we know. On the other hand we have

$$\langle\tilde{2}|A^\dagger|\tilde{1}\rangle = \int dxdx'\langle\tilde{2}|x\rangle\langle x|A^\dagger|x'\rangle\langle x'|\tilde{1}\rangle = \int dxdx'\langle\tilde{2}|x\rangle\langle x|A^\dagger|x'\rangle\langle x'|\tilde{1}\rangle \tag{4.130}$$

$$= \int dxdx'\tilde{\psi}_2^*(x)\tilde{\psi}_1(x')\langle x'|A|x\rangle^* \tag{4.131}$$

which is the same as eq.(4.129) in view of $\tilde{\psi}_{1,2}(x) = \psi_{1,2}^*(x)$.

Consider now a hermitian operator $A = A^\dagger$ with a given commutation relation with time reversal:

$$\Theta A = \epsilon_A A\Theta \tag{4.132}$$

where $\epsilon_A = \pm 1$. For example for $\hat{x}$ we have $\epsilon_x = +1$ and for ϕ we have $\epsilon_p = -1$. Now, taking into account that $\Theta^2 = 1$ (for states with integer spin) we find

$$\langle 1|A|2\rangle = \langle 1|\Theta\Theta A\Theta\Theta|2\rangle = \epsilon_A\langle 1|\Theta A\Theta|2\rangle = \epsilon_A\langle\tilde{2}|A^\dagger|\tilde{1}\rangle \tag{4.133}$$

$$= \epsilon_A\langle\tilde{2}|A|\tilde{1}\rangle \tag{4.134}$$

To obtain a selection rule we need

$$|\tilde{2}\rangle = |1\rangle, \quad |\tilde{1}\rangle = |2\rangle \tag{4.135}$$

In that case we conclude

$$\langle 1|A|2\rangle = \epsilon_A\langle 1|A|2\rangle \tag{4.136}$$

which vanishes if $\epsilon_A = -1$. In words, the matrix element between time reversed states of a time-reversal odd operator vanishes. For example you can compute

$$\langle 1s|(zp_z + p_z z)|1s\rangle \tag{4.137}$$

for the hydrogen atom and see that it vanishes whereas for example $\langle 1s|z^2|1s\rangle$ does not. This is because z^2 is time-reversal even but $zp_z + p_z z$ is odd (and hermitian). This is not trivial, it does not follow from the angular integration as is the case for angular momentum and parity selection rules. Indeed let us compute the matrix element:

$$\begin{aligned}
\langle 1s|(zp_z + p_z z)|1s\rangle &= -i\hbar \int d^3r\, \psi^*_{1s}(z\partial_z\psi_{1s} + \partial_z(z\psi_{1s})) && (4.138)\\
&= -i\hbar\left(-\frac{2}{a_0}\langle 1s|\frac{z^2}{r}|1s\rangle + 1\right) && (4.139)
\end{aligned}$$

where we used

$$\partial_z\psi_{1s} = -\frac{z}{a_0 r}\psi_{1s}, \quad \psi_{1s} = \frac{1}{\sqrt{\pi}a_0^{\frac{3}{2}}}e^{-\frac{r}{a_0}} \tag{4.140}$$

A simple computation gives

$$\langle 1s|\frac{z^2}{r}|1s\rangle = \frac{a_0}{2} \tag{4.141}$$

which indeed implies

$$\langle 1s|(zp_z + p_z z)|1s\rangle = 0 \tag{4.142}$$

At first sight the detail form of the wave-function seems to play a role. However, the main ingredient is that the wave-function is real and thus time-reversal invariant. Indeed, for any real wave function we can compute

$$\begin{aligned}
\langle\psi|(zp_z + p_z z)|\psi\rangle &= -i\hbar \int d^3r\, \psi(z\partial_z\psi + \partial_z(z\psi)) && (4.143)\\
&= -i\hbar \int d^3r\, \partial_z(z\psi^2) && (4.144)\\
&= 0 && (4.145)
\end{aligned}$$

The boundary terms at infinity vanish if the wave-function is normalizable, as assumed.

5. Perturbation theory to a degenerate level

Consider again the computation of eigenvalues and eigenvectors of the Hamiltonian

$$H = H_0 + \lambda V \tag{5.1}$$

where $\lambda \ll 1$. In the non-degenerate case we can follow an eigenstate $|\epsilon(\lambda)\rangle$ as $\lambda \to 0$ when it becomes an eigenstate of H_0. In the degenerate case, as $\lambda \to 0$ the perturbed state in principle can become any state in the degenerate subspace. To find which state it becomes, we can once again write the eigenvector condition and expand in series.

$$(H_0 + \lambda V)(|E^{(0)}\rangle + \lambda|\psi^{(1)}\rangle + \ldots) = (E^{(0)} + \lambda E^{(1)} + \ldots)(|E^{(0)}\rangle + \lambda|\psi^{(1)}\rangle + \ldots) \quad (5.2)$$

where we know that $E^{(0)}$ is the unperturbed energy. On the other hand $|E^{(0)}\rangle$ is an eigenstate of H_0 with eigenvalue $E^{(0)}$ but there is a whole subspace of such states, let us call such subspace D. To be more concrete assume that the degenerate subspace D has dimension n and is spanned by an orthonormal basis labeled by an index $\nu = 1 \ldots n$. Define a projector P_0 onto such subspace:

$$P_0 = \sum_{\nu=1}^{n} |E^{(0)}, \nu\rangle\langle E^{(0)}, \nu| \quad (5.3)$$

Expanding eq.(5.2) we find at zero, first, and second orders:

$$\begin{aligned} H_0|E^{(0)}\rangle &= E^{(0)}|E^{(0)}\rangle & (5.4)\\ H_0|\psi^{(1)}\rangle + V|E^{(0)}\rangle &= E^{(0)}|\psi^{(1)}\rangle + E^{(1)}|E^{(0)}\rangle & (5.5)\\ H_0|\psi^{(2)}\rangle + V|\psi^{(1)}\rangle &= E^{(0)}|\psi^{(2)}\rangle + E^{(1)}|\psi^{(1)}\rangle + E^{(1)}|E^{(0)}\rangle & (5.6) \end{aligned}$$

The first equation simply states that $|E^{(0)}\rangle$ is in the degenerate subspace, namely it is a linear combination of $|E^{(0)}, \nu = 1 \ldots n\rangle$. Projecting the second equation onto the degenerate subspace gives

$$P_0 V|E^{(0)}\rangle = E^{(1)}|E^{(0)}\rangle \quad (5.7)$$

That means that $|E^{(0)}\rangle$ is an eigenstate of the operator $P_0 V P_0$ that acts only inside the degenerate subspace. The eigenvalues are given by $E^{(1)}$. That means we should construct the matrix

$$V_{\nu_1\nu_2} = \langle E^{(0)}, \nu_1|V|E^{(0)}, \nu_2\rangle \quad (5.8)$$

and find the n eigenvectors and eigenvalues

$$\sum_{\nu_2=1}^{n} V_{\nu_1\nu_2}\psi^{(\alpha)}_{\nu_2} = E^{(1)}_{\alpha}\psi^{(\alpha)}_{\nu_1}, \qquad \alpha = 1, \ldots n \quad (5.9)$$

In general, all eigenvalues $E^{(1)}_{\alpha=1\ldots n}$ are different and the degeneracy is lifted completely. We find n different states

$$|E^{(0)}_{\alpha}\rangle = \sum_{\nu_1} \psi^{(\alpha)}_{\nu_1}|E^{(0)}, \nu_1\rangle \quad (5.10)$$

with their corresponding energies. The states are further corrected as can be found by projecting equation (5.5) onto the subspace orthogonal to the degenerate subspace:

$$H_0|\psi^{(1)}\rangle + P_\perp V|E^{(0)}\rangle = E^{(0)}|\psi^{(1)}\rangle \tag{5.11}$$

where $P_\perp = 1 - P_0$. As for the non-degenerate case the first order correction to the states orthogoenal to the degenerate subspace D is given by

$$|\psi^{(1)}\rangle_\perp = -(H_0 - E^{(0)})^{-1} P_\perp V|E^{(0)}\rangle = -\sum_{m\notin D} |E_m^{(0)}\rangle \frac{\langle E_m^{(0)}|V|E_\alpha^{(0)}\rangle}{E_m - E^{(0)}} \tag{5.12}$$

Notice that the operator $(H_0 - E^{(0)})$ can be inverted in the orthogonal subspace since it has no zeros there. Using the last equation in (5.5) and projecting it onto the zero order eigenstate $|E_\alpha^{(0)}\rangle$ we obtain

$$\langle E_\alpha^{(0)}|V|\psi^{(1)}\rangle = E^{(2)} \tag{5.13}$$

where we used that the components of $|\psi^{(1)}\rangle$ along the degenerate subspace are orthogonal to the zero order state $|E_\alpha^{(0)}\rangle$. Namely

$$|\psi^{(1)}\rangle_\parallel = \sum_{\beta\neq\alpha} \psi_\beta^{(1)} |E_\beta^{(0)}\rangle \tag{5.14}$$

Since all $|E_\beta^{(0)}\rangle$ are eigenstates of P_0VP_0 only the perpendicular component contributes in (5.13) and we get

$$E^{(2)} = \langle E_\alpha^{(0)}|V|\psi^{(1)}\rangle_\perp = -\sum_{m\notin D} \frac{|\langle E_m^{(0)}|V|E_\alpha^{(0)}\rangle|^2}{E_m - E^{(0)}} \tag{5.15}$$

a formula very similar ot the one for a non-degenerate state, the main difference being that $|E_\alpha^{(0)}\rangle$ has to be calculated first by diagonalizing P_0VP_0 instead of being given as when there is only one state in the subspace. Finally, projecting the last equation of (5.5) onto the other states in the degenerate subspace we get after some algebra

$$\psi_\beta^{(1)} = \langle E_\beta^{(0)}|\psi^{(1)}\rangle = \sum_{m\notin D} \frac{\langle E_\beta^{(0)}|V|E_m^{(0)}\rangle\langle E_m^{(0)}|V|E_\alpha^{(0)}\rangle}{(E_m - E^{(0)})(E_\beta^{(1)} - E_\alpha^{(1)})} \tag{5.16}$$

Because of the two powers of V this looks like a second order formula but in the denominator $(E_\beta^{(1)} - E_\alpha^{(1)})$ is first order so overall it is a first order correction. Finally we have the full correction to the state

$$|\psi^{(1)}\rangle = -\sum_{m\notin D} |E_m^{(0)}\rangle \frac{\langle E_m^{(0)}|V|E_\alpha^{(0)}\rangle}{E_m - E^{(0)}} + \sum_{m\notin D}\sum_{\beta\neq\alpha} |E_\beta^{(0)}\rangle \frac{\langle E_\beta^{(0)}|V|E_m^{(0)}\rangle\langle E_m^{(0)}|V|E_\alpha^{(0)}\rangle}{(E_m - E^{(0)})(E_\beta^{(1)} - E_\alpha^{(1)})} \tag{5.17}$$

In summary, if we have to correct a degenerate subspace we

- Find a basis $\{|E^{(0)},\nu\rangle\}$, $\nu = 1\dots n$ for the degenerate subspace D.
- Write the $n \times n$ matrix of the perturbation $V_{\nu\nu'} = \langle E^{(0)},\nu|V|E^{(0)},\nu'\rangle$ in that basis and diagonalize it. Namely find the eigenvalues $E^{(1)}_\alpha$ and eigenvectors $|E^{(0)}_\alpha\rangle$, $\alpha = 1\dots n$.
- Now we use the eigenvectors $|E^{(0)}_\alpha\rangle$ as a basis for the subspace D. Those are the zero order eigenstates and $E^{(1)}_\alpha$ are the first corrections to their energies.
- If needed, starting from each $|E^{(0)}_\alpha\rangle$ compute further corrections using the formulas above.

5.1 Spin orbit interaction

The spin orbit interaction is given by

$$U = \frac{e^2}{m^2c^2}\frac{\vec{L}\vec{S}}{r^3} \tag{5.18}$$

Consider the corrections to the $2p$ level. The wave functions are

$$\psi_{2lm} = R_{21}(r)Y_{1m}(\theta,\phi) = \frac{1}{(2a_0)^{\frac{3}{2}}}\frac{1}{\sqrt{3}}\frac{r}{a_0}e^{-\frac{r}{2a_0}}\,Y_{1m}(\theta,\phi) \tag{5.19}$$

To proceed we need to diagonalize the matrix of the perturbation in the degenerate subspace which in principle includes also the state $2s$. However it is easy to see that U applied to $|2s\rangle$ vanishes since $|2s\rangle$ has zero angular momentum. Therefore we concentrate on the $2p$ states. In that case we compute first the mean value of the radial part:

$$\int R_{21}\frac{1}{r^3}R_{21} = \frac{1}{(2a_0)^3}\frac{1}{3a_0^2}\int_0^\infty \frac{r^2}{r^3}e^{-\frac{r}{a_0}}r^2dr = \frac{1}{24a_0^3} \tag{5.20}$$

We are left to diagonalize

$$U = \frac{e^2}{m^2c^2}\frac{\vec{L}\vec{S}}{24a_0^3} \tag{5.21}$$

in the subspace of $l = 1, s = \frac{1}{2}$. Notice the simple identity

$$\vec{L}\vec{S} = \frac{1}{2}(J^2 - L^2 - S^2) \tag{5.22}$$

which means that diagonalizing $\vec{L}\vec{S}$ is the same as diagonalizing J^2. Actually, we know how to do that, the possible total angular momenta are $j = \frac{1}{2}$ and $j = \frac{3}{2}$. The eigenvalues of $\vec{L}\vec{S}$ are

$$\vec{L}\vec{S} = \frac{\hbar^2}{2}(j(j+1) - l(l+1) - s(s+1)) = \frac{\hbar^2}{2}(j(j+1) - 2 - \frac{3}{4}) = \frac{\hbar^2}{2}(j(j+1) - \frac{11}{4}) \tag{5.23}$$

Therefore the zero order states and the first order energy corrections to the $2p$ level are

$$|n=2, l=1, s=\tfrac{1}{2}, j=\tfrac{1}{2}, j_z=\pm\tfrac{1}{2}\rangle, \qquad E^{(1)} = -\frac{e^2\hbar^2}{m^2c^2}\frac{1}{24a_0^3} \tag{5.24}$$

$$|n=2, l=1, s=\tfrac{1}{2}, j=\tfrac{3}{2}, j_z=\pm\tfrac{1}{2},\pm\tfrac{3}{2}\rangle, \qquad E^{(1)} = \frac{1}{2}\frac{e^2\hbar^2}{m^2c^2}\frac{1}{24a_0^3} \tag{5.25}$$

In general we have:

$$|n, l, s, j, j_z\rangle, \quad E^{(1)} = \frac{1}{2}\frac{e^2\hbar^2}{m^2c^2}\langle\frac{1}{r^3}\rangle_{nl} \;\; [j(j+1) - l(l+1) - s(s+1)] \tag{5.26}$$

6. Electron in a magnetic field

The Lagrangian for a charge moving in electric and magnetic fields can be written in terms of the scalar $\phi(x_i, t)$ and vector $A_i(x_j, t)$ potentials as

$$L = \frac{1}{2}mv^2 - q\phi(x_i, t) + qA_j(x_i, t)v_j \tag{6.1}$$

Indeed, we can check the Euler equations give the Lorentz force:

$$\frac{d}{dt}\frac{\partial L}{\partial v_i} = \frac{\partial L}{\partial x_i} \tag{6.2}$$

Evaluating the derivatives we find

$$\frac{d}{dt}\left(mv_i + qA_i(x_k, t)\right) = -q\partial_i\phi(x_k, t) + qv_j\partial_i A_j(x_k, t) \tag{6.3}$$

or

$$m\frac{dv_i}{dt} + q\partial_t A_i + q\frac{dx_j}{dt}\partial_j A_i = -q\partial_i\phi + qv_j\partial_i A_j \tag{6.4}$$

Summarizing, the equations of motion are

$$m\frac{dv_i}{dt} = -q(\partial_i\phi + \partial_t A_i) + qv_j(\partial_i A_j - \partial_j A_i) \tag{6.5}$$

Defining the Electric and Magnetic fields

$$\vec{E} = -\vec{\nabla}\phi - \partial_t\vec{A}, \qquad \vec{B} = \vec{\nabla}\times\vec{A} \tag{6.6}$$

we find

$$m\vec{a} = q(\vec{E} + \vec{v}\times\vec{B}) \tag{6.7}$$

The last term follows form the identity

$$\left[\vec{v} \times (\nabla \times \vec{A})\right]_i = v_j(\partial_i A_j - \partial_j A_i) \tag{6.8}$$

which is a version of the well-known identity

$$\vec{A} \times (\vec{B} \times \vec{C}) = (\vec{A}\vec{C})\vec{B} - (\vec{B}\vec{C})\vec{A} \tag{6.9}$$

Computing the momentum

$$p = \frac{\partial L}{\partial v} = mv + qA \tag{6.10}$$

the Hamiltonian follows as

$$H = pv - L = \frac{1}{2}mv^2 + q\phi = \frac{1}{2m}(p - qA)^2 + q\phi \tag{6.11}$$

6.1 Electron in constant magnetic field

Suppose we have a constant magnetic field $\vec{B} = B\hat{z}$. It can be derived from the vector potential

$$A_x = -\frac{1}{2}By, \qquad A_y = \frac{1}{2}xB, \tag{6.12}$$

$$\begin{aligned}
H &= \frac{1}{2m}\left[\left(p_x + e\frac{1}{2}yB\right)^2 + \left(p_y - e\frac{1}{2}xB\right)^2 + p_z^2\right] && (6.13)\\
&= \frac{p_x^2 + p_y^2}{2m} + \frac{e^2B^2}{8m}(x^2 + y^2) + \frac{p_z^2}{2m} - \frac{eB}{2m}(xp_y - yp_x) && (6.14)\\
&= H_{ho} + \frac{p_z^2}{2m} - \frac{eB}{2m}L_z && (6.15)
\end{aligned}$$

where

$$H_{ho} = \frac{p_x^2 + p_y^2}{2m} + \frac{e^2B^2}{8m}(x^2 + y^2) \tag{6.16}$$

describes a two dimensional harmonic oscillator with frequency

$$\omega_x = \omega_y = \omega = \frac{eB}{2m} \tag{6.17}$$

The three terms in the Hamiltonian commute. To compute the eigenstates we need to classify the Harmonic oscillator eigenstates according to their angular momentum. Let us define $a_{x,y}$ and $a_{x,y}^\dagger$ in the usual manner

$$x = \sqrt{\frac{\hbar}{2m\omega}}(a_x + a_x^\dagger), \quad y = \sqrt{\frac{\hbar}{2m\omega}}(a_y + a_y^\dagger), \tag{6.18}$$

$$p_x = i\sqrt{\frac{m\hbar\omega}{2}}(a_x^\dagger - a_x), \quad p_y = i\sqrt{\frac{m\hbar\omega}{2}}(a_y^\dagger - a_y), \tag{6.19}$$

Let us further define

$$a_\pm = \frac{1}{\sqrt{2}}(a_x \pm i a_y), \quad a_\pm^\dagger = \frac{1}{\sqrt{2}}(a_x^\dagger \mp i a_y^\dagger) \tag{6.20}$$

The operators $a_\pm, a_\pm^\dagger$ define two independent harmonic oscillator as can be checked from the commutation relation

$$[a_+, a_+^\dagger] = 1, \quad [a_-, a_-^\dagger] = 1, \quad [a_+^\dagger, a_-] = 0, \quad [a_-^\dagger, a_+] = 0 \tag{6.21}$$

The occupation number operators $N_+ = a_+^\dagger a_+$ and $N_- = a_-^\dagger a_-$ allow to classify states by their eigenvalues:

$$N_\pm |n_+, n_-\rangle = n_\pm |n_+, n_-\rangle \tag{6.22}$$

The full Hamiltonian can be written as

$$H = \frac{\hbar e B}{2mc}(N_+ + N_- + 1) + \frac{\hbar e B}{2mc}(N_+ - N_-) + \frac{p_z^2}{2m} \tag{6.23}$$

$$= \frac{\hbar e B}{mc}(N_+ + \frac{1}{2}) + \frac{p_z^2}{2m} \tag{6.24}$$

Therefore the eigenstates and eigenvalues of energy are given by

$$H|n_+, n_-, p_z\rangle = E|n_+, n_-, p_z\rangle \tag{6.25}$$

$$E = \frac{\hbar e B}{mc}(n_+ + \frac{1}{2}) + \frac{p_z^2}{2m} \tag{6.26}$$

The spectrum is highly degenerate since the value of n_- does not affect the energy. The degeneracy is then infinite. In practice however it is bounded by the size of the region where the magnetic field acts. The lowest energy states are those with $n_+ = 0$ and they are said to be in the lowest Landau level. There is a gap

$$E_{gap} = \frac{\hbar e B}{mc} \tag{6.27}$$

to the next Landau level. The Landau levels continue to higher energy as n_+ is increase. For a field of $|\vec{B}| = 10T$ the gap is around $1.2 \times 10^{-3} eV$. This gap can be observed in a metal where electrons in the conduction band move (approximately) freely. Remembering that the Boltzmann constant implies that a temperature $T = 300\,^oK$ corresponds to $0.025 eV$, it is clear that such phenomena can be observed only at very low temperature $T \ll 10\,^oK$.

It is interesting to discuss the wave functions of the lowest Landau level states. There is a wave-function easy to compute, namely, the ground state of the harmonic oscillator

$$\langle x,y|n_+=0,n_-=0\rangle = \frac{1}{\sqrt{\pi}x_0}e^{-\frac{1}{2}\frac{x^2+y^2}{x_0^2}}, \qquad x_0=\sqrt{\frac{\hbar}{m\omega}} \tag{6.28}$$

We can introduce a complex variable

$$w=x+iy, \quad \bar{w}=x-iy \tag{6.29}$$

in terms of which the wave-function reads

$$\langle w,\bar{w}|n_+=0,n_-=0\rangle = \frac{1}{\sqrt{\pi}x_0}e^{-\frac{1}{2}\frac{w\bar{w}}{x_0^2}}, \tag{6.30}$$

For a generic state in the lowest Landau level we have

$$\langle w,\bar{w}|n_+=0,n_-\rangle = F(w,\bar{w})\frac{1}{\sqrt{\pi}x_0}e^{-\frac{1}{2}\frac{w\bar{w}}{x_0^2}}, \tag{6.31}$$

The condition for being in the lowest Landau level is

$$a_+|n_+=0,n_-\rangle = 0, \quad \Rightarrow \quad \partial_{\bar{w}}F=0 \quad \to F=F(w) \tag{6.32}$$

as can be seen from the representation

$$a_+ = \frac{1}{2x_0}w + x_0\partial_{\bar{w}} \tag{6.33}$$

of a_+ acting on these states. Eq.(6.32) means that F is a holomorphic (or analytic) function. This is very important in theoretical physics since the properties of analytic functions are vastly more interesting that those of real functions.

7. Hydrogen atom in magnetic field

As follows from the previous section, the Hamiltonian of a hydrogen atom in a uniform magnetic field $\vec{B}=B\hat{z}$ is

$$H=\frac{p^2}{2m}-\frac{e^2}{r}+\frac{eB}{2mc}(L_z+2S_z)+\frac{e^2B^2}{8mc^2}(x^2+y^2)+\frac{e^2}{m^2c^2}\frac{LS}{r^3} \tag{7.1}$$

where we included the contribution from the magnetic moment of the electron and the spin-orbit interaction since those corrections can be of the same order or even larger depending on the strength of the magnetic field.

7.1 Spin-orbit correction smaller than magnetic correction

Consider first the case of strong magnetic field. In this case we start from the usual eigenstates

$$H_0|n,l,l_z,s_z\rangle = -\frac{E_0}{n^2}|n,l,l_z,s_z\rangle \tag{7.2}$$

and diagonalize the perturbation

$$V = \frac{eB}{2mc}(L_z + 2S_z) \tag{7.3}$$

in the degenerate subspace characterized by the radial quantum number n. This step however is not necessary since the operators L_z and S_z are already diagonal in the chosen basis. We therefore find the first correction to be

$$E^{(1)} = \frac{\hbar eB}{2mc}(l_z + 2s_z) \tag{7.4}$$

Now we have to consider the spin-orbit interaction. The first thing to check is if the magnetic field lifted the degeneracy completely. It is obviously not the case since the following states have the same correction to the energy:

$$|1\rangle = |n,l_1,l_z,s_z = -\tfrac{1}{2}\rangle, \quad |2\rangle = |n,l_2,l_z-2,s_z = \tfrac{1}{2}\rangle \tag{7.5}$$

where l_1 can be different from l_2 but l_z jumps by two units. Now we have to diagonalize the spin-orbit interaction in this degenerate subspace. Once again we are lucky and find the the interaction is diagonal. In fact, the operator LS can change the component l_z only by 0 or ± 1. Moreover it cannot change the total angular momentum. Therefore it is diagonal and the diagonal element is easy to compute:

$$\begin{aligned} \langle n,l,l_z,s_z|\frac{e^2}{m^2c^2}\frac{LS}{r^3}|n,l,l_z,s_z\rangle &= \frac{e^2}{m^2c^2}\langle\frac{1}{r^3}\rangle_{n,l}\langle n,l,l_z,s_z|L_zS_z + \frac{1}{2}(L_+S_- + L_-S_+)|n,l,l_z,s_z\rangle \\ &= \frac{e^2\hbar^2}{m^2c^2}\langle\frac{1}{r^3}\rangle_{n,l}\ l_z s_z \end{aligned} \tag{7.6}$$

where we used that $L_\pm$ and $S_\pm$ have no diagonal elements. The mean value

$$\langle\frac{1}{r^3}\rangle_{n,l} = \int_0^\infty r^2 dr \frac{1}{r^3} R_{nl}^2(r) \tag{7.7}$$

has to be computed in each case. In total we obtain for a strong magnetic field

$$E^{(1)}_{n,l,l_z,s_z} = \frac{\hbar eB}{2mc}(l_z + 2s_z) + \frac{e^2\hbar^2}{m^2c^2}\langle\frac{1}{r^3}\rangle_{n,l}\ l_z s_z \tag{7.8}$$

The term proportional to B^2 is too small to contribute at this order

7.2 Spin-orbit correction larger than the magnetic correction

. In this case we do the spin orbit correction first. As we know we should consider now eigenstates of J^2, J_z where $\vec{J}=\vec{L}+\vec{S}$. The zero order states and the first order energy correction are

$$|n,l,s=\tfrac{1}{2},j,j_z\rangle \qquad E^{(1)}=\frac{e^2\hbar^2}{2m^2c^2}\langle\frac{1}{r^3}\rangle_{nl}\ \ [(j+1)-l(l+1)-s(s+1)] \tag{7.9}$$

Now we have to compute the matrix of the perturbation due to the magnetic field in this subspace. Since L_z and S_z commute with J_z the perturbation is diagonal. We take advantage of this fact and compute the correction

$$E_B^{(1)}=\frac{eB}{2mc}\langle n,l,s,j,j_z|(L_z+2S_z)|n,l,s,j,j_z\rangle=\frac{eB}{2mc}(\hbar j_z+\langle n,l,s,j,j_z|S_z|n,l,s,j,j_z\rangle) \tag{7.10}$$

where we used $j_z=l_z+s_z$. Still we need to compute the mean value of s_z. We can do that by the following consideration. When composing l with $s=\frac{1}{2}$ the total angular momentum can be $j=l\pm\frac{1}{2}$. For a given j_z, there are two states:

$$|l,j=l+\tfrac{1}{2},j_z\rangle=\alpha|l,l,j_z-\tfrac{1}{2},s_z=\tfrac{1}{2}\rangle+\beta|l,l,j_z+\tfrac{1}{2},s_z=-\tfrac{1}{2}\rangle \tag{7.11}$$

$$|l,j=l-\tfrac{1}{2},j_z\rangle=-\beta|l,l,j_z-\tfrac{1}{2},s_z=\tfrac{1}{2}\rangle+\alpha|l,l,j_z+\tfrac{1}{2},s_z=-\tfrac{1}{2}\rangle \tag{7.12}$$

where we used that the two states should be orthogonal. We can now compute

$$\langle l,j=l+\tfrac{1}{2},j_z|S_z|l,j=l+\tfrac{1}{2},j_z\rangle=\frac{\hbar}{2}(|\alpha|^2-|\beta|^2) \tag{7.13}$$

$$\langle l,j=l-\tfrac{1}{2},j_z|S_z|l,j=l-\tfrac{1}{2},j_z\rangle=\frac{\hbar}{2}(-|\alpha|^2+|\beta|^2)=-\langle l,j=l+\tfrac{1}{2},j_z|S_z|l,j=l+\tfrac{1}{2},j_z\rangle \tag{7.14}$$

we also have

$$|\alpha|^2+|\beta|^2=1 \tag{7.15}$$

from the normalization condition. Now, we only have to compute the coefficient α. In order to do that we have to use the definition of the states. Namely

$$J^2|l,j=l+\tfrac{1}{2},j_z\rangle=\hbar^2 j(j+1)|l,j=l+\tfrac{1}{2},j_z\rangle=\hbar^2(l+\frac{1}{2})(l+\frac{3}{2})|l,j=l+\tfrac{1}{2},j_z\rangle \tag{7.16}$$

Now let us use

$$LS=\frac{1}{2}(J^2-L^2-S^2) \tag{7.17}$$

to find

$$(LS)|l,j=l+\tfrac{1}{2},j_z\rangle=\hbar^2\frac{1}{2}\left[(l+\frac{1}{2})(l+\frac{3}{2})-l(l+1)-\frac{3}{4}\right]\ |l,j=l+\tfrac{1}{2},j_z\rangle=\hbar\frac{l}{2}|l,j=l+\tfrac{1}{2},j_z\rangle \tag{7.18}$$

a very simple answer. Using $LS = L_zS_z + \frac{1}{2}(L_+S_- + L_-S_+)$ we find

$$\frac{1}{\hbar^2}(LS)|l, j = l + \tfrac{1}{2}, j_z\rangle = \frac{\alpha}{2}(j_z - \frac{1}{2})|j_z - \tfrac{1}{2}, \tfrac{1}{2}\rangle + \frac{\alpha}{2}\sqrt{l(l+1) - (j_z - \frac{1}{2})(j_z + \frac{1}{2})}|j_z + \tfrac{1}{2}, -\tfrac{1}{2}\rangle$$
$$-\frac{\beta}{2}(j_z + \frac{1}{2})|j_z + \tfrac{1}{2}, -\tfrac{1}{2}\rangle + \frac{\beta}{2}\sqrt{l(l+1) - (j_z + \frac{1}{2})(j_z - \frac{1}{2})}|j_z - \tfrac{1}{2}, \tfrac{1}{2}\rangle \tag{7.19}$$

The eigenvalue condition (7.18) gives two equations

$$\frac{\alpha}{2}(j_z - \frac{1}{2}) + \frac{\beta}{2}\sqrt{l(l+1) - (j_z + \frac{1}{2})(j_z - \frac{1}{2})} = \frac{l}{2}\alpha \tag{7.20}$$

$$\frac{\alpha}{2}\sqrt{l(l+1) - (j_z - \frac{1}{2})(j_z + \frac{1}{2})} - \frac{\beta}{2}(j_z + \frac{1}{2}) = \frac{l}{2}\beta \tag{7.21}$$

plus the normalization condition $\alpha^2 + \beta^2 = 1$. This is now an algebraic problem that can be solved straight-forwardly giving

$$\alpha = \frac{\sqrt{l + j_z + \frac{1}{2}}}{\sqrt{2l+1}}, \qquad \beta = \frac{\sqrt{l - j_z + \frac{1}{2}}}{\sqrt{2l+1}} \tag{7.22}$$

Replacing in the previous formula we get the simple result

$$\langle l, j = l \pm \tfrac{1}{2}, j_z|S_z|l, j = l \pm \tfrac{1}{2}, j_z\rangle = \pm\frac{\hbar j_z}{2l+1} \tag{7.23}$$

Altogether the correction is

$$E^{(1)}_{j=\ell\pm\frac{1}{2}} = \frac{e^2\hbar^2}{2m^2c^2}\langle\frac{1}{r^3}\rangle_{nl}\ \left[j(j+1) - l(l+1) - s(s+1)\right] + \frac{\hbar eB}{2mc}j_z\left[1 \pm \frac{1}{2l+1}\right] \tag{7.24}$$

8. Identical Particles

Quantum mechanics implies a notion of identical particles that goes much further than the statement that, for example, all electrons (or protons, etc.) have the same properties. Clasically, although particles can be similar, we can follow their trajectories and thus distinguish them. Quantum mechanically there is no notion of trajectory and therefore if at time t_1 one has let's say two electrons at positions x_1, x_1' and at later time t_2 one also has two electrons at positions x_2 , x_2', it is impossible, in principle, to know if the electron at x_2 is the electron that was at x_1 or the one at x_1'. There is no experiment that can be done to distinguish those two possibilities and therefore it is not meaningful to distinguish them. Formally one has to add (or subtract) the amplitudes of both processes happening, namely (x_1, x_1') goes to (x_2, x_2') and the exchange process (x_1, x_1') goes to (x_2', x_2). For bosons, amplitudes should be added and for fermions they should be subtracted. Each type of particle is either a boson or a fermion. In general particles with integer spin are bosons and with half-integer spin are fermions. It may happen that one of the two processes has negligible probability (that depends on the Hamiltonian) in which case one can basically ignore it and consider the particles distinguishable. For example, if two Helium atoms collide at atomic energies, the probability of them interchanging protons from inside the nucleus is negligible and we can ignore processes where a proton of one nucleus is interchanged with a proton of the other nucleus. At even lower energies not even electrons can be interchanges an we can consider the atoms as single entities. In the case of He_4 the atom is a boson and for He_3 it is a fermion. At very low energies we need to consider processes where atoms are interchanged but not its individual components.

There are two main formalisms to deal with identical particles. The one that we are going to use consists simply in considering the particles to be distinguishable, and add a label $j = 1 \ldots N$ where N is the number of particles. The property of being identical implies that all operators should be completely symmetrical under interchange of the labels j whereas the wave-functions should be completely symmetrical for bosons and completely anti-symmetrical for fermions.

The other formalism is called the occupation number formalism. In that case a basis of states is chosen for single particle states (namely one particle). Then, a basis for multi-particle states is constructed by giving the occupation number of each state. In the case of bosons we can put an arbitrary number of particles in the same state whereas for fermions we can only put either zero or one particle. Operators are then constructed in terms of basic operators that add or subtract one particle from each state. In this formalism particles (of the same species) are considered identical form the very beginning. The fact that we can only put one fermion in each state is called the *Pauli exclusion principle* and follows from the fact that the wave-function has to be anti-symmetric.

8.1 Helium atom

The Hamiltonian for the Helium atom is

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - Z\frac{e^2}{r_1} - Z\frac{e^2}{r_2} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \tag{8.1}$$

where $Z = 2$ is the number of protons in the nucleus. The ground state cannot be found exactly. Experimentally, Helium has an ionization energy of 24.6 eV, the largest for any atom. The remaining electron will be in a hydrogen-like $1s$ state whose energy can be easily computed as $E = -4 \times 13.6\,\mathrm{eV} = 54.4\,\mathrm{eV}$. In total the ground state energy is $E_{He} = -24.6\,\mathrm{eV} - 54.4\,\mathrm{eV} = -79\,\mathrm{eV}$. The simplest approach is to ignore the Coulomb repulsion and solve the Hamiltonian

$$H_0 = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - Z\frac{e^2}{r_1} - Z\frac{e^2}{r_2} \tag{8.2}$$

This Hamiltonian corresponds to two non-interacting electrons and can be easily solved by putting each electron in a one-particle state while taking into account the Pauli exclusion principle. The ground state is

$$\psi_0(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}\psi_{1s}(r_1)\psi_{1s}(r_2)\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right) = \psi_{1s}(r_1)\psi_{1s}(r_2)|S=0\rangle \tag{8.3}$$

where we included the spin part which has to be antisymmetric since the spatial part is symmetric. The energy is

$$E^{(0)}_{He} = -2 \times 4 \times 13.6\,\mathrm{eV} = -108.8\,\mathrm{eV} \tag{8.4}$$

clearly overestimating the binding energy since the Coulomb repulsion gives a positive contribution. We can apply perturbation theory and compute the correction

$$E^{(1)} = \langle\psi_0|V|\psi_0\rangle = e^2 \int d^3\vec{r}_1 d^3\vec{r}_2 \frac{|\psi_{1s}(r_1)|^2|\psi_{1s}(r_2)|^2}{|\vec{r}_1 - \vec{r}_2|} \tag{8.5}$$

and use that

$$\psi_{1s}(r_1)\psi_{1s}(r_2) = \frac{Z^3}{\pi a_0^3}\; e^{-\frac{Z}{a_0}(r_1+r_2)} \tag{8.6}$$

This is the same as the hydrogen atom with the replacement $a_0 \to a_0/Z$, namely the Bohr radius is reduced by half. The integral is interesting to compute in itself, so let us consider

$$\int d^3\vec{r}_1 d^3\vec{r}_2 \frac{e^{-ar_1-ar_2}}{|\vec{r}_1 - \vec{r}_2|} = \frac{1}{a^5}\int d^3\vec{r}_1 d^3\vec{r}_2 \frac{e^{-r_1-r_2}}{|\vec{r}_1 - \vec{r}_2|} \tag{8.7}$$

The trick is now to consider the integral over $\vec{r}_2$ by itself. At this point, the vector $\vec{r}_1$ is a fixed vector. We can then choose our coordinates such that the z axis points along $\vec{r}_1$. The integral can be simplified in polar coordinates giving

$$\int d^3\vec{r}_2 \frac{e^{-r_1-r_2}}{|\vec{r}_1 - \vec{r}_2|} = \int_0^\infty r_2^2 dr_2 \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\,\phi\; \frac{e^{-r_2}}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2\cos\theta}} \tag{8.8}$$

$$= 2\pi \int_0^\infty r_2^2 dr_2\; e^{-r_2} \int_{-1}^1 \frac{d\mu}{\sqrt{r_1^2 + r_2^2 - 2r_1 r_2 \mu}} \tag{8.9}$$

$$= -2\pi \int_0^\infty r_2^2 dr_2\; e^{-r_2} \frac{1}{r_1 r_2}\left(|r_1 - r_2| - (r_1 + r_2)\right) \tag{8.10}$$

where we used the change of variables $\mu = \cos\theta$. Notice that the result depends now on the modulus of $\vec{r}_1, \vec{r}_2$ and not on their orientation. Therefore we can do the integral over $\vec{r}_1$ in polar coordinates obtaining

$$\int d^3\vec{r}_1 d^3\vec{r}_2 \frac{e^{-ar_1-ar_2}}{|\vec{r}_1-\vec{r}_2|} = -\frac{8\pi^2}{a^5}\int_0^\infty r_1^2 r_2^2 dr_1 dr_2 \ \frac{e^{-r_1-r_2}}{r_1 r_2}\left(|r_1-r_2| - (r_1+r_2)\right) \tag{8.11}$$

Therefore, the original six dimensional integral has been reduced to a simpler two dimensional integral. The only complication is the absolute value $|r_1 - r_2|$ that requires to separate the region of integration in two regions: $r_1 > r_2$ and $r_1 < r_2$. Since the integrand is symmetric under interchange of $r_1 \leftrightarrow r_2$ we can just compute one of them and multiply by two:

$$\begin{aligned}\int d^3\vec{r}_1 d^3\vec{r}_2 \frac{e^{-ar_1-ar_2}}{|\vec{r}_1-\vec{r}_2|} &= -\frac{16\pi^2}{a^5}\int_0^\infty dr_2 \int_{r_2}^\infty dr_1 r_1 r_2 e^{-r_1-r_2}(r_1-r_2-r_1-r_2) \\ &= \frac{32\pi^2}{a^5}\int_0^\infty dr_2 \int_{r_2}^\infty dr_1 r_1 r_2^2 e^{-r_1-r_2} \\ &= \frac{32\pi^2}{a^5}\int_0^\infty dr_2 \int_0^\infty d\tilde{r}_1(\tilde{r}_1+r_2) r_2^2 e^{-\tilde{r}_1-2r_2} \\ &= \frac{20\pi^2}{a^5}\end{aligned} \tag{8.12}$$

where we used the change of variables $\tilde{r}_1 = r_1 - r_2$ and the well-known integral $\int_0^\infty dr\, r^n e^{-r} = n!$. Armed with this result we immediately find the perturbative correction to the Helium atom ground state to be

$$\langle\psi_0|V|\psi_0\rangle = \frac{5}{8}\frac{Ze^2}{a_0} \tag{8.13}$$

In total we evaluate the energy to be

$$E = -2\frac{Z^2e^2}{2a_0} + \frac{5}{8}\frac{Ze^2}{a_0} = -108.8\,\text{eV} + 34\,\text{eV} = -74.8\,\text{eV} \tag{8.14}$$

Although this is a much better result it shows that the perturbative correction is significant and therefore higher order terms should also be important.

An alternative method is to use the variational approach. The simplest trial function is the same function we used but allowing for the Bohr radius to be different, namely instead of $a_0 \to a_0/Z$ we take $a_0 \to a_0/Z_{eff}$ where Z_{eff} is a variational parameter:

$$\psi_0(\vec{r}_1, \vec{r}_2) = \frac{Z_{eff}^3}{\pi a_0^3}\ e^{-\frac{Z_{eff}}{a_0}(r_1+r_2)}|S=0\rangle \tag{8.15}$$

This wave-function takes into account the partial screening of the nuclear charge by the electrons but still ignores correlations between electrons. That is, the probability of finding an electron in a given position is independent of where the other electron is. This ignores the fact that the two electrons tend to be as far from each other as they can because of the Coulomb repulsion. Nevertheless it is an improved approximation over the perturbative result which is simply the variational result for $Z_{eff} = Z = 2$. To proceed we have to compute the mean value of the Hamiltonian in such state. The easiest way is to write the Hamiltonian as a hydrogen atom with eZ_{eff} nuclear charge plus extra terms:

$$H = \frac{p_1^2}{2m} + \frac{p_2^2}{2m} - Z_{eff}\frac{e^2}{r_1} - Z_{eff}\frac{e^2}{r_2} + (Z_{eff} - Z)\frac{e^2}{r_1} + (Z_{eff} - Z)\frac{e^2}{r_2} + \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \tag{8.16}$$

Furthermore it is easy to find that

$$\langle 1s|\frac{1}{r}|1s\rangle = \frac{Z}{a_0} \tag{8.17}$$

which, using the previous results for the Coulomb repulsion gives

$$\langle H\rangle = (Z_{eff}^2 - 2ZZ_{eff} + \frac{5}{8}Z_{eff})\frac{e^2}{a_0} \tag{8.18}$$

The minimum is at

$$Z_{eff} = Z - \frac{5}{16} = \frac{27}{16} \tag{8.19}$$

giving an energy

$$E = -\frac{729}{128}\frac{e^2}{2a_0} = -77.5\,\mathrm{eV} \tag{8.20}$$

The answer is within 2% of the experimental value. It can be improved by adding additional terms to the variational wave-function

Let us now consider briefly the excited states. In the non-interacting case, the first excited state is obtained by leaving one electron in the $1s$ state and putting the other either in the $2s$ or $2p$ states. The total spin can be either $S = 0$ or $S = 1$ since now the spatial wave-function can be symmetric of anti-symmetric. The Coulomb interaction splits these levels and therefore the $S = 0$ and $S = 1$ states differ in energies of the order of eVs. To see why let us write the wave-functions:

$$\psi_A = \frac{1}{\sqrt{2}}\left(\psi_{1s}(\vec{r}_1)\psi_{nlm}(\vec{r}_2) - \psi_{1s}(\vec{r}_2)\psi_{nlm}(\vec{r}_1)\right)|S = 1, S_z = -1, 0, 1\rangle \tag{8.21}$$

$$\psi_S = \frac{1}{\sqrt{2}}\left(\psi_{1s}(\vec{r}_1)\psi_{nlm}(\vec{r}_2) + \psi_{1s}(\vec{r}_2)\psi_{nlm}(\vec{r}_1)\right)|S = 0\rangle \tag{8.22}$$

It is clear that in the ψ_A (triplet) state, the wave-function vanishes when the two electrons are on top of each other whereas in the singlet ψ_S it does not. Therefore the Coulomb repulsion will be larger for the latter one and the triplet will have significantly lower energy. More precisely

$$\langle \phi_{A,S}|\frac{e^2}{|\vec{r}_1-\vec{r}_2|}|\phi_{A,S}\rangle = e^2\int \frac{d^3\vec{r}_1 d^3\vec{r}_2}{|\vec{r}_1-\vec{r}_2|}|\psi_{1s}(\vec{r}_1)|^2|\psi_{nlm}(\vec{r}_2)|^2 \tag{8.23}$$

$$\pm e^2\int \frac{d^3\vec{r}_1 d^3\vec{r}_2}{|\vec{r}_1-\vec{r}_2|}\psi^*_{1s}(\vec{r}_1)\psi_{nlm}(\vec{r}_1)\psi_{1s}(\vec{r}_2)\psi^*_{nlm}(\vec{r}_2) \tag{8.24}$$

The second term, called the exchange energy receives its largest contribution from the region $\vec{r}_1 \simeq \vec{r}_2$ where the integrand is positive. The energy difference is

$$\Delta E_e = 2e^2\int \frac{d^3\vec{r}_1 d^3\vec{r}_2}{|\vec{r}_1-\vec{r}_2|}\psi^*_{1s}(\vec{r}_1)\psi_{nlm}(\vec{r}_1)\psi_{1s}(\vec{r}_2)\psi^*_{nlm}(\vec{r}_2) \tag{8.25}$$

It is purely an effect of the Coulomb repulsion but, because of the relation between symmetry in the spatial and spin parts it can be simulated by a term in the Hamiltonian

$$V_{eff} = -\frac{1}{\hbar^2}\Delta E_e(\vec{S}_1\cdot\vec{S}_2) \tag{8.26}$$

This effective term favors the parallel spin state $S=1$ over the $S=0$ state by the same energy difference ΔE_e. Therefore the Coulomb repulsion generates an effective ferromagnetic coupling between the spins with energy of the order of eV instead of the direct spin-spin magnetic interaction which is of the order of 10^{-4} eV. Such interactions are responsible for ferromagnetism in solids.

8.2 Magnetic susceptibility of Helium

The Hamiltonian of a Helium atom in a uniform magnetic field $\vec{B}=B\hat{z}$ is

$$H = \frac{p_1^2}{2m}+\frac{p_2^2}{2m}-Z\frac{e^2}{r_1}-Z\frac{e^2}{r_2}+\frac{e^2}{|\vec{r}_1-\vec{r}_2|} \tag{8.27}$$

$$+\frac{eB}{2mc}(L_{1z}+L_{2z}+2S_{1z}+2S_{2z}) \tag{8.28}$$

$$+\frac{e^2B^2}{8mc^2}(x_1^2+y_1^2+x_2^2+y_2^2) \tag{8.29}$$

For the ground state the second line is irrelevant since $L_{1z}+L_{2z}=0$ and $S_{1z}+S_{2z}=0$. The third line gives a correction to the energy that is given by first order perturbation theory as

$$E^{(1)} = \frac{e^2B^2}{8mc^2}\langle g.s.|(x_1^2+y_1^2+x_2^2+y_2^2)|g.s.\rangle \tag{8.30}$$

Since the ground state is spherically symmetric $\langle x^2\rangle = \langle y^2\rangle = \frac{1}{3}\langle r^2\rangle$. Therefore

$$E^{(1)} = \frac{e^2B^2}{8mc^2}\frac{4}{3}\langle g.s.|r^2|g.s.\rangle \tag{8.31}$$

The variational wave-function gives

$$\langle g.s.|r^2|g.s.\rangle = 3\frac{a_0^2}{Z_{eff.}^2} \tag{8.32}$$

and then

$$E^{(1)} = \frac{e^2B^2a_0^2}{2mc^2Z_{eff.}^2} \tag{8.33}$$

In general, for a material with no permanent magnetic moment, the energy, in the presence of a magnetic field is given by

$$E = -\frac{1}{2}\chi B^2 \tag{8.34}$$

where χ is the magnetic susceptibility. The induced magnetic moment is given by $\vec{M} = \chi\vec{B}$. If $\chi < 0$ the medium is diamagnetic and if $\chi > 0$ it is paramagnetic. If it has permanent magnetic moment is ferromagnetic. In this case a mole of Helium atoms has a magnetic susceptibility equal to

$$\chi = -\frac{e^2a_0^2}{mc^2Z_{eff.}^2}N_A \tag{8.35}$$

where $N_A = 6.02 \times 10^{23}$ is the Avogadro number. Doing the calculation we obtain

$$\chi = -1.6\,10^{-6}\frac{\mathrm{cm}^3}{\mathrm{mole}} \tag{8.36}$$

The experimental value is $\chi = -1.88\,10^{-6}\frac{\mathrm{cm}^3}{\mathrm{mole}}$ meaning that our results is not bad considering the simple trial wave-function used.

9. Time dependent perturbation theory

In quantum mechanics, as in classical mechanics, it becomes important to compute the evolution of a system given an initial state. In the quantum case this requires solving the Schroedinger equation

$$\frac{\partial|\psi(t)\rangle}{\partial t} = -\frac{i}{\hbar}H(t)|\psi(t)\rangle, \qquad |\psi(t=0)\rangle = |\psi_0\rangle \tag{9.1}$$

If the Hamiltonian is time independent $H(t) = H$ and we know its exact eigenstates $|E_n\rangle$ this is solved by

$$|\psi(t)\rangle = \sum_n c_n e^{-\frac{i}{\hbar}E_n t}|E_n\rangle, \qquad c_n = \langle E_n|\psi_0\rangle \tag{9.2}$$

If the Hamiltonian is time dependent, or the eigenstates are not known we need to resort to some approximation method. In the case where we can write

$$H = H_0 + \lambda V(t) \tag{9.3}$$

where H_0 is time independent and exactly solvable, and $\lambda V(t)$ is a perturbation such that the transition probabilities to other states are small, the method to use is an expansion in powers of λ, namely perturbation theory.

9.1 An exact computation

We start by considering a case that can be solved exactly. It is a two state system with Hamiltonian

$$H = \begin{pmatrix} \epsilon_1 & 0 \\ 0 & \epsilon_2 \end{pmatrix} + \begin{pmatrix} 0 & \gamma e^{i\omega t} \\ \gamma e^{-i\omega t} & 0 \end{pmatrix} \tag{9.4}$$

where $\gamma \in \mathbb{R}$. Let us consider the initial state to be

$$|\psi_0\rangle = |1\rangle \tag{9.5}$$

We have to find

$$|\psi(t)\rangle = c_1(t)e^{-\frac{i}{\hbar}\epsilon_1 t}|1\rangle + c_2(t)e^{-\frac{i}{\hbar}\epsilon_2 t}|2\rangle \tag{9.6}$$

where we extracted the trivial time dependence so that $c_{1,2}(t)$ become time independent if $\gamma = 0$. After some algebra, the Schroedinger equation gives

$$\dot{c}_1 = -\frac{i\gamma}{\hbar}\, e^{i(\omega-\omega_{21})t}c_2 \tag{9.7}$$

$$\dot{c}_2 = -\frac{i\gamma}{\hbar}\, e^{-i(\omega-\omega_{21})t}c_1 \tag{9.8}$$

where the dots indicate time derivatives and

$$\hbar\omega_{21} = \epsilon_2 - \epsilon_1 \tag{9.9}$$

We can convert this system into an equation for just c_2 by using

$$-\frac{i\gamma}{\hbar}\partial_t c_1 = \partial_t(e^{i(\omega-\omega_{21})t}\dot{c}_2) = -\frac{i\gamma}{\hbar}\ e^{i(\omega-\omega_{21})t}c_2 \tag{9.10}$$

Expanding

$$\ddot{c}_2 + i(\omega - \omega_{21})\dot{c}_2 + \frac{\gamma^2}{\hbar^2}c_2 = 0 \tag{9.11}$$

This can be solved by proposing an exponential solution. The result is

$$c_2 = Ae^{q_1 t} + Be^{q_2 t} \tag{9.12}$$

with

$$q_{1,2} = \frac{i}{2}\left[(\omega - \omega_{21}) \pm \sqrt{(\omega - \omega_{21})^2 + 4\frac{\gamma^2}{\hbar^2}}\right] \tag{9.13}$$

Defining

$$\Omega = \frac{1}{2}\sqrt{(\omega - \omega_{21})^2 + 4\frac{\gamma^2}{\hbar^2}} \tag{9.14}$$

and taking into account the initial conditions we determine

$$|c_2|^2 = \frac{1}{1 + \frac{\hbar^2(\omega-\omega_{21})^2}{4\gamma^2}}\ \sin^2\Omega t \tag{9.15}$$

The result is physically interesting. The probability of being in state $|2\rangle$ oscillates with frequency Ω but it does not quite reach the value 1 unless we are in resonance, namely $\omega = \omega_{21}$. In that case the system oscillates between state $|1\rangle$ and state $|2\rangle$.

In perturbation theory we can only access these results as an expansion in powers of γ. For the probability of being in state two we find

$$|c_2|^2 \simeq \frac{4\,\gamma^2}{\hbar^2(\omega - \omega_{21})^2}\sin^2\frac{(\omega - \omega_{21})t}{2} \tag{9.16}$$

away from resonance and

$$|c_2|^2 = \sin^2\frac{\gamma t}{\hbar} \simeq \frac{\gamma^2 t^2}{\hbar^2} \tag{9.17}$$

at resonance $\omega = \omega_{21}$. In this last case the result is only valid when $t \ll \hbar/\gamma$ since only then the approximation $\sin\gamma t \simeq \gamma t$ is valid. From a physical point of view, at resonance, even a tiny perturbation can, over time, take the system to state $|2\rangle$. On the other hand, perturbation theory assumes $|c_2|^2 \ll 1$ from the outset and therefore is only valid for a short time.

9.2 Perturbative calculation

Consider the case where we can write the Hamiltonian as

$$H = H_0 + \lambda V(t) \tag{9.18}$$

such that H_0 is a Hamiltonian that we know how to diagonalize exactly and $\lambda V(t)$ is a small perturbation in that the transition probabilities to states other than the initial state are small. Denote the eigenvectors of H_0 as $|E_n\rangle$ and take one of them $|E_i\rangle$ as the initial state. At any time t we write the state of the system as

$$|\psi(t)\rangle = \sum_n c_n(t) e^{-\frac{i}{\hbar}E_n t}|E_n\rangle \tag{9.19}$$

The initial condition reads

$$c_i(t=0) = 1, \quad c_{n\neq i}(t=0) = 0 \tag{9.20}$$

The Schroedinger equation

$$\partial_t|\psi(t)\rangle = -\frac{i}{\hbar}H|\psi(t)\rangle \tag{9.21}$$

reads

$$\partial_t c_n(t) = -\frac{i}{\hbar}\lambda\sum_m c_m(t) e^{-\frac{i}{\hbar}(E_m-E_n)t}\langle E_n|V(t)|E_m\rangle \tag{9.22}$$

If we propose a series expansion

$$c_n(t) = \sum_{j=0}^{\infty}\lambda^j c_n^{(j)}(t) \tag{9.23}$$

the equation give a simple recursive relation

$$\partial_t c_n^{(j)}(t) = -\frac{i}{\hbar}\sum_m c_m^{(j-1)}(t) e^{-i\omega_{mn}t}\langle E_n|V(t)|E_m\rangle \tag{9.24}$$

where $\hbar\omega_{mn} = E_m - E_n$. These are simple to solve but we need initial conditions. First we have that

$$c_i^{(0)}(t=0) = 1, \quad c_i^{(j>0)}(t=0) = 0, \quad c_{n\neq i}^{(j)}(t=0) = 0 \tag{9.25}$$

Furthermore, the zeroth order coefficients $c_n^{(0)}$ are time-independent since for $\lambda = 0$ all the time dependence is taken into account by the phase factors $e^{-\frac{i}{\hbar}E_n t}$. Therefore

$$c_i^{(0)}(t) = 1, \quad c_{n\neq i}^{(0)}(t) = 0 \tag{9.26}$$

The solution is now obtained recursively as

$$c_n^{(0)}(t) = \delta_{ni} \tag{9.27}$$

$$c_n^{(1)}(t) = -\frac{i}{\hbar}\int_0^t e^{i\omega_{ni}t'} V_{ni}(t')\, dt' \tag{9.28}$$

$$c_n^{(2)}(t) = \left(-\frac{i}{\hbar}\right)^2 \int_0^t e^{i\omega_{nm}t'} V_{nm}(t')\, dt' \int_0^{t'} e^{i\omega_{mi}t''} V_{mi}(t'')\, dt'' \tag{9.29}$$

$$c_n^{(j+1)}(t) = -\frac{i}{\hbar}\int_0^t e^{-i\omega_{mn}t'} c_m^{(j)}(t') V_{nm}(t')\, dt' \tag{9.30}$$

although, for most of our calculations, we are going to consider only the first order.

These formulas describe the general case. It is useful to consider a particular form of the perturbation which appears quite often, the so called monochromatic or harmonic perturbation:

$$V = \mathcal{V} e^{i\omega t} + \mathcal{V}^\dagger e^{-i\omega t} \tag{9.31}$$

It includes the particular case $\omega = 0$, namely constant perturbation. The integrals are pretty straight-forward giving

$$c_{n\neq i}^{(1)}(t) = -\frac{2i}{\hbar} e^{i\frac{(\omega_{ni}+\omega)}{2}t} \frac{\sin(\frac{\omega_{ni}+\omega}{2}t)}{\omega_{ni}+\omega}\ \langle E_n|\mathcal{V}|E_i\rangle - \frac{2i}{\hbar} e^{i\frac{(\omega_{ni}-\omega)}{2}t} \frac{\sin(\frac{\omega_{ni}-\omega}{2}t)}{\omega_{ni}-\omega}\ \langle E_n|\mathcal{V}^\dagger|E_i\rangle \tag{9.32}$$

As a function of ω, the coefficient has peaks at $\omega = \pm\omega_{ni}$. This is the resonance phenomenon that we described in the previous section for the two state system. Away from resonance the coefficients are small therefore we can make the approximation

$$|c_n^{(1)}(t)|^2 \simeq \frac{|\mathcal{V}_{ni}^\dagger|^2}{\hbar^2} \frac{\sin^2(\frac{\omega_{ni}-\omega}{2}t)}{\left(\frac{\omega_{ni}-\omega}{2}\right)^2} \quad \text{for} \quad \omega \simeq \omega_{ni} \tag{9.33}$$

$$|c_n^{(1)}(t)|^2 \simeq \frac{|\mathcal{V}_{ni}|^2}{\hbar^2} \frac{\sin^2(\frac{\omega_{ni}+\omega}{2}t)}{\left(\frac{\omega_{ni}+\omega}{2}\right)^2} \quad \text{for} \quad \omega \simeq -\omega_{ni} \tag{9.34}$$

As a function of ω, $|c_n^{(1)}(t)|^2$ is a typical diffraction pattern with a peak of width $\delta\omega = \frac{2\pi}{t}$. For large enough times the peak becomes narrower than the level spacing and therefore the initial state can transition only to the energy level determined by the resonance. For those states the probability, as computed in perturbation theory, increases quadratically in time a result that can only be valid for a short initial time. However, knowing that for a given frequency ω the system can only transition to those states with energy $E_n = E_i \pm \hbar\omega$ allows us to restrict the problem to just those states. Thus, the problem reduces to a finite number of states and can be treated exactly. In fact, this is what we did when we discussed a two state system in the previous section. There are no two state systems, but in many physical situation such as this one, only two states are relevant, namely those connected by the frequency ω.

One interesting point of view is that, for short times $t = \Delta t$, the peak is broad and the uncertainty in energy is of order

$$\Delta E \geq \frac{\hbar}{\Delta t} \tag{9.35}$$

This is known as the energy uncertainty principle. There is no presumed uncertainty in measuring time, it means that if two energy measurements are done with a time difference Δt, one is going to find the same energy only up to a dispersion ΔE. In that sense is different from the position and momentum uncertainty principle but has a similar spirit.

9.3 Transition into the continuum spectrum

The case in which the final state is in the continuum is of great physical interest since it describes the decay of a particle into others, scattering processes etc. In such situation, even in a narrow resonance peak there is a large number of states. The probability is a continuous function of ω_{ni} since $\omega_n = \frac{E_n}{\hbar}$ takes continuous values. In that case what is important is the area under the main resonance peak. Since its height is proportional to t^2 and its width to $\frac{1}{t}$, the total transition probability grows linearly in t. It makes sense to define a transition rate, namely probability divided by time. More formally, we can take the time derivative

$$\partial_t |c_n^{(1)}|^2 = \frac{2|\mathcal{V}^\dagger_{ni}|^2}{\hbar^2} \frac{\sin(\omega_{ni} - \omega)t}{\omega_{ni} - \omega} \tag{9.36}$$

When t becomes sufficiently large, we can use the approximation

$$\frac{\sin \omega t}{\omega} \xrightarrow{t \to \infty} \pi \delta(\omega) \tag{9.37}$$

Therefore the time derivative becomes constant and defines a transition rate, namely a probability per unit time. There is a probability of increasing and other of decreasing the energy

$$w_{i \to n} = \frac{2\pi}{\hbar} |\mathcal{V}^\dagger_{ni}|^2 \delta(E_n - E_i + \hbar\omega) \tag{9.38}$$

$$w_{i \to n} = \frac{2\pi}{\hbar} |\mathcal{V}_{ni}|^2 \delta(E_n - E_i - \hbar\omega) \tag{9.39}$$

These formulas are known as the Fermi golden rule. Consider now an application. The problem we are interested in is the atomic photoelectric effect, namely the ejection of an electron from an atom due to the action of external electromagnetic radiation. In any application of the Fermi golden rule we need to perform three important steps:

- Identify the perturbation V and compute the transition rate w.
- Convert the transition rate into an experimentally useful quantity such as a mean-life or a cross section.
- Identify the possible final states and sum or integrate over them to compute the total cross section or mean-life.

In this case the perturbation is due to an electromagnetic standing wave whose vector potential can be written as

$$\vec{A} = 2A_0\hat{\epsilon}\cos(\vec{k}\vec{x} - \omega t) \tag{9.40}$$

Here, A_0 is the amplitude of the wave, $\hat{\epsilon}$ is the polarization vector. Also, $\vec{k}$ is the wave number, which determines the direction of propagation, and $\omega = |\vec{k}|c$ is the frequency. The polarization is always transverse, namely $\vec{k}\hat{\epsilon} = 0$. The electric and magnetic fields follow as

$$\vec{E} = -\frac{1}{c}\frac{\partial \vec{A}}{\partial t} = -\frac{2A_0\omega}{c}\hat{\epsilon}\sin(\vec{k}\vec{x} - \omega t) \tag{9.41}$$

$$\vec{B} = \nabla \times \vec{A} = -2A_0\ (\vec{k} \times \hat{\epsilon})\ \sin(\vec{k}\vec{x} - \omega t) \tag{9.42}$$

As we saw before, the Hamiltonian for an electron in an electromagnetic field is

$$H = \frac{1}{2m}\left(\vec{p} - \frac{e}{c}\vec{A}\right)^2 + e\phi \tag{9.43}$$

where ϕ is the scalar potential (which in this case is due to the atomic nucleus). Expanding at first order and taking into account that $[p_i, A_i] = -i\hbar\nabla \cdot \vec{A} = 0$ we find the perturbation to be

$$V = -\frac{e}{mc}A_0(\hat{\epsilon}\vec{p})\ \left(e^{i\vec{k}\vec{x}-i\omega t} + e^{-i\vec{k}\vec{x}+i\omega t}\right) \tag{9.44}$$

The first term is the one relevant for absorption and gives a transition rate

$$w_{i\to n} = \frac{2\pi}{\hbar}\frac{e^2A_0^2}{m^2c^2}\left|\langle E_n|e^{i\vec{k}\vec{x}}(\hat{\epsilon}\vec{p})|E_i\rangle\right|^2 \delta(E_n - E_i - \hbar\omega) \tag{9.45}$$

Now let's convert this into a useful quantity that we can measure. Since the energy absorbed is proportional to the energy flux of the radiation and to the overall time, it is convenient to define a normalized quantity, the cross section σ_{abs}. It is defined as an area such that the energy flux of the incident beam across such an area is equal to the energy absorbed by the sample (per electron) in the unit time. Namely:

$$\text{Energy flux } \times\ \sigma_{abs} = \frac{\text{Energy absorbed}}{\text{time}} \tag{9.46}$$

Therefore it is measured in m^2. In particle and nuclear physics it is more common to use the unit "barn" given by $1b = 100\,\mathrm{fm}^2$. In this case it can be measured from the attenuation rate of the radiation inside the material. Indeed, imagine radiation traveling inside this material. In the density of the material is ρ (in number of atoms per unit volume) we have that the intensity of the radiation $\mathcal{I}(x)$ obeys

$$\mathcal{I}(x+\Delta x) - \mathcal{I}(x) = -\mathcal{I}(x)\sigma_{abs}\rho\Delta x \tag{9.47}$$

implying

$$\mathcal{I}(x) = \mathcal{I}(0)e^{-\rho\sigma_{abs}x} \tag{9.48}$$

The exponential decay with the thickness of the material is much easier to measure than the absolute value of the intensity. The energy flux of the electromagnetic radiation follows from

$$\text{Energy flux} = c\,\mathcal{U} = \frac{c}{2}\left(\frac{E_{max}^2}{8\pi} + \frac{B_{max}^2}{8\pi}\right) = \frac{1}{2\pi}\frac{\omega^2}{c}|A_0|^2 \tag{9.49}$$

where $\mathcal{U}$ is the energy density of the radiation. The energy absorbed per unit time is

$$\frac{\text{Energy absorbed}}{\text{time}} = \sum_n w_{i\to n}\hbar\omega \tag{9.50}$$

where the sum is over all possible final states of the electron and we took into account that each process absorbs an energy $\hbar\omega$. Due to the $\delta(E_n - E_i - \hbar\omega)$ only states with given energy need to be summed. The last step is to perform such sum. The only thing we have to do is to integrate over all possible directions in which the electron can emerge. However we have to have an adequate measure of integration. In order to do that consider the system confined to a large box of linear size L and use periodic boundary conditions. The electron wave-functions are

$$\psi_f(\vec{x}) = \frac{1}{L^{\frac{3}{2}}}e^{i\vec{k}_f\vec{x}}, \qquad \vec{k}_f = \frac{2\pi}{L}(n_x, n_y, n_z) \tag{9.51}$$

where the n's are integers. In the space of n's there is one state per unit volume, and for large L they are closely spaced so we can replace the sum by an integral:

$$\sum_{n_x,n_y,n_z} = \int d^3n = L^3\int\frac{d^3k_f}{(2\pi)^3} = \frac{L^3}{(2\pi)^3}\frac{m}{\hbar^2}k_f dE_f\,d\Omega, \qquad k_f = \sqrt{\frac{2mE_f}{\hbar^2}} \tag{9.52}$$

where we used $E_f = \frac{\hbar^2 k_f^2}{2m}$ and $d\Omega = \sin\theta d\theta d\phi$ denotes the solid angle into which the electron is ejected. We can then write the differential absorption cross section as

$$d\sigma_{abs} = \frac{4\pi^2\hbar}{m^2\omega}\frac{e^2}{\hbar c}\frac{L^3}{(2\pi)^3}\frac{m}{\hbar^2}\int k_f|\langle k_f|e^{i\vec{k}\vec{x}}(\hat{\epsilon}\cdot\vec{p})|E_i\rangle|^2\delta(E_f - E_i - \hbar\omega)dE_f\,d\Omega \tag{9.53}$$

$$= \frac{4\pi^2\hbar}{m^2\omega}\frac{e^2}{\hbar c}\frac{L^3}{(2\pi)^3}\frac{mk_f}{\hbar^2}\int|\langle k_f|e^{i\vec{k}\vec{x}}(\hat{\epsilon}\cdot\vec{p})|E_i\rangle|^2 d\Omega \tag{9.54}$$

The matrix element can be computed as

$$\langle k_f|e^{i\vec{k}\vec{x}}(\hat{\epsilon}\cdot\vec{p})|E_i\rangle = \int d^3x \frac{1}{L^{\frac{3}{2}}} e^{-i\vec{k}_f\vec{x}+i\vec{k}\vec{x}}(-i\hbar)\hat{\epsilon}\cdot\nabla\psi_i(\vec{x}) \tag{9.55}$$

$$= \frac{i\hbar}{L^{\frac{3}{2}}}(-i\vec{k}_f\cdot\hat{\epsilon})\int d^3x e^{i(\vec{k}-\vec{k}_f)\vec{x}}\psi_i(\vec{x}) \tag{9.56}$$

$$= \frac{\hbar}{L^{\frac{3}{2}}}(\vec{k}_f\cdot\hat{\epsilon})\tilde{\psi}(\vec{k}-\vec{k}_f) \tag{9.57}$$

where we integrated by parts and defined the Fourier transform

$$\tilde{\psi}(\vec{k}-\vec{k}_f) = \int d^3x\; e^{i(\vec{k}-\vec{k}_f)\vec{x}}\psi_i(\vec{x}) \tag{9.58}$$

The final expression for the differential cross section is

$$\frac{d\sigma_{abs}}{d\Omega} = \frac{1}{2\pi}\frac{e^2}{m\omega c}k_f(\vec{k}_f\cdot\hat{\epsilon})^2|\tilde{\psi}(\vec{k}-\vec{k}_f)|^2 \tag{9.59}$$

Here the modulus of $\vec{k}_f$ is determined by energy conservation. The angles in $d\Omega$ should be integrated to obtain the total cross section.

A simple example is hydrogen atom in the ground state. In that case the wave function is

$$\psi_{1s} = \frac{1}{\sqrt{\pi}a_0^{\frac{3}{2}}}\, e^{-\frac{r}{a_0}} \tag{9.60}$$

The Fourier transform is

$$\tilde{\psi}(\vec{k}) = \int d^3r\, e^{i\vec{k}\vec{r}}\psi_{1s} = \frac{8\sqrt{\pi}a_0^{\frac{3}{2}}}{(1+k^2a_0^2)^2} \tag{9.61}$$

and then

$$\frac{d\sigma_{abs}}{d\Omega} = \frac{32e^2a_0^3}{m\omega c}\frac{k_f(\vec{k}_f\hat{\varepsilon})^2}{(1+(\vec{k}-\vec{k}_f)^2a_0^2)^4} \tag{9.62}$$

The first result is that electron will be ejected primarily in the direction of $\hat{\varepsilon}$ due to the factor $(\vec{k}_f\hat{\varepsilon})^2$ in the numerator. The reason is that $\hat{\varepsilon}$ is the direction in which the electric field points. Finally, during the calculation we ignored the spin of the electron. The reason is that this perturbation, at lowest order, does not couple to the spin and therefore if the elecron is *e.g.* with spin up in the atom, it will be ejected with spin up.

9.4 $2p \to 1s$ transition

In an spontaneous atomic transition only a few, usually one, photons are produced and therefore the electromagnetic field needs to be quantized. Imagine the field inside a box with periodic boundary conditions. The solutions to the Maxwell equations is a superposition of non-interacting plane waves of momenta $\vec{k} = \frac{2\pi}{L}(n_x, n_y n_z)$ with $n_{x,y,z}$ integers. For each mode, the fields oscillate with frequency $\omega = |\vec{k}|c$. Clearly, the plane waves are the normal modes of oscillation of the field and should be quantized as a set of independent harmonic oscillators. With this in mind we introduced the quantum vector potential

$$\vec{A}(x) = \sqrt{\frac{4\pi}{V}} \sum_{\vec{k},\, \alpha=1,2} c\sqrt{\frac{\hbar}{2\omega_k}} \epsilon^{(\alpha)} \left[a_{\vec{k},\alpha} e^{i\vec{k}\vec{x}} + a^{\dagger}_{\vec{k},\alpha} e^{-i\vec{k}\vec{x}} \right] \tag{9.63}$$

where $a^{\dagger}_{\vec{k},\alpha}$, $a_{\vec{k},\alpha}$ are the usual creation and annihilation operators associated with each mode. Their commutation relation is

$$[a^{\dagger}_{\vec{k},\alpha}, a_{\vec{k}',\alpha'}] = -\delta_{\vec{k},\vec{k}'} \delta_{\alpha,\alpha'} \tag{9.64}$$

the index $\alpha = 1, 2$ indicates the polarization and ϵ_α are two unit vectors orthogonal to $\vec{k}$ and orthogonal to each other. The Hamiltonian is given by

$$H = \sum_{\vec{k},\alpha} \hbar\omega_k \; a^{\dagger}_{\vec{k},\alpha} a_{\vec{k},\alpha} \tag{9.65}$$

The coefficients on the mode expansion of $\vec{A}$ are chosen such that

$$H = \frac{1}{8\pi} \int d^3x (\vec{E}^2 + \vec{B}^2) \tag{9.66}$$

The eigenstates of the Hamiltonian are given by a set of integers $N_{\vec{k},\alpha}$ that determine the occupation state of each mode.

$$|N_{\vec{k},\alpha}\rangle, \qquad E = \sum_{\vec{k},\alpha} N_{\vec{k},\alpha} \, \hbar\omega_k \tag{9.67}$$

After this brief description of the quantization of the electromagnetic field, let us go back to our problem of computing the atomic transition probabilities. As said before, first we have to identify the interaction responsible for the transition. This is the familiar term in the interaction of a charged particle with an electromagnetic field:

$$V = -\frac{e}{2mc}(\vec{A}\vec{p} + \vec{p}\vec{A}) \tag{9.68}$$

Where we now have to take into account that $\vec{A}$ is an operator in the photon space. Now we use Fermi's golden rule

$$w_{i\to f} = \frac{2\pi}{\hbar} \; |\langle f|V|i\rangle|^2 \; \delta(E_f - E_i) \tag{9.69}$$

Notice that this is a transition in the continuum spectrum because the photon can have any value of (positive) energy. The initial and final states are

$$|i\rangle = |nlm; N_{\vec{k},\alpha} = 0\rangle, \qquad |f\rangle = |n'l'm'; N_{\vec{k},\alpha} = 1\rangle \tag{9.70}$$

for some mode $\vec{k}$, α.

Finally we have to sum over final states of the photon. That's done by using

$$\sum_{n_x,n_y,n_z} = \frac{L^3}{(2\pi)^3} \int d^3k \tag{9.71}$$

and also a discrete sum over the two possible polarizations. In computing the transition probability, only the creation part of the operator $\vec{A}$ needs to be kept, resulting in

$$\langle f|V|i\rangle = \langle n'l'm'; N_{\vec{k},\alpha} = 1| - \frac{e}{mc}\sqrt{\frac{4\pi}{V}} \sum_{\vec{k}\alpha} c\sqrt{\frac{\hbar}{2\omega_k}} \epsilon^{(\alpha)} \vec{p} a^\dagger_{\vec{k},\alpha} e^{-i\vec{k}\vec{x}} |nlm; N_{\vec{k},\alpha} = 0\rangle \tag{9.72}$$

The easiest part is the photon part since it gives

$$\langle N_{\vec{k},\alpha} = 1 | a^\dagger_{\vec{k},\alpha} | N_{\vec{k},\alpha} = 0\rangle = 1 \tag{9.73}$$

Putting everything together including the sum over final states gives

$$w_{i\to f} = \frac{L^3}{(2\pi)^3} \sum_\alpha \int d^3k \frac{4\pi^2 e^2}{m^2\omega L^3} |\epsilon^{(\alpha)} \langle n'l'm'| e^{-i\vec{k}\vec{x}} \vec{p} |nlm\rangle|^2 \; \delta(E_{n',l',m'} + \hbar\omega_k - E_{nlm}) \tag{9.74}$$

Since $\omega_k = kc$ we can do the radial integral in momentum using the delta function. Thus

$$w_{i\to f} = \sum_\alpha \int d\Omega \frac{e^2\omega}{2\pi\hbar c m^2 c^2} |\epsilon^{(\alpha)} \langle n'l'm'| e^{-i\vec{k}\vec{x}} \vec{p} |nlm\rangle|^2 \tag{9.75}$$

where $d\Omega = \sin\theta d\theta d\phi$ is the differential of solid angle for the emitted photon. This is now a calculable atomic matrix element. However, it is useful to simplify the calculation a bit by using the dipole approximation. Indeed, for example for the transition $2p \to 1s$, the energy is

$$\hbar\omega = \frac{3}{4}\frac{e^2}{2a_0} = 10.2\,\mathrm{eV}, \qquad \text{equivalently} \qquad k \simeq \frac{1}{2\times 10^{-8} m} \tag{9.76}$$

Since the wave function of the states is exponentially small for $r \gg a_0$ we have $\vec{k}\vec{x} \sim 10^{-2}$ and an appropriate expansion is

$$e^{-i\vec{k}\vec{x}} = 1 - i\vec{k}\vec{x} + \dots \tag{9.77}$$

Keeping the first term corresponds to the so called $E1$ electric dipole transition, giving

$$w_{i\to f} = \sum_\alpha \int d\Omega \frac{e^2\omega}{2\pi\hbar c m^2 c^2} |\epsilon^{(\alpha)}\langle n'l'm'|\vec{p}|nlm\rangle|^2 \tag{9.78}$$

The only dependence on the direction of $\vec{k}$ is now in the polarization vectors. The integral and sum over polarizations can be done using that

$$\sum_\alpha \int d\Omega \epsilon_i^{(\alpha)}\epsilon_j^{(\alpha)} = B\delta_{ij} \tag{9.79}$$

which follows from rotational invariance. The constant B can be computed by taking the trace on both sides using that $\epsilon^{(\alpha)}$ are unit vectors

$$\sum_\alpha \int d\Omega \epsilon_i^{(\alpha)}\epsilon_i^{(\alpha)} = 2\int d\Omega = 8\pi = 3B \quad \Rightarrow \quad B = \frac{8\pi}{3} \tag{9.80}$$

Finally there is a useful trick to compute the matrix element of the momentum:

$$\langle n'l'm'|\vec{p}|nlm\rangle = \langle n'l'm'|\frac{im}{\hbar}[H,\vec{x}]|nlm\rangle \tag{9.81}$$

$$= \frac{im}{\hbar}(E_{n'l'm'} - E_{nlm})\langle n'l'm'|\vec{x}|nlm\rangle \tag{9.82}$$

$$= im\omega\langle n'l'm'|\vec{x}|nlm\rangle \tag{9.83}$$

Finally

$$w_{i\to f} = \frac{4}{3}\alpha\frac{\omega^3}{c^2}\ |\langle n'l'm'|\vec{x}|n,lm,\rangle|^2 \tag{9.84}$$

which agrees with the one obtained from the Einstein relations. For the particular case $2p \to 1s$ the result is

$$|\langle 1s|\vec{x}|2pm=0\rangle|^2 = \frac{2^{15}}{3^{10}}\ a_0^2 \tag{9.85}$$

where we used

$$\psi_{1s} = \frac{1}{\sqrt{4\pi}}\frac{1}{a_0^{\frac{3}{2}}}2e^{-\frac{r}{a_0}} \tag{9.86}$$

$$\psi_{2p} = \sqrt{\frac{3}{4\pi}}\cos\theta\ \frac{1}{(2a_0)^{\frac{3}{2}}}\frac{r}{\sqrt{3}a_0}e^{-\frac{r}{2a_0}} \tag{9.87}$$

Using that

$$\hbar\omega = \frac{3}{4}\frac{e^2}{2a_0} \tag{9.88}$$

we obtain

$$w_{2p\to 1s} = \frac{2^8}{3^8}\alpha^5\frac{mc^2}{\hbar c}c = \frac{1}{1.6\,10^{-9}s} \tag{9.89}$$

Therefore the mean life of the $2p$ state is

$$\tau_{2p} = 1.6\,ns \tag{9.90}$$

10. Scattering

Scattering is one of the most important processes in physics from an experimantal point of view. It consists of sending a beam of particles towards a target and detecting the resulting products of the collision. A detector usually measures the direction in which the particles come out together with their energy, charge and mass.

A particular case is ellastic scattering where incoming particles are scattered in different directions but without changing their nature, that is no new particles are created in the collision. The most standard case is the scattering of particles by a potential. This case has applications for example in atomic and molecular physics.

Scattering process are characterized by the total σ_T, partial σ_λ differential $\frac{d\sigma}{d\Omega}$ cross sections.

$$\text{Incident flux } \times \ \sigma_T = \frac{\text{Number of particles scattered}}{\text{time}} \tag{10.1}$$

$$\text{Incident flux } \times \ \sigma_l = \frac{\text{Number of particles scattered in given channel } l}{\text{time}} \tag{10.2}$$

$$\text{Incident flux } \times \ \frac{d\sigma}{d\Omega} = \frac{\text{Number of particles scattered into a solid angle } d\Omega}{\text{time}} \tag{10.3}$$

A channel means scattering taking place through a particular process, for example oinvloving waves with angular momentum l. The unit of measure for the cross ection is area, namely m^2. Some times the unit $1\text{barn} = 1\text{b} = 10^{-28} m^2 = 100\text{fm}^2$ is used.

10.1 Scattering as a time dependent problem, Born approximation

Ellastic scattering is a time-dependent process where the initial sate is a particle in a definite sate of momentum and the final state is the same particle with a different momentum. If hte process can be treated perturbatively, using the Fermi golden rule, the probabilty per unit time is

$$w_{i\to f} = \sum_{\text{final states}} \frac{2\pi}{\hbar} |\langle f|V|i\rangle|^2 \delta(E_f - E_i) \tag{10.4}$$

The cross section is then

$$\sigma = \frac{w_{i\to f}}{\text{incident flux}} \tag{10.5}$$

The cross section is the total cross section if we sum over all final states and the differential cross section if we sum over states with momentum inside the differential of solid angle $d\Omega$. Here V is the perturbation responsible for the scattering.

To be more specific consider the scattering of particles by a potential $V(\vec{x})$. Normalizig the wave functions to unit in a large volume L^3, the incident and outgoing wave functions are

$$\psi_{i,f} = \frac{1}{L^{\frac{3}{2}}} e^{i\vec{k}_{i,f}\vec{x}} \tag{10.6}$$

The momenta are quantized as

$$\vec{k} = \frac{2\pi}{L}(n_x, n_y, n_z), \qquad n_{x,y,z} \in \mathbb{Z} \tag{10.7}$$

Therefore the sum over final states is done as

$$\sum_{n_x,n_y,n_x} \simeq \int d^3n = \frac{L^3}{(2\pi)^3} \int d^3k \tag{10.8}$$

valid in the limit $L \to \infty$. Finally, the incident flux is given by

$$\vec{j} = -i\frac{\hbar}{2m}\left(\psi^* \nabla \psi - \psi \nabla \psi^*\right) = \frac{1}{L^3}\frac{\hbar \vec{k}}{m} \tag{10.9}$$

since $\hbar\vec{k}$ is the momentum, the current can be interpreted as the density $\frac{1}{L^3}$ times the velocity $\frac{\hbar\vec{k}}{m}$ Putting all the pieces together we can compute the total cross section:

$$\begin{aligned}
\sigma_T &= \frac{w_{i\to f}}{\text{incident flux}} && (10.10)\\
&= \frac{m\,L^3}{\hbar k}\frac{L^3}{(2\pi)^3}\int d^3k \frac{2\pi}{\hbar}|\langle f|V|i\rangle|^2 \delta(E_f - E_i) && (10.11)\\
&= \frac{m\,L^3}{\hbar k}\frac{L^3}{(2\pi)^3}\int d^3k \frac{2\pi}{\hbar}|\frac{1}{L^3}\int d^3x e^{i(\vec{k}-\vec{k}')\vec{x}} V(\vec{x})|^2 \delta(\frac{\hbar^2 k_f^2}{2m} - \frac{\hbar^2 k_i^2}{2m}) && (10.12)\\
&= \frac{m^2}{4\pi^2\hbar^4}\int d\Omega |\tilde{V}(\vec{k}-\vec{k}')|^2 && (10.13)
\end{aligned}$$

where we defined the Fourier transform

$$\tilde{V}(\vec{k}-\vec{k}') = \int d^3x e^{i(\vec{k}-\vec{k}')\vec{x}} V(\vec{x}) \tag{10.14}$$

The differential cross section is given by

$$\frac{d\sigma}{d\Omega} = \frac{m^2}{4\pi^2\hbar^4}|\tilde{V}(\vec{k}-\vec{k}')|^2 \tag{10.15}$$

This gives the first order approximation to scattering by a potential also known as the Born approximation.

10.1.1 Radial potential

If the potential only depends on the distance to the origin, namely $V = V(r)$, we have

$$\tilde{V}(\vec{k}-\vec{k}') = \int d^3x e^{i(\vec{k}-\vec{k}')\vec{x}} V(r) \tag{10.16}$$

$$= \int_0^\infty r^2 dr \int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi e^{i|\vec{k}-\vec{k}'|r\cos\theta} V(r) \tag{10.17}$$

$$= \frac{4\pi}{|\vec{k}-\vec{k}'|} \int_0^\infty rV(r)\sin(r|\vec{k}-\vec{k}'|)dr \tag{10.18}$$

which involves only a single integral and is therefore simpler to compute. Consider the example of a Yukawa potential

$$V(r) = \frac{V_0}{\mu r} e^{-\mu r} \tag{10.19}$$

The integral can be done in closed form

$$\tilde{V}(q = |\vec{k}-\vec{k}'|) = \frac{4\pi}{q} \int_0^\infty r \frac{V_0}{\mu r} e^{-\mu r} \sin qr \tag{10.20}$$

$$= \frac{4\pi}{q} \frac{V_0}{2i\mu} \int_0^\infty e^{-\mu r}(e^{iqr} - e^{-iqr})dr \tag{10.21}$$

$$= \frac{4\pi V_0}{\mu} \frac{1}{\mu^2 + q^2} \tag{10.22}$$

The differential cross section is therefore

$$\frac{d\sigma}{d\Omega} = \frac{m^2}{4\pi^2\hbar^4} \frac{V_0^2}{\mu^2} \frac{16\pi^2}{(\mu^2+q^2)^2} = \frac{4m^2V_0^2}{\mu^2\hbar^4} \frac{1}{(\mu^2+q^2)^2} \tag{10.23}$$

Using now that

$$q^2 = (\vec{k}-\vec{k}')^2 = k^2 + k'^2 - 2\vec{k}\vec{k}' = k^2(2 - 2\cos\theta) = 4k^2 \sin^2 \frac{1}{2}\theta \tag{10.24}$$

where we defined θ as the angle between $\vec{k}$ and $\vec{k}'$ and used that $k^2 = k'^2$ from energy conservation, we can get

$$\frac{d\sigma}{d\Omega} = \left(\frac{2mV_0}{\mu\hbar^2}\right)^2 \frac{1}{(\mu^2 + 4k^2\sin^2\frac{1}{2}\theta)^2} \tag{10.25}$$

The total cross section is

$$\sigma = \int d\sigma = \left(\frac{2mV_0}{\mu\hbar^2}\right)^2 2\pi \int_0^\pi \frac{\sin\theta d\theta}{(\mu^2 + 4k^2\sin^2\frac{1}{2}\theta)^2} \tag{10.26}$$

$$= \left(\frac{2mV_0}{\mu\hbar^2}\right)^2 \frac{2\pi}{\mu^2(\mu^2+4k^2)} \tag{10.27}$$

Interestingly, if we take $V_0 = e^2\mu$ and take the limt $\mu \to 0$ we get the Coulomb differential cross section

$$\left(\frac{d\sigma}{d\Omega}\right)_{Coulomb} = \left(\frac{2me^2}{\hbar^2}\right)^2 \frac{1}{16k^4 \sin^4 \frac{1}{2}\theta} \tag{10.28}$$

10.2 Scattering by a potential, time-independent approach

In the case of scattering by a potential it is actually possible to give a solution to all orders in perturbation theory if we are able to solve the problem of finding the Energy eigenstates for a particle in such potential. This can be done analytically or perhaps numerically. Although showing the equivalence between the time dependent and independent methods is a bit lengthy the result is very simple to understand.

If the incident particles have energy E then we need to look for an eigensate of energy E. In the continuum spectrum there is an infinte number of states with a given energy. Among those states we have to find a linear combination that behaves at inifity as a superposition of an incident plane wave and and outgoing spherical wave:

$$\psi_E(\vec{x}) \simeq_{|\vec{x}|=r\to\infty} \frac{1}{(2\pi)^{\frac{3}{2}}} \left(e^{i\vec{k}\vec{x}} + \frac{e^{ikr}}{r} f(\hat{r}, \vec{k})\right) \tag{10.29}$$

Here $\vec{k}$ is the momentum of the incident wave and $\vec{x} = r\hat{r}$. The outgoing spherical waves represent the scattered particles and therefore the differential cross section is given by

$$d\sigma = \frac{\text{outgoing flux} \times r^2 d\Omega}{\text{ingoing flux}} = \frac{\frac{\hbar k}{m}\frac{1}{r^2}|f(\hat{r},\vec{k})|^2 \times r^2 d\Omega}{\frac{\hbar k}{m}} \tag{10.30}$$

$$= |f(\hat{r},\vec{k})|^2 \, d\Omega \tag{10.31}$$

10.3 Central potential and phase shifts

If the potential depends only on the distance to the origin, $V = V(r)$ then the angular momentum is conserved. In this case it is more likely that we can solve the Schroedinger problem analytically or numerically. The reason is that due to angular momentum conservation, the three dimensional Schroedinger equation reduces to an independent set of one-dimensional equation. Moreover, since the centrifugal barrier grows near the origin, for a finite incident energy, only a finite set of angular momenta contribute to the scattering. More precisely, the wave function is decomposed as

$$\psi_E = \sum_{\ell,m} R_\ell(r) Y_{\ell m}(\theta,\phi) = \sum_{\ell,m} \frac{1}{r}\chi_\ell(r) Y_{\ell m}(\theta,\phi) \tag{10.32}$$

The equation for $\chi_\ell(r)$ is

$$-\frac{\hbar^2}{2m}\chi_\ell''(r) + \left(V(r) + \frac{\ell(\ell+1)\hbar^2}{2mr^2}\right)\chi_\ell(r) = E\chi_\ell(r) \tag{10.33}$$

From now on we are going to assume that the potential has range a, namely that for $r > a$ the potential vanish (or can be well approximated by zero, *e.g.* Yukawa potential that vanishes exponentially). A particle of energy $E = \frac{\hbar^2k^2}{2m}$ cannot penetrate the centrifugal barrier much beyond a distance $\bar{r}$ such that

$$\frac{\hbar^2k^2}{2m} = \frac{\ell^2\hbar^2}{2m\bar{r}^2}, \qquad \bar{r} = \frac{\ell}{k} \tag{10.34}$$

Thus, if $\bar{r} > a$ such particle will not be affected by the potential. That means that only waves with angular momentum

$$\ell < \ell_{max} = ka \tag{10.35}$$

are affected by the potential (for a given k). The next question is how are the waves with $\ell < ka$ affected. At infinity χ_ℓ behaves as a superposition of an incoming and outgoing waves:

$$\chi_\ell(r) \simeq_{r\to\infty} A_\ell e^{-ikr} + B_\ell e^{ikr} \tag{10.36}$$

Since the coordinate r ends at $r = 0$ the incoming and outgoing fluxes have to tbe the same $|A| = |B|$. There can only be a phase difference between A and B:

$$B_\ell = (-)^{\ell+1}e^{2i\delta_\ell(E)}A_\ell \tag{10.37}$$

Such phase difference, up to the minus sign introduced by convenience, defines the phase shift $\delta_\ell(E)$ for that given incident energy E. The set of numbers δ_ℓ, $\ell < ka$ are the whole information we can get from solving the Schroedinger equation and therefore should determine the scattering cross section for that energy. Both, theoretically and experimentally it is convenient to characterize the scattering from the phase shifts $\delta_\ell(E)$.

To see how to compute the cross section we consider the Schroedinger equation in the region $r \gg a$ where the potential vanishes. The equation reduces to

$$-\chi_\ell'' + \frac{\ell(\ell+1)}{r^2}\chi_\ell = \frac{2mE}{\hbar^2}\chi_\ell \tag{10.38}$$

This is a from of the Bessel equation whose solution are $\frac{1}{r}J_{\ell+\frac{1}{2}}(kr)$ and $\frac{1}{r}N_{\ell+\frac{1}{2}}(kr)$. This is conveniently written in terms of the radial wave function as

$$R_\ell(r) = C_1j_\ell(kr) + C_2n_\ell(kr) \tag{10.39}$$

with j_ℓ , n_ℓ called spherical Bessel functions and given by

$$j_\ell(\rho) = \sqrt{\frac{\pi}{2\rho}} J_{\ell+\frac{1}{2}}(\rho), \qquad n_\ell(\rho) = \sqrt{\frac{\pi}{2\rho}} (-)^{\ell+1} N_{\ell+\frac{1}{2}}(\rho) \tag{10.40}$$

Some properties are

$$j_\ell(\rho) \sim \frac{2^\ell\,\ell!}{(2\ell+1)!}\rho^\ell, \qquad \rho \to 0, \qquad j_\ell(\rho) \simeq \frac{1}{\rho}\cos(\rho - \frac{1}{2}(\ell+1)\pi), \quad \rho \to \infty \tag{10.41}$$

$$n_\ell(\rho) \sim \rho^{-\ell-1}, \qquad \rho \to 0, \qquad n_\ell(\rho) \simeq \frac{1}{\rho}\sin(\rho - \frac{1}{2}(\ell+1)\pi), \quad \rho \to \infty \tag{10.42}$$

and some particular values are

$$j_0(\rho) = \frac{1}{\rho}\sin\rho, \quad n_0(\rho) = -\frac{1}{\rho}\cos\rho \tag{10.43}$$

$$j_1(\rho) = -\frac{1}{\rho}\cos\rho + \frac{1}{\rho^2}\sin\rho, \quad n_1(\rho) = -\frac{1}{\rho}\sin\rho - \frac{1}{\rho^2}\cos\rho \tag{10.44}$$

According to the definition of phase shifts the radial wave function should behave asymptotically as

$$R_\ell(r) = \frac{1}{r}\chi_\ell(r) \simeq \frac{1}{r}\left(A_\ell e^{-ikr} + B_\ell e^{ikr}\right) \simeq \frac{1}{r}A_\ell\left(e^{-ikr} + (-)^{\ell+1}e^{2i\delta_\ell}e^{ikr}\right) \tag{10.45}$$

From the asymptotic form of the spherical Bessel functions we find

$$j_\ell(kr) + in_\ell(kr) = \frac{1}{kr}e^{ikr}(-i)^{\ell+1}, \quad j_\ell(kr) - in_\ell(kr) = \frac{1}{kr}e^{-ikr}i^{\ell+1} \tag{10.46}$$

implying that the wave-function for $r > a$ is

$$\begin{aligned} R_\ell &= A_\ell\left(k(-i)^{\ell+1}(j_\ell - in_\ell) + (-)^{\ell+1}e^{2i\delta_\ell}i^{\ell+1}k(j_\ell + in_\ell)\right) && (10.47)\\ &= 2k(-i)^{\ell+1}A_\ell e^{i\delta_\ell}(j_\ell(kr)\cos\delta_\ell - n_\ell(kr)\sin\delta_\ell) && (10.48) \end{aligned}$$

Moreover, since the potential is spherically symmetric we can choose the axis any way we want. It is convenient to choose z along the incident beam. In that way the wave function we are looking for is independent of ϕ and can be written in terms of Legendre polynomials $P_\ell(\cos\theta)$. Altogether, for $r > a$ the wave-function can be written as

$$\psi^E(r) = \sum_\ell 2k(-i)^{\ell+1}A_\ell e^{i\delta_\ell}(j_\ell(kr)\cos\delta_\ell - n_\ell(kr)\sin\delta_\ell)P_\ell(\cos\theta) \tag{10.49}$$

The phase shifts should be computed by matching this expression to the wave-function for $r < a$ that can follow only from solving the Schroedinger equation in the potential in question. Equivalently, we can match equation (10.39) to the aymptotic form of the wave-function and find

$$C_1 + iC_2 = |C_1 + iC_2| e^{-i\delta_\ell} \qquad \Rightarrow \qquad \delta_\ell = \arg(C_1 - iC_2) \tag{10.50}$$

To summarize, the phase shift is computed by solving the Schroedinger equation and matching the aymptotic form of the wave-function to eq.(10.45)

The next step is to compute the scattering cross section. For that we have to match with the asymptotic form

$$\psi^E(\vec{x}) \simeq_{|\vec{x}|=r\to\infty} \frac{1}{(2\pi)^{\frac{3}{2}}} \left(e^{ikz} + \frac{e^{ikr}}{r} f(\hat{r}, \vec{k}) \right) \tag{10.51}$$

The plane wave can be written as

$$\begin{aligned} e^{ikz} &= \sum_\ell (2\ell+1) i^\ell j_\ell(kr) P_\ell(\cos\theta) && (10.52) \\ &\simeq_{r\to\infty} \sum_\ell \frac{2\ell+1}{2ikr} P_\ell(\cos\theta) \left(e^{ikr} + (-)^{\ell+1} e^{-ikr} \right) && (10.53) \end{aligned}$$

and therefore

$$\begin{aligned} \psi^E(\vec{x}) &\simeq_{r\to\infty} \frac{1}{(2\pi)^{\frac{3}{2}}} \sum_\ell \frac{2\ell+1}{2ikr} P_\ell(\cos\theta) \left(e^{2i\delta_\ell} e^{ikr} + (-)^{\ell+1} e^{-ikr} \right) && (10.54) \\ &\simeq_{r\to\infty} \frac{1}{(2\pi)^{\frac{3}{2}}} \sum_\ell \frac{2\ell+1}{2ikr} P_\ell(\cos\theta) \left[\left(e^{2i\delta_\ell} - 1 + 1 \right) e^{ikr} + (-)^{\ell+1} e^{-ikr} \right] && (10.55) \end{aligned}$$

where we used eq.(10.37) to relate the incoming and outgoing waves. Thus the asymptotic wave-function is written as a sum of a plane wave and outgoing spherical waves allowing us to identify:

$$\begin{aligned} f(\hat{r}, \vec{k}) &= \sum_\ell \frac{2\ell+1}{2ik} P_\ell(\cos\theta) \left(e^{2i\delta_\ell} - 1 \right) && (10.56) \\ &= \sum_\ell \frac{2\ell+1}{k} P_\ell(\cos\theta) e^{i\delta_\ell} \sin\delta_\ell && (10.57) \end{aligned}$$

The total cross section is given by

$$\begin{aligned} \sigma &= \int d\Omega |f(\hat{r}, \vec{k})|^2 && (10.58) \\ &= 2\pi \int_0^\pi d\theta \sin\theta \sum_{\ell,\ell'} \frac{(2\ell+1)(2\ell'+1)}{k^2} \sin\delta_l \sin\delta_{\ell'} e^{i(\delta_\ell - \delta_{\ell'})} P_\ell(\cos\theta) P_{\ell'}(\cos\theta) && (10.59) \\ &= \frac{4\pi}{k^2} \sum_\ell (2\ell+1) \sin^2\delta_\ell && (10.60) \end{aligned}$$

where we have used

$$\int_{-1}^{1} P_\ell(x) P_{\ell'}(x)\, dx = \frac{2}{2\ell+1}\,\delta_{\ell\ell'} \tag{10.61}$$

It interesting to note that

$$\sigma = \frac{4\pi}{k^2}\sum_\ell (2\ell+1)\sin^2\delta_\ell = \frac{4\pi}{k}\mathrm{Im} f(\theta=0) \tag{10.62}$$

that is known as the optical theorem.

10.4 Hard spheres example

The hard sphere potential is defined as

$$V(r) = \begin{cases} \infty & r<a \\ 0 & r>a \end{cases} \tag{10.63}$$

The wave equation is the one for a free particle for $r > a$ and has to vanish at $r = a$. Form equation (10.49) we immediately find

$$j_\ell(ka)\cos\delta_\ell - n_\ell(ka)\sin\delta_\ell = 0 \tag{10.64}$$

namely

$$\tan\delta_\ell = \frac{j_\ell(ka)}{n_\ell(ka)} \tag{10.65}$$

that completely solves the problem of computing the phase shifts. In hte case of $\ell = 0$ we simply have

$$\tan\delta_0 = \frac{j_0(ka)}{n_0(ka)} = -\tan ka \qquad \Rightarrow \qquad \delta_0 = -ka \tag{10.66}$$

Atlow energy, namely $ka \ll 1$ we can use the behavior of the Bessel functions to find

$$\delta_\ell \sim (ka)^{2\ell+1} \to 0 \tag{10.67}$$

Therefore, in the low energy regime, the scattering is dominated by the s-waves. It follows that

$$\sigma = \frac{4\pi}{k^2}(ka)^2 = 4\pi a^2 \tag{10.68}$$

larger than the classical cross section which is πa^2 at all energies. This motivates the following definition, for a generic system, the cross section at low energies the cross section is dominated by s-waves and therefore

$$\sigma_T(k\to 0) \to 4\pi a_s^2 \tag{10.69}$$

for some quantity a_s with units of length that is called the *scattering length.*

At large energies all angular momenta up to $l_{max} \sim ka$ contribute, as discussed at the beginning of this section. For large ka we have

$$\tan\delta_\ell \simeq \frac{\cos(ka - \frac{1}{2}(\ell+1)\pi)}{\sin(ka - \frac{1}{2}(\ell+1)\pi)} = -\tan(ka - \frac{1}{2}\ell\pi) \qquad \Rightarrow \qquad \delta_\ell \simeq -ka + \frac{1}{2}\ell\pi \tag{10.70}$$

Therefore

$$\sigma \simeq \frac{4\pi}{k^2}\sum_{\ell}^{l_{max}}(2\ell+1)\sin^2(ka - \frac{1}{2}\ell\pi) = \frac{2\pi}{k^2}\sum_{\ell}^{l_{max}}(2\ell+1)(1-(-)^\ell\cos(2ka)) \tag{10.71}$$

The sums can be done exactly now. The leading behavior is

$$\sigma \simeq \frac{2\pi}{k^2}\ell_{max}^2 = 2\pi a^2 \tag{10.72}$$

Notice that is $\ell_{max} = ka + \Delta$ for Δ of order one in ka, the leading expansion is still the same.

10.5 Shallow bound state

Consider the case where we have a deep potential $V(r)$ that vanishes for $r > a$. Suppose there is a shallow bound state, namely a bound state of energy $E = -\epsilon$ whose value is small compared with the potential. Also assume we are interested in low energy scattering $ka \ll 1$ and such that E is also small compared with the potential, but not necessarily with ϵ. In this situation scattering is dominated by s-waves and

$$\sigma = \frac{4\pi}{k^2}\sin^2\delta_0 \tag{10.73}$$

To compute the phase shift δ_0 we write the wave function for $r > a$ which is

$$\chi(r > a) = A\sin(kr + \delta_0) \tag{10.74}$$

by definition of phase shift. We need to match the function and the derivative to the function inside the potential. To compute the boundary condition we use the fact that there is a shallow bound state. Indeed, inside the potential the scattering wave-function satisfies

$$-\frac{\hbar^2}{2m}\partial^2\chi + V(r)\chi = E\chi \tag{10.75}$$

Since the energy E is small compared to the potential we can assume the wave-function changes little when we change E. However, we know that for $E = -\epsilon$ the wave function inside matches a decaying exponential outside:

$$\chi(r > a) = Be^{-\kappa r}, \qquad \kappa = \sqrt{\frac{2m\epsilon}{\hbar^2}}, \qquad \Rightarrow \qquad \frac{\chi'(r=a)}{\chi(r=a)} = -\kappa \tag{10.76}$$

and then we should also have the same value for the scattering state

$$k\frac{\cos(ka+\delta_0)}{\sin(ka+\delta_0)} = -\kappa \tag{10.77}$$

Since $ka \ll 1$ we find

$$\cot\delta_0 = -\frac{\kappa}{k} \tag{10.78}$$

and then

$$\sin^2\delta_0 = \frac{k^2}{k^2+\kappa^2} \qquad \Rightarrow \sigma = \frac{4\pi}{k^2+\kappa^2} = \frac{2\pi\hbar^2}{m}\frac{1}{E+\epsilon} \tag{10.79}$$

The cross section at zero energy is given by

$$\sigma = \frac{2\pi\hbar^2}{m}\frac{1}{\epsilon} \tag{10.80}$$

This cross section can be very large compared to the value $4\pi a^2$ that we could have expected at low energy. In fact, if the bound state is at $\epsilon = 0$ the cross section is

$$\sigma = \frac{4\pi}{k^2} \tag{10.81}$$

which is called the unitarity limit and is discussed more generally in the next subsection.

10.6 Unitarity limit

Consider the case of low energy that is dominated by s-wave scattering:

$$\sigma = 4\pi|f_0|^2 \tag{10.82}$$

The optical theorem gives

$$\sigma = \frac{4\pi}{k}\mathrm{Im}f_0 \tag{10.83}$$

Hence

$$(\mathrm{Im}f_0)^2 = \frac{\sigma^2k^2}{16\pi^2} \le |f_0|^2 = \frac{\sigma}{4\pi} \tag{10.84}$$

Implying

$$\sigma \le \frac{4\pi}{k^2} \tag{10.85}$$

which is known as the unitarity limit. In terms of the phase shift

$$\sigma = \frac{4\pi}{k^2}\sin^2\delta_0 \tag{10.86}$$

The unitarity limit is reached at resonance $\delta_0 = \frac{\pi}{2}$:

$$\sigma = \frac{4\pi}{k^2} \tag{10.87}$$

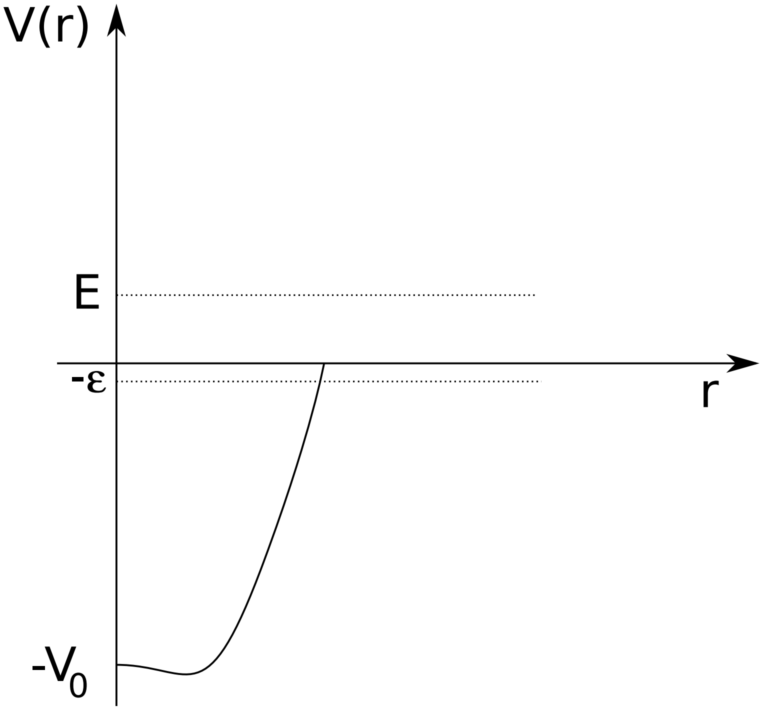


Figure 5: Sacttering with energy E in the presence of a shallow bound state with energy $-\epsilon$.

The cross section has no parameters and is completely fixed by dimensional reasons. The absence of a scale suggest that the system can display scale invariance. In atomic physics it is possible to have a gas of particles such that the typical interactions occur at a resonance. Such gas is said to be at the unitarity limit.

10.7 Resonances

Suppose we have a negative potential surrounded by a high barrier that ends at $r = a$ after which the potential vanishes. Let us consider the case $ka \ll 1$ and study s-wave scattering. For simplicity, consider the barrier has constant potential V_0 (see figure 6) and write the wave-function as

$$\chi(r) = \begin{cases} \chi_I(r) & \text{for} \quad r < r_0 \\ \chi_{II}(r) = Ae^{\kappa r} + Be^{-\kappa r} & \text{for } r_0 < r < a \\ \chi_{III}(r) = C\sin(kr + \delta_0) & \text{for} \quad r > a \end{cases} \tag{10.88}$$

with

$$k = \sqrt{\frac{2mE}{\hbar^2}}, \quad \kappa = \sqrt{\frac{2m(V_0 - E)}{\hbar^2}}, \tag{10.89}$$

We do not know the wave-function $\chi_I(r)$ since we assume some general potential in the region $r < r_0$. On the other hand, matching the wave-functions at $r = a$ we obtain

$$\frac{\kappa A e^{\kappa a} - \kappa B e^{-\kappa a}}{\kappa A e^{\kappa a} + \kappa B e^{-\kappa a}} = k \cot(ka + \delta_0) \tag{10.90}$$

For most values of energy, we have $e^{\kappa a} \gg e^{-\kappa a}$ and therefore (recall $ka \ll 1$)

$$\cot \delta_0 \simeq \frac{k}{\kappa} \tag{10.91}$$

a slowly varying function of energy. However, for a quasi-bound state at $E = E_0$ we have $A(E_0) = 0$, namely only the decaying exponential survives. At $E = E_0$ we have

$$\cot \delta_0 \simeq -\frac{k}{\kappa} \tag{10.92}$$

namely a sign change. It is clear that when going from $E < E_0$ to $E > E_0$ the phase shift abruptly increases by π. For some value of energy $E = E_R$ close to E_0 we should have $\delta_0 = \frac{\pi}{2}$ giving a peak in the cross section (since $\sin \delta_0(E_R) = 1$). In principle the phase shift could decrease by π instead but we are going to rule out that case later on. If we assume δ_0 is small away from the resonance, the cross section will increase and have a peak whose highest value is $\sigma = \frac{4\pi}{k^2}$, namely the unitarity limit. If the cross section is large (more rare case), namely $\delta_0 \simeq 1$ then it will dip to zero. The shape of the peak can be computed using the approximation that

$$\cot \delta_0 \simeq -2\frac{E - E_R}{\Gamma} \quad \Rightarrow \quad \sin^2 \delta_0 \simeq \frac{\Gamma^2/4}{(E - E_R)^2 + \Gamma^2/4} \tag{10.93}$$

and the cross section

$$\sigma \simeq \frac{4\pi}{k^2} \frac{\Gamma^2/4}{(E - E_R)^2 + \Gamma^2/4} \tag{10.94}$$

that is superimposed to the "normal" cross section computed from $\cot \delta_0 \simeq \frac{k}{\kappa}$

10.8 Equivalence of time-independent and dependent approaches

Consider the eigenstate of the Hamiltonian with energy $E = \frac{\hbar^2 k^2}{2m}$ such that at infinity behaves as

$$\psi_E \simeq \frac{1}{(2\pi)^{\frac{3}{2}}} \left\{ e^{ikz} + \frac{1}{r} f(\theta, k) e^{ikr} \right\} \tag{10.95}$$

with

$$f(\theta) = \sum_{\ell} \frac{2\ell + 1}{2ik} P_\ell(\cos\theta)(e^{2i\delta_\ell} - 1) \tag{10.96}$$

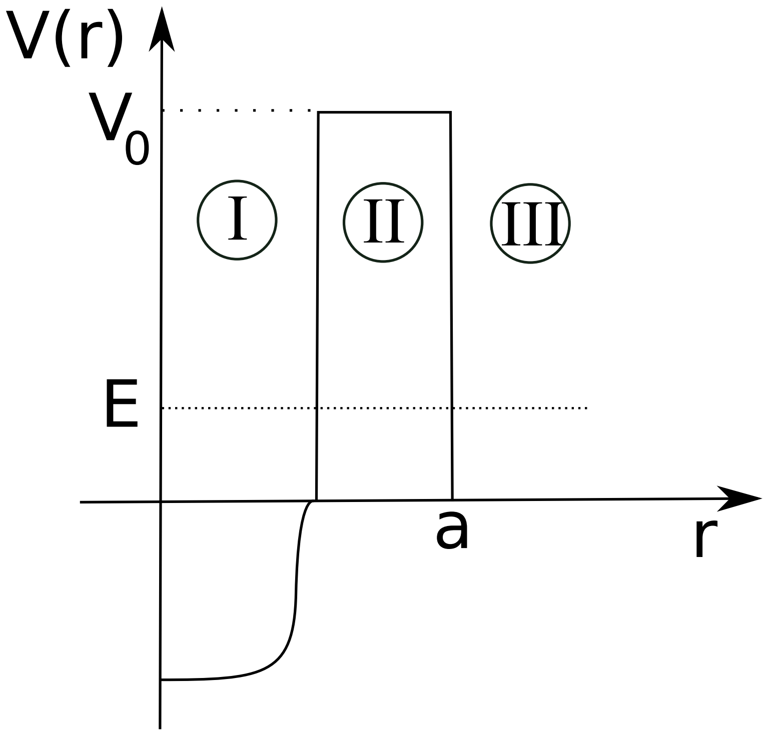


Figure 6: Sacttering with energy E in the presence of a resonance.

Create now a wave packet

$$\psi_g = \int dk g(k)\psi_E(x), \qquad g(k) = Ae^{-\frac{a^2}{2}(k-k_0)^2} \tag{10.97}$$

The time dependent wave function will be

$$\psi_g(\vec{x},t) = A\int dk e^{-\frac{a^2}{2}(k-k_0)^2} e^{-i\frac{\hbar k^2}{2m}t}\psi_E(x), \tag{10.98}$$

We assume that this gaussian is sharply peaked and with small uncertainty in position and momentum. For large values of $|\vec{x}|$ we can use the expression of the wave function that we had before. The first term gives a wave packet propagating towards the scattering center:

$$\psi_{g1} = \sqrt{\frac{2}{a}}\pi^{\frac{1}{4}}\frac{1}{\sqrt{1+\frac{i\hbar}{ma^2}t}}e^{-\frac{(z-\frac{\hbar k_0}{m}t)^2}{2a^2(1+\frac{i\hbar}{ma^2}t)}} \tag{10.99}$$

as can be seen from its modulus squared:

$$|\psi_{g1}|^2 = \sqrt{\frac{4\pi}{a^2+\frac{\hbar^2 t^2}{m^2a^2}}}e^{-\frac{1}{2}\frac{(z-\frac{\hbar k_0}{m}t)^2}{a^2+\frac{\hbar^2 t^2}{m^2a^2}}} \tag{10.100}$$

The position of the wave packet is given by

$$z = \frac{\hbar k_0}{m} t = v_0 t, \quad v_0 = \frac{\hbar k_0}{m} \tag{10.101}$$

For the second term we first ignore the dependence of $f(\theta, k)$ on k and get the same result as for the first term but replacing $z \to r$:

$$\psi_{g2} \simeq \frac{1}{r}\sqrt{\frac{2}{a}}\pi^{\frac{1}{4}} \frac{1}{\sqrt{1 + \frac{i\hbar}{ma^2}t}} e^{-\frac{(r - \frac{\hbar k_0}{m}t)^2}{2a^2(1 + \frac{i\hbar}{ma^2}t)}} \tag{10.102}$$

This represents a spherical wave whose radius grows as

$$r = \frac{\hbar k_0}{m} t = v_0 t, \tag{10.103}$$

However, for $t < 0$ the gaussian is localized around an unphysical negative value of r. Therefore, for $r > 0$ the wave functions is essentially zero. That is, for negative t we only have a plane wave and for $t > 0$ we have a superposition of a plane wave and a spherical wave as desired. More detail can be found by using the previous expression for $f(\theta)$ and expanding

$$\delta_\ell(k) \simeq \delta_\ell(k_0) + \frac{\partial \delta_\ell(k_0)}{\partial k_0}(k - k_0) + \ldots \tag{10.104}$$

In this case we obtain a spherical wave of radius

$$r = \frac{\hbar k_0}{m} t - 2\frac{\partial \delta_\ell(k_0)}{\partial k_0} = \frac{\hbar k_0}{m}(t - \Delta t) \tag{10.105}$$

with

$$\Delta t = 2\hbar \frac{\partial \delta_\ell(E)}{\partial E} \tag{10.106}$$

It should be noted that a very rapid decrease of the phase shift would lead to a negative time delay, in the extreme case implying that the spherical wave packet appears before the plane wave reaches the scattering region. Since this is impossible, very rapid decreases of the phase shift are ruled out. If the potential is non-zero within a radius a we have a bound for the case $\Delta t < 0$

$$|\Delta t| < \frac{a}{v_0} \Rightarrow E|\delta'(E)| < ka \tag{10.107}$$

10.9 Inelastic Scattering

Assuming a central potential but also the possibility of other processes happening, the amplitude of the outgoing wave in each angular momentum channel should be equal or smaller that the incoming one. Taking this into account, the elastic scattering amplitude can be written as

$$f(\theta) = \sum_{\ell=0}^{\infty} \frac{2\ell+1}{2ik} P_\ell(\cos\theta)\,(S_\ell - 1), \qquad |S_\ell| \leq 1 \tag{10.108}$$

The total elastic cross section is given by

$$\sigma_e = \int d\Omega |f|^2 = \frac{\pi}{k^2} \sum_{\ell=0}^{\infty} (2\ell+1)|S_\ell - 1|^2 \tag{10.109}$$

For each channel, $1 - |S_\ell|^2$ represents the probability going into other channels, for example particle production. Therefore, the inelastic cross section is

$$\sigma_i = \frac{\pi}{k^2} \sum_{\ell=0}^{\infty} (2\ell+1)(1 - |S_\ell|^2) \tag{10.110}$$

The total cross section is

$$\sigma_T = \sigma_e + \sigma_i = \frac{2\pi}{k^2} \sum_{\ell=0}^{\infty} (2\ell+1)(1 - \mathrm{Re} S_\ell) \tag{10.111}$$

If $|S_\ell| = 1$ then we only have elastic scattering, but if $|S_\ell| = 0$ then $\sigma_e = \sigma_i$, that is we cannot have just inelastic scattering. Finally, the optical theorem is

$$\mathrm{Im} f(0) = \sum_{\ell=0}^{\infty} \frac{2\ell+1}{2k} (1 - \mathrm{Re} S_\ell) = \frac{k}{4\pi} \sigma_T \tag{10.112}$$

That means the imaginary part of the forward *elastic* cross section determines the total cross section, including elastic and inelastic.