Quantum Mechanics II

George Siopsis

Department of Physics and Astronomy
The University of Tennessee
Knoxville, TN 37996-1200
U.S.A.
e-mail: `siopsis@tennessee.edu`

Lecture notes by students

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Contents

UNIT 1

Scattering

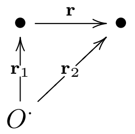
Notes by C. Hartnett and K. Yeter

Scattering is such an important phenomenon that is used in high energy physics to understand the forces of the nature and the properties of the materials. In general, there are two types of scattering used in the scientific research.One type uses colliding beams of high energy particles to produce new particles. Looking at the by products of such collisions gives scientists insgiht into the fundamental forces of nature. The LHC (*Large Hadron Collider*) is the biggest examples for this kind of scattering, and it's very important. The other type is to scatter beams of particles, like neutrons, off a stationary material target.This type of experiment is used to understand the property of the target material. A prime example of this type is the SNS (*Spallation Neutron Source*) at Oak Ridge National Laboratory. It is one-of-a-kind facility provides the most intense pulsed neutron beams in the world for scientific research and industrial development.

Since we can consider the two colliding particle beams in the rest frame of one of the beams, studying these kinds of scattering phenomena is not as hard as it seems to be.

First of all, let me ask the question of whether two electrons will meet once they are directed to each other for collision. Since electrons are fundamental particles they are exact points and laws of classical mechanics cannot be used to answer this question. As an answer for this question we can say that there is a probability for these electrons to meet.Another question that begs an answer is: if electrons do not meet *how do they scatter then*? The Coulomb force causes the electrons to be deflected. On the other hand, for two particles attracting each other we can say that there is a certain possibility of these particles' positions therefore there is a finite possibility for these particles to find each other.

We are going to assume that what governs the force between each particle is the potential which only depends on the relative position $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ of the particles.



where,
r: distance between particle m_1 and m_2
$\mathbf{r}_1$: distance of particle m_1 from the origin
$\mathbf{r}_2$: distance of particle m_2 from the origin

In the center-of-mass reference frame of the two particles the problem will be reduced to the study of *the scattering of a single particle by the potential V(**r**).* Therefore, the mass of the particles also will be reduced to a value of $\mu = \frac{m_1 m_2}{m_1+m_2}$. This μ value is called the *effective* or *reduced* mass and it is the mass of the "relative particle".
In the rest frame of a scattering, in which there is a particle beam directed towards a target, we see the distribution of the particles on the detector.

1-Dimensional Case

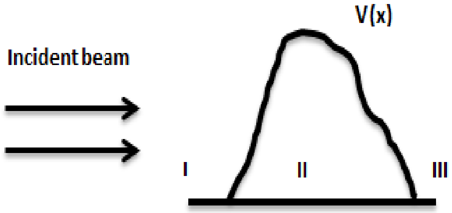


Figure 1: 1-d potential

Figure 1 shows the incident beam interacting with an arbitrary one dimensional potential. In case of interacting with a potential there will be transmitted and reflected beam of particles. As you may remember from the previous semester a square potential was given as an example for this type of scattering. For particles whose energy greater than zero there will be a continuous spectrum and the Schrodinger equation can be written as,

$$-\frac{\hbar^2}{2m}\varphi'' + V\varphi = E\varphi, \qquad E > 0 \tag{1}$$

Since the spectrum is continuous solution of the Schrodinger equation for scattering potential gives a plane and non-normalizable wavefunction. It is,

$$\varphi_{inc} = Ae^{ikx}, \qquad x \to -\infty \tag{2}$$

where $k = \frac{\sqrt{2mE}}{\hbar}$. The solutions for reflected and transmitted beam of particles are respectively,

$$\varphi_r = Be^{-ikx} \tag{3}$$

$$\varphi_t = Ce^{ikx} \tag{4}$$

The wave function incident in region I would be the sum of the wavefunctions which are incident and reflected.

$$\varphi_I = \varphi_{inc} + \varphi_r \tag{5}$$

The wavefunction transmitted in region III, where the potential ends, is,

$$\varphi_{III} = Ce^{ikx}, \qquad x \to +\infty \tag{6}$$

The wavefunction is not a physical quantity therefore we cannot measure it in the experiments. What we measure in the experiments is the probability current. Probability current is defined as $\mathbf{J} = \frac{i\hbar}{2m}(\psi\nabla\psi^* - \psi^*\nabla\psi)$. There is a continuity equation for probability current and current density which gives the conservation law of probability current, $\mathbf{J}$. For this scattering case the probability current density,ρ, does not depend explicitly on time.

$$\frac{\partial\rho}{\partial t} + \frac{\partial J}{\partial x} = 0 \tag{7}$$

Once we do the calculation,

$$J = -\frac{i\hbar}{2m}\varphi^*\varphi'' + C.C. \tag{8}$$

$$J' = -i\frac{i\hbar}{2m}\varphi^*\varphi' - \frac{i\hbar}{2m}\varphi^*\varphi'' + C.C. \tag{9}$$

As you measure the physical quantities in the scattering process you stay away from the scattering potential therefore from the Schrodinger equation

$$\varphi'' = -\frac{2mE}{\hbar^2}\varphi \tag{10}$$

$$J' = -\frac{i\hbar}{2m}\mid \varphi' \mid^2 + C.C. = 0 \tag{11}$$

From equation (1.11) we can easily see that probability current, J, is conserved - i.e. it does not depend explicitly on x and it is just a number.
As $x \to -\infty$ there will be two contributions to the wavefunction, φ, i.e. one from incident beam of particles and one from reflected beam of particles. Therefore J becomes,

$$J = --i\frac{i\hbar}{2m}(A^*e^{-ikx} + B^*e^{ikx})ik(Ae^{ikx} - Be^{-ikx}) + C.C. = \frac{\hbar k}{m}(|A|^2 - |B|^2) \tag{12}$$

$$J_{inc} = \frac{\hbar k}{m} \mid A \mid^2, \qquad J_r = \frac{\hbar k}{m} \mid B \mid^2 \tag{13}$$

As $x \rightarrow +\infty$ the only contribution comes from the transmitted probability current density.

$$J_t = \frac{\hbar k}{m} \mid C \mid^2 \tag{14}$$

Since J is a conserved quantity no matter how complicated the Schrodinger equation is the incident probability current is equal to the sum of the reflected probability current and the transmitted probability current.

$$J_{inc} = J_r + J_t. \tag{15}$$

If equation (1.15) is divided by J_{inc} then we obtain that

$$1 = \frac{J_r}{J_{inc}} + \frac{J_t}{J_{inc}}. \tag{16}$$

In the equation above the $\frac{J_r}{J_{inc}}$ value is called the reflection coefficient and denoted as R. The $\frac{J_t}{J_{inc}}$ value is called the transmission coefficient and denoted as T. Therefore,

$$R + T = 1 \tag{17}$$

The most interesting point of the scattering phenomenon is that the reflected particles are the scattered particles from the scattering potential. The number of reflected particles is about 10^{20}. Say we have a beam of particles which consists of N number of particles. The probability density, ρ, for such a beam is

$$\rho = \mid \varphi \mid^2 \qquad and \qquad \int \rho dx = 1 \tag{18}$$

If we measure a number of particles given a certain distance then,

$$\frac{\#\, of\, particles}{length} = N\rho = \#density \tag{19}$$

If the N number of particles are electrons with charge e then what you measure in the experiment is the charge density.

$$charge\, density = eN\rho \tag{20}$$

The *electrical current* is defined as the number of particles passing through a certain point in unit time. Therefore, the electrical current for this beam of particles is

$$electricalcurrent = eNJ = \frac{charge}{time} \tag{21}$$

Since the electrical current is directly proportional to the probability current density, J, reflection and transmission coefficients can be written as the ratio of the reflected and transmitted currents to the incident current.

$$R = \frac{reflected\, current}{incident\, current} \quad and \quad T = \frac{transmitted\, current}{incident\, current}. \tag{22}$$

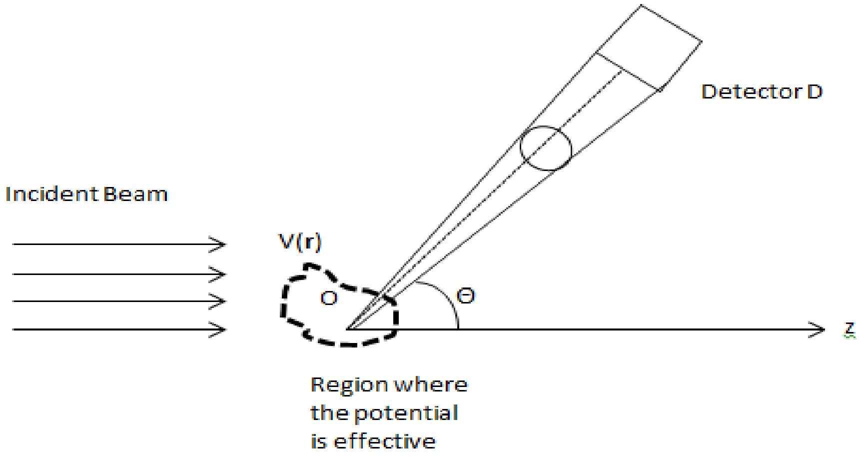


Figure 2: 3-d potential

3-Dimensional Case

In 3-d case we are going to introduce current density. To use the current density we need to introduce the concept of flux- the number of particles per unit time which traverse a unit surface perpendicular to direction of the beam. The flux of the incident particles beam is F_{inc}.

$$F_{inc} = \frac{\#\, of\, particles}{(area)(time)} \tag{23}$$

$$current\, density = J = \frac{charge}{(area)(time)} = \frac{I}{area} \tag{24}$$

In Figure 2 a detector is placed far from the region under the influence of the potential. The number of particles, dn, scattered per unit time into the solid angle $d\Omega$ about the direction (θ, φ) is

$$dn = F_{inc}\sigma(\theta, \varphi)d\Omega \tag{25}$$

where $\sigma(\theta, \varphi)$ is the *differential scattering cross section* in the direction (θ, φ). Scattering cross section is the coefficient of proportionality between dn and $F_{inc}d\Omega$. In other words, the scattering cross section is

$$\frac{\#\, of\, deflected\, particles/time}{incident\, flux} \tag{26}$$

The scattering cross section has the dimension of area which is on the order of $\approx 10^{-24}cm^2$. Since $10^{-24}cm^2$ is small the unit of barn is used.

$$1barn = 10^{-24}cm^2 \tag{27}$$

The total cross section is the integral over the solid angle, that is,

$$\sigma = \int d\Omega \frac{d\sigma}{d\Omega} \tag{28}$$

The second term on the right-hand-side of the equation above is called the differential cross section and it is rather useful.
Now, let us find a simple expression for scattering cross section, σ. As far as the incident beam is concerned the wavefunction is $\varphi = Ae^{ikz}$, where
$k = \frac{\sqrt{2mE}}{\hbar}$ and m is the reduced mass. For simplicity we set A=1, therefore the wavefunction for the incident beam is $\varphi = e^{ikz}$. On the other hand, reflected and transmitted wavefunctions are more complicated.
To find the scattered wavefunction we shall solve the Schrodinger equation. Since the detector is far from the scattering potential we can neglect the potential in the Schrodinger equation. Therefore,

$$-\frac{\hbar^2}{2m}\nabla^2\varphi = E\varphi \tag{29}$$

$$\nabla^2\varphi + k^2\varphi = 0 \tag{30}$$

We assume that there is a spherical symmetry and we shall use the spherical coordinates to solve the equation above.

$$\frac{1}{r}(r\varphi)'' + k^2\varphi = 0 \tag{31}$$

Let's denote $(r\varphi)$ as u, that is,

$$u'' + k^2\varphi = 0 \qquad \Rightarrow \qquad u = e^{\pm ikr} \tag{32}$$

Since the particles are scattering we choose e^{ikr} as a solution for u. Therefore the generalized solution for the scattered wavefunction is,

$$\varphi = \frac{1}{r}e^{ikr}. \tag{33}$$

Figure 2 *does not* have spherical symmetry therefore we hope to manipulate φ in such a way as to arrive at an appropriate solution for φ. We therefore need to solve an equation that is a little more general,

$$\nabla^2\varphi + k^2\varphi = \rho \tag{34}$$

Where ρ will be something that I have to figure out if it means anything at all. If we have to solve Eq. (3) the solution is known because all one has to do is look to electrostatics for the necessary steps. And that will give me φ at r, that is,

$$\varphi(\vec{r}) = -\int d^3r'\rho(\vec{r'})G_+(\vec{r},\vec{r'}) \qquad G_\pm(\vec{r},\vec{r'}) = -\frac{e^{ik|\vec{r}-\vec{r'}|}}{4\pi|\vec{r}-\vec{r'}|} \tag{35}$$

$G(\vec{r}, \vec{r'})$ is a Green's function, and $\varphi(\vec{r})$ is now a general solution to Eq. (3). So this Green function is the same as φ, the spherically symmetric case, so it must obey the Schrodinger equation.

$$\nabla^2 G_\pm + k^2 G_\pm = 0 \tag{36}$$

Have to be careful here because as $\vec{r} \to 0$ you get a singularity, so it's zero everywhere except exactly at the origin, therefore,

$$\nabla^2 G_\pm + k^2 G_\pm = \delta^3(\vec{r}) \tag{37}$$

Integrating Eq. (6),

$$\int d^3r'(\nabla^2 G_\pm + k^2 G_\pm) = \int d^3r' \delta^3(\vec{r}) \tag{38}$$

$$\int \vec{\nabla} G_\pm \cdot d\vec{S} + k^2 \int d^3r G_\pm = 1 \tag{39}$$

And as the spherical volume element within the integral shrinks to zero Eq. (8) becomes one as it should.

$$1 + 0 = 1 \tag{40}$$

And now we understand how to solve Eq. (3), in general. But no matter what, we want to go far away from the scattering potential and we want to put the detector way out so it's not effected by what's happening. So we look at the behavior as $\vec{r} \to \infty$.

$$|\vec{r} - \vec{r'}| = \sqrt{r^2 + r'^2 - 2rr'\cos\beta} \approx r - r'\cos\beta \tag{41}$$

Where β is the angle between $\vec{r}$ and $\vec{r'}$. If we go back to the expression for $\varphi(\vec{r})$ and use the approximation for $|\vec{r} - \vec{r'}|$,

$$\varphi(\vec{r}) = -\int d^3r' \rho(\vec{r'}) \frac{e^{ikr - ikr'\cos\beta}}{4\pi r} = -\frac{e^{ikr}}{4\pi r} \int d^3r' \rho(\vec{r'}) e^{-ikr'\cos\beta} \tag{42}$$

Notice the factor outside the integral it's a nice spherical wave traveling outward, and then there's the integral. What is this integral a function of? After integrating over r' this integral is going to be a function of $\vec{r}$, which has three component in spherical coordinates $f(r, \theta, \varphi)$. But because there is no r (the distance r not the vector $\vec{r}$) f will be a function of the angles only. So we have a nice spherical wave as it goes out but it's modulated as you go around the angles. We don't quite understand $\rho(\vec{r})$ yet but at least we can write $\varphi(\vec{r})$ as,

$$\varphi(\vec{r}) = -\frac{e^{ikr}}{4\pi r} f(\theta, \varphi) \tag{43}$$

So this is our equation for the out going scattered wave. The entire wave function will be the combination of the incoming wave, e^{ikz}, and the outgoing wave.

$$\Phi = e^{ikz} + \frac{e^{ikr}}{r} f(\theta, \phi) \tag{44}$$

The minus and factor of 4π were absorbed in the arbitrary function $f(\theta, \phi)$. This generalizes what we found in one dimension. Next, we're going to take a look at the probability current and try to generalize from one to three dimensions. Recall that the probability current and the gradient in spherical coordinates are given by,

$$\vec{J} = -\frac{i\hbar}{2m} \Phi^* \vec{\nabla} \Phi + C.C. \tag{45}$$

$$\vec{\nabla} = \frac{\partial}{\partial r}\hat{r} + \frac{1}{r}\frac{\partial}{\partial \theta}\hat{\theta} + \frac{1}{r \sin\theta}\frac{\partial}{\partial \phi}\hat{\phi} \tag{46}$$

The incident current $\vec{J_i} = \frac{\hbar k}{m}\hat{z}$. Now the scattered wave, or the out going wave, it's going to have three components.

$$(J_{out})_r = -\frac{i\hbar}{2m}\frac{e^{-ikr}}{r} f^* f[\frac{ike^{ikr}}{r} - \frac{e^{ikr}}{r^2}] + C.C. = \frac{\hbar k}{m}\frac{|f|^2}{r^2} \tag{47}$$

$$(J_{out})_\theta = -\frac{i\hbar}{2m}\frac{1}{r^3} f^* \frac{\partial f}{\partial \theta} + C.C. \tag{48}$$

$$(J_{out})_\phi = -\frac{i\hbar}{2m}\frac{1}{r^3 \sin\theta} f^* \frac{\partial f}{\partial \phi} + C.C. \tag{49}$$

The currents are very complicated. So what can we do about it? Now remember we want to know what happens very far away from the scattering potential, as $\vec{r} \to \infty$. That's where the detector is going to be and that's where I'm going to observe the currents. The angular components of the probability currents fall off like r^{-3} and we can forget about them. The current represents particles that come out so it has to be conserved. It's all coming out in the radial direction. The total out going current is given by integrating over a sphere.

$$I_{out} = \int J_r dS = \frac{\hbar k}{m} \int d\Omega |f|^2 \tag{50}$$

It turns out that I_{out} is a constant, no r dependence and only the solid angle. Which it needs to be because probability currents need to be conserved. Now we can build an expression for the scattering cross section.

$$\sigma = \frac{I_{out}}{J_{in}} = \int d\Omega |f|^2 \tag{51}$$

If we care about the distribution of particles then we need the differential cross section. You can see that the differential cross section is given precisely by the function f. This is a very important function because this is what we're going to be able to measure.

$$\sigma = \int d\Omega |f|^2 = \int d\Omega \frac{d\sigma}{d\Omega} \qquad \rightarrow \qquad \frac{d\sigma}{d\Omega} = |f|^2 \tag{52}$$

Where do we even find this $f(\Omega)$? We turn back to our old friend the Schrodinger equation. And when it is written in this way we can see that it's form is similar to that of Eq. (3). Except now we can see that ρ comes from φ itself.

$$\nabla^2\varphi + k^2\varphi = \frac{2m}{\hbar^2}V\varphi \qquad k = \frac{\sqrt{2mE}}{\hbar} \tag{53}$$

If we can say $\rho = \frac{2m}{\hbar^2}V\varphi$ then we already know of the solution to Eq. (22). It is an integral equation and nobody can solve it.

$$\varphi(\vec{r}) = e^{ikz} + \frac{2m}{\hbar^2}\int d^3r' G_+(\vec{r}, \vec{r'})V(\vec{r'})\varphi(\vec{r'}) \tag{54}$$

But, if you can solve it you're going to get the function f. Well, like before we only care about what happens really far away at the detector. We have the right ρ now so f is therefore given by,

$$f(\theta, \phi) = -\frac{1}{4\pi}\frac{2m}{\hbar^2}\int d^3r' e^{ik\vec{r}\cdot\hat{r}}V(\vec{r'})\varphi(\vec{r'}) \tag{55}$$

Now let's calculate this. To do so we need to use the Born approximation. Let $\varphi \approx e^{ikz}$. Then for Eq. (24),

$$f(\theta, \phi) \approx -\frac{1}{4\pi}\frac{2m}{\hbar^2}\int d^3r' e^{ik\vec{r}\cdot\hat{r}}V(\vec{r'})e^{ikz'} \tag{56}$$

And if we look in the direction of r we can write $kz' = \vec{k_i} \cdot \vec{r'}$. Which is the definition of the Fourier transform of V.

$$f_B = -\frac{1}{4\pi}\frac{2m}{\hbar^2}\int d^3r' e^{-i(\vec{k_s}-\vec{k_i})\cdot\vec{r'}}V(\vec{r'}) = -\frac{1}{4\pi}\frac{2m}{\hbar^2}\tilde{V}(\vec{k_s} - \vec{k_i}) \tag{57}$$

We can improve our Born approximation through iterations.

$$\varphi_0 = e^{ikz} \tag{58}$$

$$\varphi_1 = e^{ikz} + \frac{2m}{\hbar}\int d^3r' G_+(\vec{r}, \vec{r'})V(\vec{r'})e^{ikz'} \tag{59}$$

$$\varphi_2 = e^{ikz} + \frac{2m}{\hbar}\int d^3r' G_+(\vec{r}, \vec{r'})V(\vec{r'})\varphi(\vec{r'}) \tag{60}$$

Instead of having a plane wave let's try spherical wave. How do we find all solutions? Need to solve the equation $\nabla^2\varphi + k^2\varphi = 0$, and find the eigenvalues, of which will commute with a set of operators $\{H, L^2, L_z\}$.

$$\varphi_{klm} = R_{kl}Y_{lm}(\theta, \phi) \tag{61}$$

$$-\frac{\hbar^2}{2m}\frac{1}{r}(rR)'' + \frac{l(l+1)\hbar^2}{2mr^2}R = ER \qquad let \quad u = rR \tag{62}$$

$$-\frac{\hbar^2}{2m}u'' + \frac{l(l+1)\hbar^2}{2mr^2}u = Eu \tag{63}$$

Now as $r \rightarrow 0$ there is asymptotic behavior.

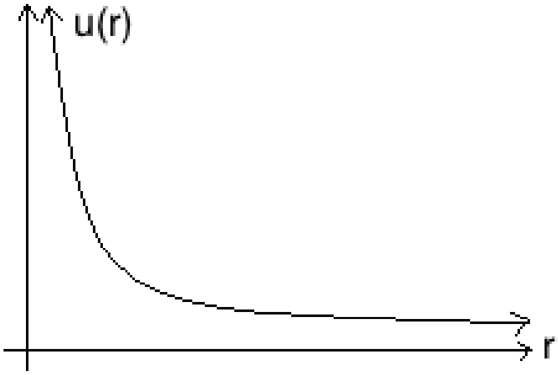


Figure 3: asymptotic behavior

Therefore,

$$-u'' + \frac{l(l+1)}{r^2}u = Eu \approx 0 \tag{64}$$

Solution of the differantial equation above is done by writing $u = r^\lambda$ instead of u and then,

$$\lambda(\lambda+1) = l(l+1) \qquad \Longrightarrow \lambda = -l \, or \, l+1 \tag{65}$$

We choose the solution of $\lambda = l + 1$ therefore the solution of this differential equation is r^{l+1} for $r \rightarrow 0$.
On the other hand, as $r \rightarrow \infty$, u becomes that of a free particle.

$$-\frac{\hbar^2}{2m}u'' = Eu \qquad \Longrightarrow u = e^{\pm ikr} \tag{66}$$

We have found the general solution valid for a far away detector and the boundary conditions examined. For instance as r→0 we have found that u also goes to zero therefore u≈ r^{l+1} and as r→ ∞ u≈ $e^{\pm ikr}$. Let us do an example about this kind of situation. We are going to examine them for different l and now we are going to start with the simplest case which is l=0.

- <u>$l = 0$</u>

  When we are far away from the potential there are two solutions and the most general solution is

$$u = A'e^{ikr} + B'e^{-ikr} \tag{67}$$

If we *Taylor expand* the function u it becomes

$$u = A' + B' + ik(A' - B')r + \dots . \tag{68}$$

In the limit when r goes to zero we find that

$$A' = -B' \tag{69}$$

Using this relation between A' and B' we can write u as

$$u = A'(e^{ikr} - e^{-ikr}) = A\sin(kr) \tag{70}$$

then the radial part of the wavefunction which is R will be

$$R = A\frac{\sin(kr)}{r} \tag{71}$$

In this case it is very simple because l is zero and then to find the wavefunction we need to multiply this by spherical harmonics which is constant for $l = 0$. Now it can be seen that this radial wavefunction, R, is a mixture of incoming and outgoing waves which has to be in this way because we want a valid solution for everywhere so as r→0 this wavefunction needs to satisfy this condition as well. In case of the Hydrogen atom the radial part of the wavefunction needs to be normalized. But here we don't have normalization because the energy of the particles are greater than zero and we have a continuous spectrum therefore to normalize this radial wavefunction we are going to use the *delta function.* Let us write the inner product for the wavefunction.

$$I = \int d^3r \varphi^*_{k'0}(\vec{r})\varphi_{k0}(\vec{r}) \tag{72}$$

If we separate this into radial and angular parts we find

$$I = \int_0^\infty dr u^*_k(r)u_{k'}(r)\int d\Omega|Y_{00}|^2 \tag{73}$$

Since spherical harmonics are normalized the second integral term will be equal to 1. Now to calculate the integral for the radial part let us substitute the value of $u = A\sin(kr)$ in the integral.

$$I = A^*_k A_{k'}\int_0^\infty dr \sin(kr)\sin(k'r) \tag{74}$$

To solve this integral we are going to write the sine functions in terms of exponentials.

$$I = A^*_k A_{k'}\int_0^\infty dr \frac{(e^{ikr} - e^{-ikr})}{2i}\frac{(e^{ik'r} - e^{-ik'r})}{2i} \tag{75}$$

$$I = \frac{A_k^* A_{k'}}{(2i)^2} \int_0^\infty dr[e^{i(k+k')r} - e^{-i(k-k')r} - e^{i(k'-k)r} + e^{-i(k+k')r}] \quad (76)$$

If we do change of variable from r→-r the first and the last terms in the integral will be the same except for their limits. For the last term the limit of the integral is going to be from $-\infty$ to zero.

$$I = \frac{A_k^* A_{k'}}{(2i)^2} \int_{-\infty}^\infty dr[e^{i(k+k')r} - e^{-i(k-k')r}] = 2\pi \frac{A_k^* A_{k'}}{(2i)^2} [\delta(k+k') - \delta(k-k')] \quad (77)$$

Since both k, k' are positive the first delta function goes to zero and the integral becomes

$$I = |A_k|^2 \frac{\pi}{2} \delta(k-k') \quad (78)$$

The normalization for a continuous spectrum will be equal to the delta function therefore the normalization constant, A_k, is

$$A_k = \sqrt{\frac{2}{\pi}} \quad (79)$$

This normalization constant is the same for the plane waves as well because $< k|k' >= \delta(k-k')$.

- <u>*l*=1</u>

  To calculate the wavefunction for the case of $l = 1$ we are going to use the wavefunction we obtained for $l = 0$ and we shall define the momentum operator, $P_+ = P_x + iP_y$. The momentum operator commutes with the Hamiltonian which means that they have the same eigenfunction. Let us apply the Hamiltonian and P_+ operator to the eigenfunction of the Hamiltonian.

$$H|\varphi\rangle = E|\varphi\rangle \quad (80)$$

$$HP_+|\varphi\rangle = P_+H|\varphi\rangle = EP_+|\varphi\rangle \quad (81)$$

Once we apply this momentum operator, P_+, to the wavefunction for the case of $l = 0$ we can find the wavefunction for the case of $l = 1$.

$$P_+ \frac{\sin(kr)}{r} = -i\hbar(\frac{\partial}{\partial x} + i\frac{\partial}{\partial y})\frac{sin(kr)}{r} \quad (82)$$

The derivative of r with respect to x and y is respectively,

$$\frac{\partial r}{\partial x} = \frac{x}{r}, \qquad \frac{\partial r}{\partial y} = \frac{y}{r} \quad (83)$$

Therefore,

$$P_+ \frac{\sin(kr)}{r} = -i\hbar(\frac{x+iy}{r})(\frac{\sin(kr)}{r})' \quad (84)$$

and

$$\frac{x+iy}{r} = \sin\theta e^{i\varphi} = (constant)Y_{11} \quad (85)$$

$$\varphi_{k11} = AY_{11}(\theta,\phi)\left[\frac{k\cos(kr)}{r} - \frac{\sin(kr)}{r^2}\right] \tag{86}$$

For $l = 1, m = -1, 0, 1$ therefore there are three wavefunctions and they are

$$-\varphi_{k11} = \varphi_{k10} \qquad \mathit{and} \qquad -\varphi_{k10} = \varphi_{k1-1} \tag{87}$$

- <u>l=2</u>

  Let us apply the momentum operator, P_+, for the second time to find the wavefunctions for the case of $l = 2$.

$$P_+^2\frac{\sin(kr)}{r} = A'P_+\frac{x+iy}{r}(\frac{\sin(kr)}{r})' \tag{88}$$

Here one thing that you need to realize is that P_+ operator commutes with (x+iy). Therefore,

$$P_+^2\frac{\sin(kr)}{r} = A'(x+iy)P_+\frac{1}{r}(\frac{\sin(kr)}{r})' \tag{89}$$

$$P_+^2\frac{\sin(kr)}{r} = A'(x+iy)^2\frac{1}{r}(\frac{1}{r}\frac{\sin(kr)}{r})' \tag{90}$$

As you look for different l's you shall realize that there is a pattern which gives the wavefunction for a general l.

$$P_+^l\frac{\sin(kr)}{r} = A'(x+iy)^l\frac{1}{r}(\frac{1}{r}\frac{d}{dr})^l\frac{\sin(kr)}{r} = \varphi_{kll} \tag{91}$$

The term of $(x+iy)^l = r^lY_{ll}$ and then if we define $\rho = kr$ then the equation above will become,

$$j_l(\rho) = (-\rho)^l(\frac{1}{\rho}\frac{d}{d\rho})^l\frac{\sin\rho}{\rho}. \tag{92}$$

The functions which satisfy the equation above are called the *Spherical Bessel Functions*. The most general solution for the wavefunction written in terms of spherical Bessel functions is therefore,

$$\varphi_{klm} = Aj_l(kr)Y_{lm}(\theta,\phi) \tag{93}$$

where $A = k\sqrt{\frac{2}{\pi}}$ is the same for every l.

The differential equation for the spherical Bessel function is the radial part of the Schrodinger equation.

$$\frac{1}{r}(rR)'' - \frac{l(l+1)}{r^2}R + k^2R = 0 \tag{94}$$

$$j'' + \frac{2}{\rho}j_l' + [1 - \frac{l(l+1)}{\rho^2}]j_l = 0 \tag{95}$$

The asymptotic behaviour of the spherical Bessel functions which is important for physics as r→ ∞ is known.

$$r \to \infty; \qquad j_l(kr) \approx \frac{\sin(kr - l\frac{\pi}{2})}{r} \tag{96}$$

Because of the sine function above j_l is a mixture of incoming and outgoing waves. Now, let us expand sine in exponentials

$$j_l(kr) \approx \frac{e^{i(kr-l\frac{\pi}{2})} - e^{-i(kr-l\frac{\pi}{2})}}{r} \tag{97}$$

$$j_l(kr) \approx \frac{e^{ikr}}{r}e^{-il\frac{\pi}{2}} - \frac{e^{-ikr}}{r}e^{il\frac{\pi}{2}} \tag{98}$$

If we take the first phase $e^{-il\frac{\pi}{2}}$ as a constant then the equation becomes

$$j_l(kr) \approx \frac{e^{ikr}}{r} - \frac{e^{-ikr}}{r}e^{il\pi} \tag{99}$$

$e^{il\pi} = \pm 1$ so we obtain a phase difference between the first term in the equation above (the outgoing wave) and the second term (the incoming wave). This phase different is fixed by the behaviour of the wavefunction where r→ 0. Generally near zero when there is a potential we cannot just go to zero and keep the same Schrodinger equation. In this type of situation what changes is this phase difference between the incoming and outgoing waves. Now we shall examine the behaviour of the wavefunction as r→ 0 to understand the physics. We know that as r→ 0 the wavefunction behaves like $r^{(l+1)}$. On the other hand, the spherical Bessel function's behaviour near r→ 0 is

$$j_l(kr) \approx (kr)^l \tag{100}$$

In figure 4, as r→ 0, j_l goes to zero as well. Where it starts picking up from zero is a number that is approximately l. Therefore, the larger l is, the more j_l stays at zero. The role that case plays in physics is that if $kr \lesssim l$ then the wavefunction R≈ 0. This means that the probability of finding a particle there is zero. Even if it is not exactly zero it will be very very small.

Now if we switch on a potential, for example a nuclear potential, whose range is $\lesssim \frac{l}{k}$ (shown in the figure above with the dashed lines) then the particles that you send for scattering shall not feel the potential because the probability of them being there is very very small. In other words, these particles will never see the potential. We know that $k = \frac{\sqrt{2mE}}{\hbar}$ therefore, it is directly proportional to the energy of the particles. The higher the energy, the smaller the ratio of $\frac{l}{k}$ which is the reason why we want to have high energy. With high energy you can go smaller distances.

l is a quantum number, so large l means that we are in the limit of classical physics. Let us consider the classical limit in more detail.

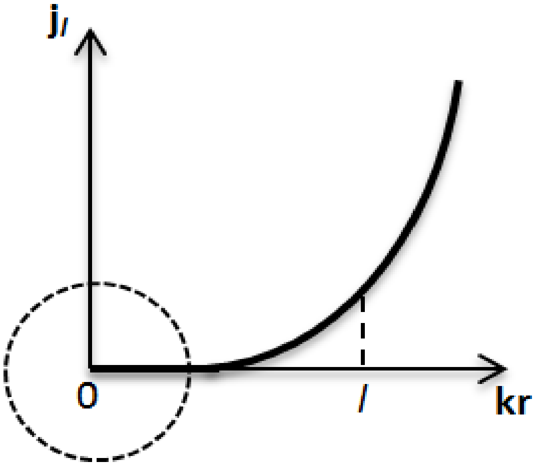


Figure 4: Plot of j_l *vs.* kr

CLASSICAL PHYSICS

Say we send a classical particle for scattering which has a momentum of $\vec{p}$ as shown in figure 5. The distance b shown in the figure is called the *impact parameter* which is defined as the perpendicular distance between the path of a particle and the center of the scattering potential. The angular momentum of the particle is then,

$$L = pb = \hbar\sqrt{l(l+1)} \approx \hbar l \tag{101}$$

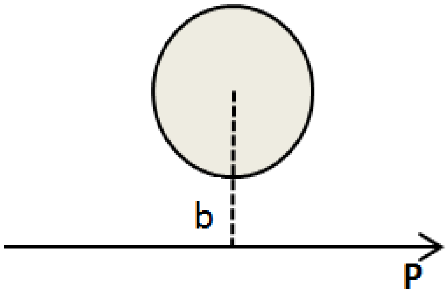


Figure 5: Scattering from a potential

The momentum of the particle and the angular momentum for large l where we are expecting to see the classical results are

$$p = \hbar k \qquad and \qquad L \approx \hbar l \tag{102}$$

respectively. Using these two equalities for the impact parameter we obtain

$$b = \frac{L}{p} = \frac{\hbar l}{\hbar k} = \frac{l}{k} \tag{103}$$

In quantum mechanical perspective we have found that if the range is $\lesssim \frac{l}{k}$ then the particle does not feel the potential. On the other hand, in classical perspective we also see that if the range of the potential is less than the ratio $\frac{l}{k}$ then the particle doesn't see the potential. Therefore, this case makes sense for both perspectives and this explains the physical meaning of this kind of wavefunctions.
Now let us assume that we have a central potential, V(r). Then we still have a general solution which is

$$\varphi_{klm}(\vec{r}) = R_{kl}(r)Y_{lm}(\theta,\varphi) \tag{104}$$

We write $R = \frac{u_{kl}}{r}$ and then the wavefunction becomes

$$u'' + k^2 u - \left[\frac{l(l+1)}{r^2} + \frac{2mV}{\hbar^2}\right] u = 0 \tag{105}$$

We have solved this equation without any potential and we have found that the solution was spherical Bessel functions but now we have a potential. This equation becomes a one dimensional equation as r turns to be x. The limits for r is $0 \rightarrow \infty$ but for x is $-\infty \rightarrow \infty$. Fortunately we know the boundary condition for $r = 0$. This boundary condition says us that there is a wall at $r = 0$. so we can think of r from $-\infty \rightarrow \infty$ with a wall at $r = 0$. Therefore the potential will be complicated for $r > 0$ and infinite for $r < 0$. This way we can think of this case in one dimension. From the one dimensional point of view the scattering means reflection only. If we think of e^{ikr} as the incident wave and e^{-ikr} as the reflected wave then the wavefunction when you look at r$\rightarrow \infty$ is

$$u = Ae^{ikr} + Be^{-ikr} \tag{106}$$

When $r < 0$ then

$$u = 0 \tag{107}$$

Since the potential is infinite in $r < 0$ this means there is no transmission. Hence, the transmission coefficient, T=0 and since R+T=0, R=1=$|\frac{A}{B}|^2$. This simple argument tells us that

$$|A| = |B| \tag{108}$$

A and B are comlex numbers so even though their norms are equal there will be a phase difference between them. If we set A=1 then

$$B = e^{i\beta} \tag{109}$$

New form of the wavefunction u is

$$u \approx e^{ikr} + e^{i\beta} e^{-ikr} \tag{110}$$

$$u \approx e^{-\frac{i\beta}{2}} e^{ikr} + e^{\frac{i\beta}{2}} e^{-ikr} \tag{111}$$

$$u \approx 2\cos(kr - \frac{\beta}{2}) \tag{112}$$

This is the behaviour at infinity. We don't know β unless we solve the equation but we know how it should be. We can write the cosine in terms of sine.

$$u \approx 2\sin(kr - \frac{\beta}{2} - \frac{\pi}{2}) \tag{113}$$

To compare this solution with that of no potential we can write

$$u \approx 2\sin(kr - \frac{l\pi}{2} + \delta_l(k)) \tag{114}$$

In other words, the difference between having a potential and not having a potential is just a δ which is called the *phase shift* and δ in general will have an index of l and is a function of energy. It is very important to calculate the phase shift because it gives all of the information.

We have found the solution for particles coming from all directions. In experiments, instead of bombarding a target from every direction scientists send a beam on the target in one direction. But the solutions that we have found are the most general solutions and they form a complete set because they are the eigenfunctions of the Hamiltonian. We can write other solutions in terms of these general solutions' superposition. Hence, for any experimental arrangement you should be able to write it in terms of the eigenfunctions of Hamiltonian. In particular, the usual setup is to send the beam in z direction. It is a plane wave e^{ikz}. We can write this plane wave in terms of eigenfunctions of the Hamiltonian.

$$e^{ikz} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} a_{lm} \varphi_{klm}(\vec{r}) \tag{115}$$

The coefficients a_{lm} can be written as

$$a_{lm} = \int d^3r \varphi^*_{klm}(\vec{r}) e^{ikz} \tag{116}$$

Now we are going to write these a_{lm} in terms of spherical coordinates to calculate the integral.

$$\varphi_{klm}(\vec{r}) = C j_l(kr) Y_{lm}(\theta, \varphi) \qquad and \qquad e^{ikz} = e^{ikr\cos\theta} \tag{117}$$

$$a_{lm} = C^* \int d^3r e^{ikr\cos\theta} j_l(kr) Y^*_{lm}(\theta, \varphi) \tag{118}$$

Since the φ appears just in the last term of the integral above we can calculate the φ part separately.

$$\int_0^{2\pi} d\varphi Y_{lm}^*(\theta,\varphi) = P_l^m(\theta)\int_0^{2\pi} d\varphi e^{im\varphi} = 0\,(unless\, m=0) \tag{119}$$

This simplifies the calculation and then

$$e^{ikz} = \sum_{l=0}^{\infty} C_l' j_l(kr) Y_{l0}(\theta) \tag{120}$$

$$e^{ikz} = \sum_{l=0}^{\infty} C_l j_l(kr) P_l(\cos\theta) \tag{121}$$

where you don't even need to sum till infinity since the first three or four terms suffice. For the purpose of normalization we can calculate the C_l' and C_l.

$$C_l' = i^l\sqrt{4\pi(2l+1)} \qquad and\, C_l = i^l(2l+1). \tag{122}$$

where $i^l = e^{i\frac{\pi}{2}l}$.

It's nice to have the wave expressed in terms of the spherical harmonics because they are orthogonal functions. When you express the wave in terms of a sum you can see that the full wave is just the sum of partial waves. In practice, keeping only the first two or three terms is good enough. Depending on the value of l the partial waves will have different names. For instance, $l=0$ is called the S wave and $l=1$ is called the P wave, and so on.

So what is the wave function going to be after scattering from the potential? The incoming wave will turn into the outgoing wave, $e^{ikz} \rightarrow \varphi$, which is the sum of the incoming and outgoing wave $\varphi_{scattered}$. The entire wave will be,

$$\varphi = e^{ikz} + \varphi_s \tag{123}$$

In order to figure out the scattering cross section we need to determine the outgoing wave φ_s. To begin we look at the behavior of the wave very far away - because that's where we want to put the detector. The incoming partial wave is built with spherical Bessel functions, $j_l(kr)$, and we can expand this in the region where $r \rightarrow \infty$, where it becomes a sin function.

$$j_l(kr) \sim \frac{1}{2i}\left[\frac{e^{ikr}}{kr}e^{-il\frac{\pi}{2}} - \frac{e^{-ikr}}{kr}e^{il\frac{\pi}{2}}\right] \tag{124}$$

If we look at the total wave φ in the region $r \rightarrow \infty$ and there's gonna be a mixture of incoming and outgoing spherical waves again. And we introduced the phase shift δ_l which distinguishes the total wave from the incoming wave. The overall phase is arbitrary so we chose to put it with the first term.

$$\varphi \sim \frac{1}{2i}\left[\frac{e^{ikr}}{kr}e^{-il\frac{\pi}{2}e^{2i\delta_l}} - \frac{e^{-ikr}}{kr}e^{il\frac{\pi}{2}}\right] \tag{125}$$

That will be the behavior of the total wave and I know in general it'll behave like this. Really what I'm after is the outgoing wave, which will be the difference between the total and incoming waves. Therefore φ_s will take the form,

$$\varphi_s \sim \frac{e^{ikr}}{2ikr} e^{-il\frac{\pi}{2}}[e^{2i\delta_l} - 1] = \frac{e^{ikr}}{kr}\frac{1}{i^l} e^{i\delta_l} \sin\delta_l \tag{126}$$

We haven't really solved for anything yet. Just simplified our general expression for the outgoing wave to better see the behavior. So for each l there will be a different solution for the scattered wave. If I look at the entire wave, I just have to replace the j_l with the behavior of j_l at large r by this new behavior for φ_s.

$$e^{ikz} \to \frac{e^{ikr}}{kr}\sum_{l=0}^{\infty} \sqrt{4\pi(2l+1)} e^{i\delta_l} \sin\delta_l Y_l(\theta) \tag{127}$$

So that's the expression for the outgoing wave, the entire outgoing wave. If you remember, this whole thing multiplying $\frac{e^{ikr}}{kr}$ we called it $f(\theta, \varphi)$ before. The entire sum is then this $f(\theta, \varphi)$ function.

$$e^{ikz} \to \frac{e^{ikr}}{kr}\sum_{l=0}^{\infty} \sqrt{4\pi(2l+1)} e^{i\delta_l} \sin\delta_l Y_l(\theta) = \frac{e^{ikr}}{r} f(\theta, \varphi) \tag{128}$$

$$\Rightarrow f(\theta) = \frac{1}{k}\sum_{l=0}^{\infty} \sqrt{4\pi(2l+1)} e^{i\delta_l} \sin\delta_l Y_l(\theta) \tag{129}$$

So if I somehow manage to calculate those δ_l's I will be able to figure out the entire $f(\theta)$. Remember the cross section is given in terms of this function. Recall that $f(\theta)$ is sort of an amplitude because of the relation to the differential cross section. This is the quantity that I'm after because that's the experimental result that I'll be comparing things with.

$$\frac{d\sigma}{d\Omega} = |f|^2 \tag{130}$$

$$|f(\theta)|^2 = \frac{1}{k^2}|\sum_{l=0}^{\infty} \sqrt{4\pi(2l+1)} e^{i\delta_l} \sin\delta_l Y_l(\theta)|^2 \tag{131}$$

From this I can find the total cross section. I'll have to integrate the differential cross section over all the angles. Since the variable φ was constant I only need to integrate over θ.

$$\sigma = \int d\Omega \frac{d\sigma}{d\Omega} = \int d\Omega |f(\theta)|^2 = 2\pi \int_0^{\pi} d\theta \sin\theta |f(\theta)|^2 \tag{132}$$

I want to calculate the total cross section, so I'll plug in for $|f(\theta)|^2$ and remembering to keep track of the indices for $f^*(\theta)$ and $f(\theta)$.

$$\sigma = \frac{1}{k^2}\sum_{l,l'=0}^{\infty}\sqrt{4\pi(2l+1)}\sqrt{4\pi(2l'+1)}e^{-i\delta_l}e^{i\delta_{l'}}\sin\delta_l\sin\delta_{l'}\int d\Omega Y_l^*(\theta)Y_{l'}(\theta') \tag{133}$$

This integral we can do pretty easily because of the orthonormal nature of the spherical harmonics. It's a Kronecker delta function equal to one only when $l = l'$. So the total cross section boils down to a manageable expression in terms of the phases δ_l. And calculating the first few terms is usually good enough.

$$\sigma = \frac{1}{k^2}\sum_{l=0}^{\infty}4\pi(2l+1)\sin^2\delta_l \tag{134}$$

As an interesting aside, lets look at the function $f(\theta)$ when $\theta = 0$ and compare it to our expression for the total cross section when we look in the forward direction.

$$Y_l(0) = \sqrt{\frac{2l+1}{4\pi}} \tag{135}$$

$$f(\theta)|_{\theta=0} = \frac{1}{k}\sum_{l=0}^{\infty}\sqrt{4\pi(2l+1)}e^{i\delta_l}\sin\delta_l Y_l(0) = \frac{1}{k}\sum_{l=0}^{\infty}(2l+1)e^{i\delta_l}\sin\delta_l \tag{136}$$

Comparing this with the total cross section we see that σ has an extra factor of $\frac{4\pi}{k}$ and $\sin\delta_l$. This is a very general result and it even has it's own name, the *Optical Theorem*.

$$\sigma = \frac{4\pi}{k}Imf(0) \tag{137}$$

Example 1: Hard Sphere

We will now move on to do an example problem, scattering from a hard sphere. Hard sphere means anything you send in gets reflected. Modeled as an infinite potential wall at $r \leqslant r_0$.

$$V(r) = \begin{cases} 0 & \text{if } r > r_0 \\ \infty & \text{if } r \leqslant r_0 \end{cases}$$

So how do we solve this problem? We can actually solve it exactly. Remember that when $r > r_0$ we have a free particle and must solve the free Schrodinger equation. We already found it and lets call it $R_{k,l}(r)$, a spherical Bessel function.

$$R_{k,l}(r) = Aj_l(kr) \qquad A = constant \tag{138}$$

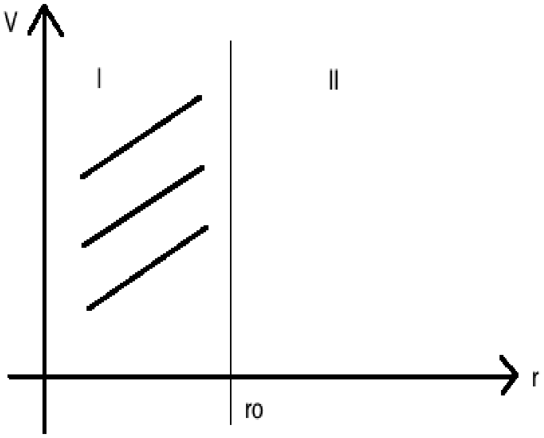


Figure 6: Hard sphere potential

Since we no longer have to worry about the behavior of the function at the origin we need to keep both pieces of the wave function. This other Bessel function we need is $n_l(kr)$. The n stands for Neumann.

$$R_{k,l}(r) = Aj_l(kr) + Bn_l(kr) \tag{139}$$

Next thing to do would be to apply the boundary conditions, and setting $A = 1$ because we arbitrarily can.

$$R_{k,l}(r = r_0) = 0 \qquad \Rightarrow \qquad \frac{B}{A} = \frac{j_l(kr_0)}{n_l(kr_0)} \tag{140}$$

So this completely determines the function but we want an expression for δ_l because this is what have expressions for. To do this we have to go far away $r \to \infty$.

$$\text{Definition of } \delta_l : \qquad R_{k,l}(r) \sim \frac{1}{kr}\sin(kr - l\frac{\pi}{2} + \delta_l) \tag{141}$$

$$j_l(kr) \sim \frac{1}{kr}\sin(kr - l\frac{\pi}{2}) \tag{142}$$

$$n_l(kr) \sim -\frac{1}{kr}\cos(kr - l\frac{\pi}{2}) \tag{143}$$

$$\Rightarrow R_{k,l}(r) = Aj_l(kr) + Bn_l(kr) \sim \frac{A}{kr}\sin(kr - l\frac{\pi}{2}) - \frac{B}{kr}\cos(kr - l\frac{\pi}{2}) \tag{144}$$

That's the behavior of my wavefunction. When we compare this expression to that of the definition of δ_l I should get δ_l. Expanding the definition in terms of a trigonometric identity comparing the coefficients to match, then taking the ratio of $\frac{B}{A}$,

$$-\frac{B}{A} = \frac{\sin(\delta_l)}{\cos(\delta_l)} = \tan(\delta_l) = \frac{j_l(kr_0)}{n_l(kr_0)} \tag{145}$$

That's the solution I'm looking for. Let's look at it and try to figure out the behavior to find the cross section. Begin with the lowest value, $l = 0$. We can look up the spherical Bessel functions $j_0(\rho) = \frac{\sin(\rho)}{\rho}$ and $n_0(\rho) = -\frac{\cos(\rho)}{\rho}$, then the first phase shift.

$$\tan(\delta_0) = -\tan(kr_0) \qquad \Rightarrow \qquad \delta_0 = -kr_0 \tag{146}$$

Plugging this into the expression for the total cross section and keeping just the first term,

$$\sigma = \frac{1}{k^2} 4\pi \sin^2(kr_0) \tag{147}$$

When is this approximation good? Remember that k has to do with the energy of the beam. If I had a very low energy beam then $kr_0 \ll 1$ then $\sigma = 4\pi r_0^2$. So in the low energy limit the cross section becomes a constant. The lower the energy the better the approximation.

So let's make this problem a little more difficult. You never really have a hard sphere but you do have a potential well of finite depth. Such is life.

Example 2: Square Well

Outside the potential we have a free particle so the equation for $R_{k,l}(r)$ will be the same as that for the hard sphere. But now we do have to consider what happens for $r < r_0$. So when we are the region of the potential we'll have a new value for k and that'll be $k' = \frac{\sqrt{2m(E+V_0)}}{\hbar}$. So in the region of the potential, where the $n_l \to 0$,

$$R_{k,l}(r) = Cj_l(k'r) \tag{148}$$

And outside the potential.

$$R_{k,l}(r) = Aj_l(kr) + Bn_l(kr) \tag{149}$$

Now we have to match the solutions at the boundary, including the derivatives.

$$Aj_l(kr_0) + Bn_l(kr_0) = Cj_l(k'r_0) \tag{150}$$

$$Akj_l'(kr_0) + Bkn_l'(kr_0) = Ck'j_l'(k'r_0) \tag{151}$$

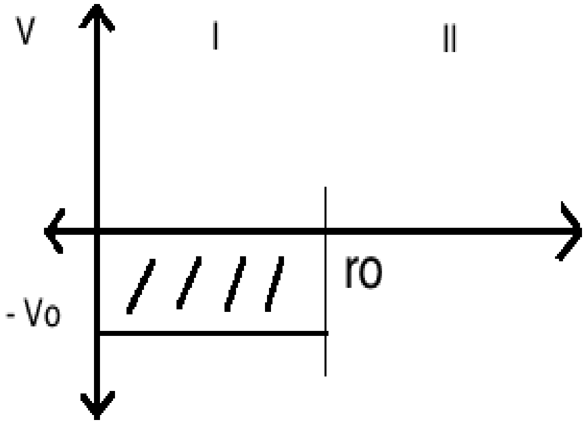


Figure 7: Potential step

Dividing the two equations and dividing through by A, and writing $-\frac{B}{A} = \tan(\delta_l)$,

$$\frac{j_l(kr_0) - tan(\delta_l)n_l(kr_0)}{kj_l'(kr_0) - \tan(\delta_l)kn_l'(kr_0)} = \frac{j_l(k'r_0)}{k'j_l'(k'r_0)} \tag{152}$$

Now we only have one constant, δ_l and if we can solve this equation that will give me δ_l and that's all we need. So let's do the case when $l = 0$. Let $\rho = kr_0$ and $\rho' = k'r_0$, and using the Bessel functions from earlier. Plugging in and doing some algebra will give,

$$[\frac{\cos(\rho)\cos(\rho')}{\rho} + \frac{\sin(\rho)\sin(\rho')}{\rho'}]\tan(\delta_l) = \frac{\sin(\rho')\cos(\rho)}{\rho'} - \frac{\sin(\rho)\cos(\rho')}{\rho} \tag{153}$$

Then going to the low energy realm, $\rho \ll 1$. In this limit $\rho' \approx \frac{r_0}{\hbar}\sqrt{2mV_0}$ and $\rho \to 0$.

$$[\frac{\cos(\rho')}{\rho}]\tan(\delta_0) = \frac{\sin(\rho')}{\rho'} - \cos(\rho') \tag{154}$$

$$\Rightarrow \qquad \tan(\delta_0) = \rho[\frac{\tan\rho'}{\rho'} - 1] \approx \sin(\delta_0) \approx \delta_0 \tag{155}$$

Now we can look into figuring out the first terms in the cross section and plugging in for $\rho = kr_0$.

$$\sigma = \frac{4\pi}{k^2}\delta_0^2 = 4\pi r_0^2[\frac{\tan\rho'}{\rho'} - 1]^2 \tag{156}$$

Again the cross section is a constant and this time it's less the four times the cross section. And how much less depends on the depth of the potential because of the dependence on ρ'. Looking at the behavior of the tangent function, it'll blow up as V_0 increases and then ρ' approaches $\frac{\pi}{2}$. Then,

$$V_0 < \frac{\pi^2\hbar^2}{8mr_0^2} \tag{157}$$

If V_0 becomes as big as this number then the cross section blows up and there is lots of scattered particles. When this happens it's called a resonance. Is the cross section itself infinite? No, because we have made an approximation for the cross section when we wrote it. When ρ' is exactly $\frac{\pi}{2}$ a value may blow up but δ_0 will not be infinite because we take the tangent of δ_0. That tells me the δ_0 will be precisely $\frac{\pi}{2}$. And if it's exactly $\frac{\pi}{2}$ I have to calculate the cross section again using the same formula.

$$\sigma = \frac{4\pi}{k^2} \tag{158}$$

So σ is not infinite but as $k \rightarrow 0$ the cross section becomes very, very large. The cross section is then large for low energies. So that means I have a resonance. Which is something we should be able to see in an experiment. Lots of particles coming out.

Lets now increase V_0 above this number. The tangent of ρ will begin to decrease and eventually you will get down to zero. If you keep increasing the potential there will be a point where $\tan(\rho') = \rho'$. If you solve that equation you'll find that $\rho' \approx 4.5$. At this point δ_0 will be exactly zero and the cross section will get a zero contribution from the first term, which is the most significant. So in practice, the other terms are going to contribute but they're going to contribute very little. If you do an experiment and you have a potential thats exactly at that value you'll see nothing.

This is a famous result that was obtained back in 1923 when people didn't know anything about quantum mechanics. They didn't have a wave equation, Schrodinger hadn't come up with it yet. So all of a sudden the experiment that they performed, which was the scattering of electrons by rare gasses, you detect nothing. They were wondering why you see nothing, and there was no explanation in terms of classical mechanics. It's a completely quantum mechanical effect, because it has to do with interference. It's only with interference that you can get absolutely nothing. This was a great mystery and is known as the Ramsauer-Townsend effect.

For E<0 the zeroth order phase shift, which is the most important term in low energies, ρ, and ρ' values are respectively,

$$\tan\delta_0 = \rho(\frac{\tan\rho'}{\rho'} - 1) \tag{159}$$

$$\rho = kr_0 = \frac{\sqrt{2mE}}{\hbar}r_0 \tag{160}$$

$$\rho' = k' r_0 = \frac{\sqrt{2m(E+V_0)}}{\hbar} r_0. \tag{161}$$

From the formula of the phase shift we can see that the resonance occurs when $\tan\rho'$ becomes infinite. In other words, the resonance occurs when ρ' takes the following values.

$$\rho' \approx \frac{\pi}{2}, \frac{3\pi}{2}, \frac{5\pi}{2}, \dots \tag{162}$$

At these points the cross section becomes large, not infinite. Now let us consider the values of V_0 that will cause the resonances.

Bound States

For the energy less than zero the spectrum will be discrete. For this kind of wavefunctions the solutions of the Schrodinger equation are

$$(I) \qquad u_I'' + k'^2 u_I = 0 \qquad \Rightarrow \qquad u_I = A\sin(k'r) + B\cos(k'r) \tag{163}$$

$$(II) \qquad u_{II}'' + k'^2 u_{II} = 0 \tag{164}$$

Since E<0 say, k=$i\kappa$ where $\kappa = \frac{\sqrt{-2mE}}{\hbar}$ and is a real number. Therefore, u$_{II}$ becomes,

$$u_{II}'' - \kappa^2 u_{II} = 0 \qquad \Rightarrow \qquad u_{II} = Ce^{\kappa r} + De^{-\kappa r} \tag{165}$$

As $r \to \infty$ $u_{II} \to 0$ and once $r = 0$, $u_I = 0$. Therefore, coefficients B and C are zero. Using the continuity, these two solutions and their derivatives need to match at the boundary, that is, r= r_0.

$$A\sin(k'r_0) = De^{-\kappa r_0} \tag{166}$$

$$k'A\cos(k'r_0) = -\kappa De^{-\kappa r_0} \tag{167}$$

To cancel the coefficients A and D we divide by the two equations above and we obtain

$$\frac{1}{k'}\tan(k'r_0) = -\frac{1}{\kappa r_0} \tag{168}$$

Once we solve this equation above we obtain the energy, E. We get discrete spectrum because the solution of this equation has finite number of solutions. To solve this equation we are going to use the graphical method and we are going to denote $k'r_0$ as x and κr_0 as y. Then the equation becomes,

$$\frac{1}{x}\tan(x) = -\frac{1}{y} \qquad \Rightarrow \qquad y = -x\cot x \tag{169}$$

If we look at the figure we see that one more function intersects with this graph.

$$x^2 + y^2 = \frac{2mV_0}{\hbar^2} r_0^2 \tag{170}$$

The circles in the figure changes according to the value of V_0. For low V_0 values there is no intersection on the graphs. But there is one intersection where we

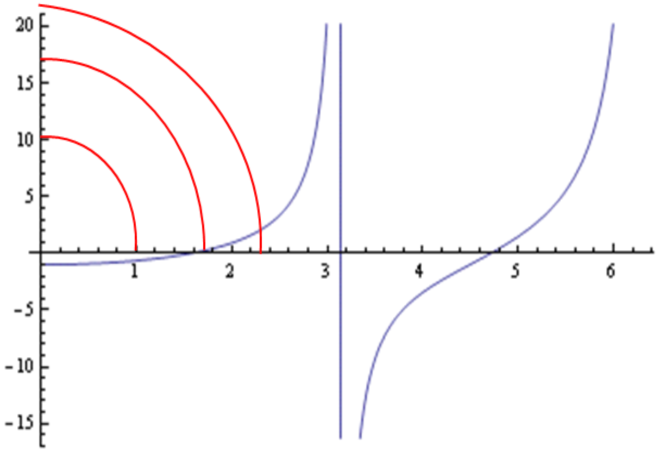


Figure 8: Plot of $k'r_0$ vs. κr_0

exactly get the *first bound state* for which $x = \frac{\pi}{2}$. We can continue in first bound state until drawing a circle intersecting with the second part of the graph and so on. Therefore,

$$x^2 + y^2 = \frac{2mV_0}{\hbar^2} r_0^2 = (\frac{\pi}{2})^2 \tag{171}$$

$$V_0 < \frac{\hbar^2 \pi^2}{8mr_0^2} \qquad \Rightarrow \qquad NO\, BOUND\, STATES! \tag{172}$$

The values $\frac{\pi}{2}$, $\frac{3\pi}{2}$, $\frac{5\pi}{2}$... are also the values for the resonance. This means that as V_0 changes, and there's a resonance, a new bound state has been added. This result relates the resonance, bound states and the cross section.

Absorption

We have been working on the elastic collisions so far but Nature does not work this way. We need to study inelastic scattering as well.

- Elastic Collisions:

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot \vec{J} = 0 \qquad \Rightarrow \qquad Conserved\, current \tag{173}$$

$$\frac{\partial \rho}{\partial t} = 0 \qquad \Rightarrow \qquad No\, dependence\, on\, time \tag{174}$$

$$\vec{\nabla} \cdot \vec{J} = 0 \qquad \Rightarrow \qquad Conservation\, law \tag{175}$$

  where

$$\vec{J} = \frac{\hbar}{2mi}(\psi^* \vec{\nabla}\psi - \psi\vec{\nabla}\psi) \tag{176}$$

- Inelastic Collisions:

$$V = V_1 + iV_2 \tag{177}$$

$$-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = i\hbar\frac{\partial\psi}{\partial t} \tag{178}$$

$$\frac{\partial\rho}{\partial t} = \psi\frac{\partial\psi^*}{\partial t} + C.C. \tag{179}$$

$$\frac{\partial\rho}{\partial t} = \frac{1}{i\hbar}[-\frac{\hbar^2}{2m}\psi^*\nabla^2\psi + V|\psi|^2 + C.C. \tag{180}$$

$$\frac{\partial\rho}{\partial t} = -\frac{\hbar}{2mi}\psi^*\nabla^2\psi + \frac{V_2}{\hbar}|\psi|^2 + C.C. \tag{181}$$

$$\frac{\partial\rho}{\partial t} = -\frac{\hbar}{2mi}\vec{\nabla}(\psi^*\vec{\nabla}\psi - \psi\vec{\nabla}\psi^*) + \frac{2V_2}{\hbar}|\psi|^2 \tag{182}$$

$$\frac{\partial\rho}{\partial t} = -\vec{\nabla}\cdot\vec{J} + \frac{2V_2}{\hbar}\rho \tag{183}$$

Since there is no time dependence,

$$\vec{\nabla}\cdot\vec{J} = \frac{2V_2}{\hbar}\rho \tag{184}$$

Using divergence theorem the total current is,

$$I = \int_S \vec{J}\cdot d\vec{S} = \int_V \vec{\nabla}\cdot\vec{J}d^3r = \int \frac{2V_2}{\hbar}\rho d^3r \tag{185}$$

We are interested in this situation because this appears in absorption. If there were no absorption then V_2 would be zero and there wouldn't be a term like I. Flux means the number of particles passing through a surface per time but they can both go out or come in.Therefore, I is the absorbed flux.

$$F_{abs} = -I \tag{186}$$

If we measure the entire cross section for the absorption it is,

$$\sigma_{abs} = \frac{F_{abs}}{J_{inc}} \tag{187}$$

We have already calculated the value of J_{inc} for incoming plane wave.

$$J_{inc} = \frac{\hbar k}{m} = Velocity \tag{188}$$

Then the absorbed cross section is calculated from

$$\sigma_{abs} = -\frac{2m}{\hbar^2 k}\int V_2\rho d^3r = -\frac{m}{\hbar k}\int \vec{J}\cdot d\vec{S}. \tag{189}$$

To calculate this integral we will go through the same steps as the elastic scattering. First of all, we place the detector far away, that is, $r \to \infty$. The incoming wave is a plane wave which is e^{ikz} and it turns into the total φ,

$$\varphi = \sum_{l=0}^{\infty} \sqrt{4\pi(2l+1)}[\frac{e^{ikr}}{2ikr} e^{-il\frac{\pi}{2}} e^{2i\delta_l} - \frac{e^{-ikr}}{2ikr} e^{il\frac{\pi}{2}}]Y_{l0}(\theta) \tag{190}$$

As you go over the same procedure as in the elastic scattering part you get exactly the same answer. The crucial difference is that since the potential has the imaginary part the phase shift, δ_l, has an imaginary part. Hence we can write $\delta_l = \alpha_l + i\beta_l$. Since we know φ we can find J and the cross section.

$$\sigma_{abs} = -\frac{m}{\hbar k} \int J_r r^2 d\Omega = -\frac{mr^2}{\hbar k} \int J_r d\Omega \tag{191}$$

$$J_r = \frac{\hbar}{2mi}(\varphi^* \frac{\partial \varphi}{\partial r} - C.C.) \tag{192}$$

Let us calculate the partial differential of φ with respect to r.

$$\frac{\partial \varphi}{\partial r} = \sum_{l=0}^{\infty} \sqrt{4\pi(2l+1)}[(\frac{e^{ikr}}{2r} - \frac{e^{ikr}}{2ikr^2})e^{-il\frac{\pi}{2}} e^{2i\delta_l} + C.C.(\delta_l = 0)]Y_{l0}(\theta) \tag{193}$$

As $r \to \infty$ the term $\frac{e^{ikr}}{2ikr^2}$ may be ignored and let us call the coefficient as b_l.

$$\frac{\partial \varphi}{\partial r} = \frac{1}{2r} \sum_l b_l Y_{l0}(\theta) \tag{194}$$

For φ we already have an expression and if we take $\frac{1}{2r}$ out and write the rest as a coefficient, c_l, then,

$$\varphi = \frac{1}{2r} \sum_l c_l Y_{l0}(\theta) \tag{195}$$

Now we can calculate the absorption cross-section.

$$\sigma_{abs} = -\frac{mr^2}{\hbar k} \frac{\hbar}{2mi} \sum_{l,l'} \frac{1}{(2r)^2} \int d\Omega b_{l'} c_l^* Y_{l'0}^*(\theta) Y_{l0}(\theta) + C.C. \tag{196}$$

Since spherical harmonics are orthogonal this expression can be simplified.

$$\sigma_{abs} = -\frac{1}{8ki} \sum_l b_l c_l^* + C.C. \tag{197}$$

As expected you can see from the equation above the cross-section does not depend on r. The cross-section should not depend on where you put the detector. The flux has to be the same no matter where you are. We need to calculate the coefficient. To do this we are going to calculate the following expression.

$$b_l c_l^* - C.C. = \frac{8\pi(2l+1)}{ik}(e^{-4\beta_l} - 1) \tag{198}$$

Then the absorption coefficient is,

$$\sigma_{abs} = \frac{\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)(1-e^{-4\beta_l}). \tag{199}$$

If the phase shift due to absorption is zero then it is obivious from the equation that the absorption coefficient is zero. Remember when there is an elastic scattering we had a very similar expression for the cross-section. To remind, the φ and the scattering amplitude, $f(\theta)$, were

$$\varphi = \frac{e^{ikr}}{r} f(\theta) \tag{200}$$

$$f(\theta) = \frac{1}{k}\sum_{l=0}^{\infty}\sqrt{4\pi(2l+1)}e^{i\delta_l}\sin\delta_l Y_{l0}(\theta) \tag{201}$$

These two expressions are still the same for the inelastic scattering. But now we need to be careful because δ_l is not real anymore. Hence, we can write the terms with

$$e^{i\delta_l}\sin\delta_l = \frac{1}{2i}(e^{2i\delta_l}-1) \tag{202}$$

Using the terms above the elastic scattering cross section becomes,

$$\sigma_{el} = \int d\Omega |f|^2 = \frac{\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)|e^{2i\delta_l}-1|^2 \tag{203}$$

Now we don't have $\sin^2\delta_l$ because δ_l is not real. For imaginary δ_l,

$$\mid e^{2i\delta_l} - 1 \mid^2 = \mid e^{2i\delta_l} \mid^2 + 1 - 2Re e^{2i\delta_l} = e^{-4\beta_l} + 1 - 2e^{-2\beta_l}\cos(2\alpha_l) \tag{204}$$

The total cross-section will be the sum of these cross-sections.

$$\sigma = \sigma_{abs} + \sigma_{el} \tag{205}$$

$$\sigma = \frac{2\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)[1-e^{-2\beta_l}\cos(2\alpha_l)] \tag{206}$$

The last term in the sum above is $Re[1-e^{2i\delta_l}]$ where,

$$S_l = e^{2i\delta_l} \tag{207}$$

S is called the *scattering matrix* and S_l is the eigenvalues of this scattering matrix.

Optical Theorem

Remember that the optical theorem relates the cross-section to the scattering amplitude in the forward direction. For the inelastic scattering case the optical theorem is,

$$f(0) = \frac{1}{2ik}\sum_{l=0}^{\infty}(2l+1)(e^{2i\delta_l}-1) \tag{208}$$

$$Imf(0) = \frac{k}{4\pi}\sigma \tag{209}$$

This shows that the optical theorem is satisfied by the inelastic scattering case as well.

UNIT 2

Angular momentum

Notes by J. Mazer, A. Holt, and M. Rezaee

Angular Momentum

The angular momentum classically is given as:

$$\vec{L} = \vec{r} \times \vec{p} \tag{1}$$

When we write this as an operator is it shown that the components satisfy the communtation relation:

$$[L_x, L_y] = i\hbar L_z \tag{2}$$

If you want to understand nature, you have to be able to ask what values of L can you get? When we call the L, J, we see the same commutation relations are satisfied.

$$[J_x, J_y] = i\hbar J_z \tag{3}$$

We can find all the possible combinations by writing:

$$J_{\pm} = J_x \pm i\hbar J_y \tag{4}$$

and if writing J^2 as a vector, it is the sum of the squares of the components:

$$J^2 = J_x^2 + J_y^2 + J_z^2 \tag{5}$$

J^2 commutes with all the components, in particular lets look atJ_z:

$$[J^2, J_z] = 0 \tag{6}$$

Since these commute we can label them with common eigenvalues. Calling the eigenvalue λ and pulling out the $\hbar^2$ for dimensional reasons we get:

$$J^2 \mid \lambda, m\rangle = \lambda^2\hbar^2 \mid \lambda, m\rangle \tag{7}$$

Now as a state of J_z:

$$J_z \mid \lambda, m\rangle = \hbar \mid \lambda, m\rangle \tag{8}$$

When acting with J_- our m state is lowered by 1.

$$J_- \mid \lambda, m\rangle \propto \mid \lambda, m-1\rangle \tag{9}$$

In order to avoid the negative norm states we take the norm of a state and square it as:

$$\parallel J_- \mid \lambda, m\rangle \parallel^2 = [\lambda^2 - m(m-1)]\hbar^2 \geq 0 \tag{10}$$

Since it has to be positive we see:

$$m^2 - m - \lambda^2 \leq 0 \tag{11}$$

When this is thought of a polynomial of m it must satisfy the relation:

$$m_- \leq m \leq m_+ \tag{12}$$

Solving the polynomial we get the following roots:

$$m_\pm = \frac{1}{2}(1 \pm \sqrt{1+4\lambda^2}) \tag{13}$$

$$m = m_- + integer \tag{14}$$

Now acting with J_+ we go through the same story.

$$J_+ \mid \lambda, m\rangle \propto \mid \lambda, m+1\rangle \tag{15}$$

Writing the norm:

$$\parallel J_+ \mid \lambda, m\rangle \parallel^2 = [\lambda^2 - m(m+1)]\hbar^2 \tag{16}$$

It follows that:

$$m^2 + m - \lambda^2 \leq 0 \tag{17}$$

Where the roots to our polynomial are:

$$m\prime_\pm = \frac{1}{2}(-1 \pm \sqrt{1+4\lambda^2}) \tag{18}$$

$$m\prime_- \leq m \leq m\prime_+ \tag{19}$$

$$m = m\prime_+ + integer \tag{20}$$

Rearranging gives:

$$m\prime_+ - m_- = integer \tag{21}$$

Writing what these numbers are in terms of λ we get:

$$\frac{1}{2}(-1 + \sqrt{1+4\lambda^2}) - \frac{1}{2}(1 - \sqrt{1+4\lambda^2}) = integer \tag{22}$$

This integer is referred to as $2j$.

$$-1+\sqrt{1+4\lambda^2} = integer = 2j \tag{23}$$

Then:

$$\sqrt{1+4\lambda^2} = integer = 2j+1 \tag{24}$$

for $j = 0, \frac{1}{2}, 1, \frac{3}{2}, ...$
Squaring we get:

$$1+4\lambda^2 = (2j+1)^2 = 4j^2+4j+1 \tag{25}$$

Solving we get:

$$\lambda^2 = j(j+1) \tag{26}$$

Now we will present the first non-trivial case of $j = \frac{1}{2}$. We all consist of spin $\frac{1}{2}$ particles. Its not angular momentum anymore because we can never have values of halves. This has no classical analog to explain this, for this case we have:

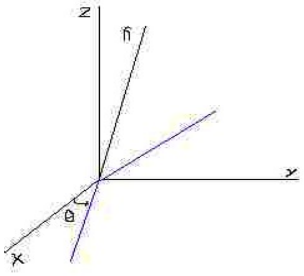
$$m = \pm\frac{1}{2} \tag{27}$$

We have two states given as:

$$\mid j,m\rangle = \begin{cases} \mid \frac{1}{2}\frac{1}{2}\rangle = \mid +\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \\ \mid \frac{1}{2}-\frac{1}{2}\rangle = \mid -\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \end{cases} \tag{28}$$

The particles that carry that spin are called spinors. Such examples are electrons (point particles) , protons, and neutrons which are made of quarks (point particles).

ROTATIONS



We want to understand what happens when you rotate something that is a spinor. Under rotation the vector components of r are transformed as:

$$\vec{r} = \begin{pmatrix} x \\ y \\ z \end{pmatrix} \Rightarrow \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} \tag{29}$$

by using the transformations for rotation about the Z-axis by an angle θ we have:

$$\begin{aligned} x\prime &= \cos(\theta)x - \sin(\theta)y \\ y\prime &= \sin(\theta)x + \cos(\theta)y \\ z\prime &= z \end{aligned} \tag{30}$$

We get the rotation matrix which is multiplied by our original vector components:

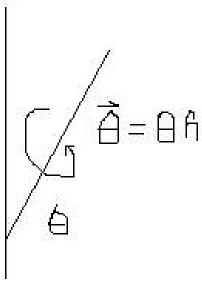
$$\begin{pmatrix} \cos(\theta) & -\sin(\theta) & 0 \\ \sin(\theta) & \cos(\theta) & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \tag{31}$$

For small θ, we make a Taylor expansion that gives:

$$\begin{pmatrix} \theta & -\theta & 0 \\ \theta & \theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \tag{32}$$

We can separate the 1's from the θ's we can write this as

$$= II \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \theta \begin{pmatrix} 0 & -1 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \tag{33}$$



The angular momentum is held responsible for generating such rotations, to see this we express this as:

$$\varphi(\vec{r}) \to \varphi(x - \theta y, y + \theta x, z) = \varphi(x, y, z) + \theta \left[-y\frac{\partial\varphi}{\partial x} + x\frac{\partial\varphi}{\partial y} \right] \tag{34}$$

where are coordinates are transformed in our function. Since we are rotating about the Z-axis, the proper component would be the Z component of the angular momentum. This is shown and then where it is converted to its operator form. Since θ is small we need to Taylor expand this function. Expanding in

θ we need to take the derivative, but we are taking the derivative of a variable that depends on another variable so we need to use the chain rule.

$$L_z = xp_y - yp_x \rightarrow -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \tag{35}$$

If we act on φ:

$$L_z\varphi = -i\hbar\left(x\frac{\partial \varphi}{\partial y} - y\frac{\partial \varphi}{\partial x}\right) \tag{36}$$

Pulling out common factors we see:

$$= \varphi(\vec{r}) + \frac{i\theta}{\hbar}L_z\varphi + ... = (II + \frac{i\theta}{\hbar}L_z)\varphi + ... = e^{i\frac{\theta}{\hbar}L_z}\varphi \tag{37}$$

This shows us that the wave equation is being operated on by an operator. If we choose another axis for rotation we can always just redefine our axis to meet the requirements. We can write the exponent as $\theta\hat{n}\cdot\vec{L} = \vec{\theta}\cdot\vec{L}$ when we have an arbitrary direction. θ is not the angle about the Z-axis, but the angle we rotate. Thinking of this as an operator, if we have a spinor, we can replace L by S:

$$\vec{S} = \frac{\hbar}{2}\vec{\sigma} \tag{38}$$

where σ is just our familiar Pauli matrices.
We can call this matrix R, and in terms of σ we have:

$$R = e^{\frac{i}{\hbar}\vec{\theta}\cdot\vec{S}} = e^{\frac{i}{2}\vec{\theta}\cdot\vec{\sigma}} \tag{39}$$

When we act on a spinor we get a 2x2 matrix. This matrix operator on a spinor rotates operator A like $A \rightarrow RAR^{-1}$. We get a 2 component object.
Lets choose $\hat{n} = \hat{z}$ to identify the Z-axis as the direction we are rotating about. Then if θ is small, keeping just the first two terms:

$$R = e^{\frac{i}{\hbar}\theta S_z} = II + \frac{i}{\hbar}\theta S_z + ... \tag{40}$$

We now want to find out what happens to S, in particular taking the component S_x and rotating we see:

$$\begin{aligned} S_x &\rightarrow RS_xR^{-1} \\ &= (II + \frac{i}{\hbar}\theta S_z)S_x(II - \frac{i}{\hbar}\theta S_z) + .. \\ &= S_x + \frac{i}{\hbar}\theta \S_z S_x - \frac{i}{\hbar}\theta S_x Sz + ... \\ &= S_x + \frac{i}{\hbar}\theta\left[S_z, S_x\right] + ... = S_x - \theta S_y + ... \end{aligned} \tag{41}$$

So now, going back to the matrix, we want to see how to write it. We want to keep $\hat{n}$ in the Z-direction. R is expressed with an exponent which can be expanded in a series to yield:

$$\begin{aligned} R = e^{\frac{i}{2}\theta\sigma_z} &= \sum_{n=0}^{\infty} \frac{1}{n!}\left(\frac{i\theta}{2}\right)^n \sigma_z^n \\ &= II\left(1 + \frac{1}{2!}\left(\frac{i\theta}{2}\right)^2 + ..\right) + \sigma_z\left(\frac{i\theta}{2} + \frac{1}{3!}\left(\frac{i\theta}{2}\right)^3 + ..\right) \\ R &= \cos\frac{\theta}{2} II + i\sin\frac{\theta}{2}\sigma_z \end{aligned} \tag{42}$$

This last equation for R is a single matrix and is what we get when we have rotation around the Z-axis. All the even terms are proportional to the identity and the odd terms are proportional to σz. If we replace $\sigma_z = \hat{n} \cdot \vec{\sigma}$ we get the rotation around an arbitrary axis.
The table below shows what σ's behavior is for different values of n.

n	σ_z^n
0	II
1	σ_z
2	II
3	σ_z
..	..

If we rotate by $\theta = 2\pi$ we get:

$$\begin{aligned} R(2\pi) &= \cos\pi II + i\sin\pi\sigma_z = -II \\ R(4\pi) &= II \end{aligned} \tag{43}$$

Therefore we see we need to rotate by 4π to get back to where we started. Our everday experiences would suggest 2π, but our everyday experience uses operator and observables. $A \to RAR^{-1} = (-II)A(-II) = A$ The physicial consequences of what we see for R is that if we operate on a spinor by rotating 2π, we get: $R(2\pi) \mid \varphi\rangle = - \mid \varphi\rangle$. Which gives us $-\varphi$, but with a phase, and as far as the probability is concerned this sign doesn't matter, but the phase is very important when dealing with interference effects.

Two Spinors

Two Spinors has four states: $\mid ++\rangle, \mid +-\rangle, \mid -+\rangle, \mid --\rangle$. They are eigenstate of spin operators: $\vec{S_1}$, and $\vec{S_2}$, so we have a total of six components. For the particles we now get states: $S_1^2, S_{1z}, S_2^2, S_{2z}$.
If we operate S_1^2 we get:

$$S_1^2 \mid \pm\pm\rangle = \frac{3}{4}\hbar^2 \mid \pm\pm\rangle \tag{44}$$

They form a basis so, S_1^2 is 4x4 diagonalizable matrix and we get this same result acting on any of our 4 initial states as indicated by the ± signs.
Since they form a basis we always get the same eigenvalue we get the same result for S_1^2 and S_2^2.

$$S_1^2 = \frac{3}{4}\hbar^2 II = S_2^2 \tag{45}$$

If we want to write S_{1z}, we act on the 1st component (1st particle) of our four initial vectors and get:

$$S_{1z} = \frac{\hbar}{2}\begin{pmatrix} +1 & 0 & 0 & 0 \\ 0 & +1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \tag{46}$$

It is diagonizable with eigenvalues 1, 1, -1, -1.
If we do the same thing for S_{2z}, we act on the 2nd component (2nd particle) of each of our four states.

$$S_{2z} = \frac{\hbar}{2}\begin{pmatrix} +1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & +1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \tag{47}$$

TOTAL SPIN

If we want to define total spin then $\vec{S} = \vec{S_1} + \vec{S_2}$ which follows the commuation relation $\left[S^2, S_z\right] = 0$. This means that they commute. We can ask what are their common eigenstates? To find them we write S_z in its matrix form and again it is diagonizable.

$$S_z = S_{1z} + S_{2z} = \hbar\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \tag{48}$$

Writing S^2, we already know S_1^2 and S_2^2 are the identity matrix.

$$\begin{aligned} S^2 &= (\vec{S_1} + \vec{S_2}) \\ &= S_1^2 + S_2^2 + 2\vec{S_1} \cdot \vec{S_2} \end{aligned} \tag{49}$$

We expand this dot product and use S_+ and S_-,

$$S_\pm = (S_x \pm iS_y) \tag{50}$$

to get:

$$\begin{aligned} 2\vec{S_1} \cdot \vec{S_2} &= 2S_{1x}S_{2x} + 2S_{1y}S_{2y} + 2S_{1z}S_{2z} \\ &= S_{1+}S_{2-} + S_{1-}S_{2+} + 2S_{1z}S_{2z} \end{aligned} \tag{51}$$

By acting on a state with S_+ and S_-, we see:

$$\begin{aligned} S_+ \mid +\rangle &= 0 \\ S_- \mid +\rangle &= \hbar \mid -\rangle \\ S_+ \mid -\rangle &= \hbar \mid +\rangle \\ S_- \mid -\rangle &= 0 \end{aligned} \tag{52}$$

Now if we act with S^2 on the first state $\mid ++\rangle$:

$$S^2 \mid ++\rangle = \frac{3}{2}\hbar^2 \mid ++\rangle + 2(\frac{\hbar}{2})^2 \mid ++\rangle = 2\hbar^2 \mid ++\rangle \tag{53}$$

And now the second state and third states. We get the same result as the $\mid +-\rangle$ when acting on $\mid -+\rangle$.

$$S^2 \mid +-\rangle = S^2 \mid -+\rangle = \hbar^2 \mid +-\rangle + \hbar^2 \mid -+\rangle \tag{54}$$

Acting on $\mid --\rangle$ we get the same result as $\mid ++\rangle$

$$S^2 \mid --\rangle = 2\hbar^2 \mid --\rangle \tag{55}$$

Since we know how to act on the basis we now know the matrix of S^2. We are no longer diagonal.

$$S^2 = \hbar^2 \begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 2 \end{pmatrix} \tag{56}$$

To find the common eigenstates we need to diagonalize this matrix. So we first need to find the eigenvalues of this matrix.

$$0 = det(S^2 - \lambda II) = \begin{pmatrix} 2-\lambda & 0 & 0 & 0 \\ 0 & 1-\lambda & 1 & 0 \\ 0 & 1 & 1-\lambda & 0 \\ 0 & 0 & 0 & 2-\lambda \end{pmatrix} \tag{57}$$

Solving for the eigenvalues by find the determinant gives:

$$= (2-\lambda)^2 \left[(1-\lambda)^2 - 1\right] = (2-\lambda)^2(\lambda^2 - 2\lambda) = \lambda(\lambda-2)^3 \tag{58}$$

with eigenvalues $\lambda = 2, 0$ The degeneracy is $2l+1$, such that $\lambda = l(l+1)$. So for $\lambda = 0 \rightarrow l = 0$ and for $\lambda = 2 \rightarrow l = 1$

2 spinors

A spinor means the particle which has spin half and when we have two spinors we have 4 states. The can be written as:

$$\mid ++\rangle \tag{59}$$

$$| +-\rangle \tag{60}$$

$$| -+\rangle \tag{61}$$

$$| --\rangle \tag{62}$$

$$S_\pm = (S_x \pm iS_y) \tag{63}$$

$$\vec{S} = \vec{S_1} + \vec{S_2} \tag{64}$$

$$[S^2, S_z] = 0 \tag{65}$$

I want to find the common eigenstates of these two.

$$S^2 = \hbar^2 \begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 1 & 1 & 0 \\ 0 & 0 & 0 & 2 \end{pmatrix} \tag{66}$$

The eigenvalues are 1 and 0. The $l = 1$ it has degeneracy of three. The $l = 0$ has the degeneracy of one. We want to figure out the eigenstates and:

$$| ++\rangle =| 11\rangle \tag{67}$$

$$| --\rangle =| 1-1\rangle \tag{68}$$

$$| --\rangle =| 1-1\rangle \tag{69}$$

$$| 10\rangle = \frac{1}{\sqrt{2}}(| +-\rangle + | -+\rangle) \tag{70}$$

$$| 10\rangle = \frac{1}{\sqrt{2}}(| +-\rangle - | -+\rangle) \tag{71}$$

$$m_1 = -\frac{1}{2}, +\frac{1}{2} \tag{72}$$

$$m_1 = -\frac{1}{2}, +\frac{1}{2} \tag{73}$$

$$m_2 = -\frac{1}{2}, +\frac{1}{2} \tag{74}$$

The original number of states, which is $3 + 1 = 4$. All three of these states have a spin of one.

$$\begin{aligned} S_+ \mid 11\rangle &= 0 \\ S_- \mid 11\rangle &=\mid 10\rangle \\ S_- \mid 10\rangle &=\mid 1-1\rangle \end{aligned} \tag{75}$$

The states correspond to: $S = 1$ being all symmetric and $S = 0$ being antisymmetric.

Alternative Derivation:

$$M = m_1 + m_2 \tag{76}$$

$$\mid ++\rangle = \mid 11\rangle \tag{77}$$

what we should do is to select highest m_1 and the highest m_2

$$m_1 = m_2 = +\frac{1}{2} \tag{78}$$

Therefore $M = 1$ and S must be equal to 1. How we can find the forth state? We know the 4th state should be orthogonal to all the previous S=1 states. Therefore:

$$\mid 00\rangle = \frac{1}{\sqrt{2}}(\mid +-\rangle - \mid -+\rangle) \tag{79}$$

So lets generalize our results: Imagine instead of two spin half particles we have one angular momentum J_1 and another angular momentum J_2. J could be the spin or a combination of angular momentum and spin. We know the eigenstates of the J_1 which is:

$$\mid j_1 m_1\rangle \tag{80}$$

and for J_2 which is

$$\mid j_2 m_2\rangle \tag{81}$$

and when we put the two particle in one system then we will have:

$$\mid j_1 j_2; m_2 m_2\rangle \tag{82}$$

for the eigenstate. Now we want to build states which belong to total angular momentum and we define the total angular momentum as:

$$\vec{J} = \vec{J_1} + \vec{J_2} \tag{83}$$

And the set of commuting observables $\{J^2, J_z\}$. So we should be able to find states which have quantum numbers appropriate for these two and they will be:

$$\mid J; M\rangle \tag{84}$$

So we want to find the common eigenstates of J^2 and J_z :

$$J^2 \mid J; M\rangle = \hbar^2 J(J+1) \mid J; M\rangle \tag{85}$$

$$J_z \mid J; M\rangle = \hbar M \mid J; M\rangle \tag{86}$$

Now we want to find all the eigenvalues. We know that $m_1 = -j_1, ..., j_1$ and $m_2 = -j_2, ..., j_2$ so we will have space with $(2j_1+1)*(2j_2+1)$ different eigenvalues and that is how many states we have the highest possible M is $j_1 + j_2$ and there is only one state which has the highest M?

$$| \, j_1 j_2; j_1 j_2 \rangle = | \, j_1 + j_2; j_1 + j_2 \rangle \tag{87}$$

and

$$M = -J, ..., J \tag{88}$$

By acting J_- we should be able to produce other states. Lets count the states which we have here.
Example:
Lets choose $j_1 = 3$ and $j_3 = 2$ how many states do we have originally:

$$(2j_1 + 1) \times (2j_2 + 1) = (2 \times 3 + 1) \times (2 \times 2 + 1) = 7 \times 5 = 35 \tag{89}$$

So $J = 5, 4, 3, 2, 1, 0$ but can we really have all these numbers? The degeneracy of $J = 5$ is $11 = 2 \times 5 + 1$ and for the other J:

J	Degeneracy
4	9
3	7
2	5
1	3
0	1

If we add all these degeneracies we will have $11 + 9 + 7 + 5 + 3 + 1 = 36$ and this tells us that we can not have $J = 0$. So the $J_{max} = 5$ and the $J_{min} = 1$. We can say:

$$J_{max} = j_1 + j_2 \tag{90}$$

$$J_{min} = j_1 - j_2 \tag{91}$$

By counting states
if $j_1 \geq j_2$ and we do know that for each J we have $2J + 1$ multiplicity

$$\sum_{j_1 - j_2}^{j_1 + j_2} (2J + 1) = 2 \sum_{j_1 - j_2}^{j_1 + j_2} J + \sum_{j_1 - j_2}^{j_1 + j_2} 1 \tag{92}$$

$$= 2(\sum_{1}^{j_1 + j_2} J - \sum_{1}^{j_1 - j_2 - 1} J) + j_1 + j_2 - (j_1 - j_2) + 1 \tag{93}$$

by using:

$$\sum_{1}^{N} J = \frac{N(N+1)}{2} \tag{94}$$

We will have:

$$(j_1+j_2)(j_1+j_2+1)-(j_1+j_2-1)(j_1-j_2)+2j_2+1 \tag{95}$$

By doing simple algebra here we will have:

$$=(j_1+j_2)^2+j_1+j_2-(j_1-j_2)^2\ +j_1-j_2+2j_2+1 \tag{96}$$

So we can write it as:

$$=4j_1j_2+2j_1+2j_2+1 \tag{97}$$

By factoring this:

$$=(2j_1+1)(2j_2+1) \tag{98}$$

That is exactly the number of states we began with and tells us that our guess was very good. So:

$$j_1+j_2\geq J\geq |j_1-j_2| \tag{99}$$

This gives the angular momentum a nice vector sense and in this picture we can visualize it as a vector. Lets construct all those eigenstates by starting from the highest eigenstate and acting J_- on that state.

$$M_{highest}=j_1+j_2 \tag{100}$$

$$\mid j_1j_2;j_1j_2\rangle=\mid j_1+j_2;j_1+j_2\rangle \tag{101}$$

The general formula for J_- is given as:

$$J_-\mid J,M\rangle=\hbar\sqrt{J(J+1)-M(M-1)}\mid J,M-1\rangle \tag{102}$$

acting J_- on the highest state we have:

$$J_-\mid j_1+j_2,j_1+j_2\rangle= \tag{103}$$
$$\hbar\sqrt{(j_1+j_2)(j_1+j_2+1)-(j_1+j_2-1)}\mid j_1+j_2,j_1+j_2-1\rangle \tag{104}$$

$$=\hbar\sqrt{(j_1+j_2)}\mid j_1+j_2,j_1+j_2-1\rangle \tag{105}$$

So this tells us we can have new state by acting J_- on the highest one the new state:

$$\mid\psi\rangle=\mid j_1+j_2,j_1+j_2-1\rangle=\frac{1}{\hbar\sqrt{2(j_1+j_2)}}J_-\mid j_1+j_2,j_1+j_2\rangle \tag{106}$$

To figure out the new state we write it as:

$$=\frac{1}{\hbar\sqrt{2(j_1+j_2)}}(J_{1-}+J_{2-})\mid j_1j_2,j_1j_2\rangle \tag{107}$$

Then we write it using J_{1-} and J_{2-}.

$$= \frac{1}{\hbar\sqrt{2\,(j_1+j_2)}}\Big(\hbar\sqrt{j_1(j_1+1)-j_1(j_1-1)}\mid j_1j_2;j_1-1j_2\rangle$$
$$+\hbar\sqrt{j_2(j_2+1)-j_2(j_2-1)}\mid j_1j_2;j_1j_2-1\rangle\ ) \tag{108}$$

So by summarizing it we have:

$$= \sqrt{\frac{j_1}{j_1+j_2}}\mid j_1j_2;j_1-1j_2\rangle + \sqrt{\frac{j_2}{j_1+j_2}}\mid j_1j_2;j_1j_2-1\rangle \tag{109}$$

So this is our new state. By repeating this procedure we can have all the M values. We started with $M = j_1 + j_2$ and we have all of them now:

$$M = j_1+j_2, j_1+j_2-1, \ldots, -j_1-j_2 \tag{110}$$

So we know two states which have the M that we want. Do we know any other states? There are no other states and we can find that by a simple arithmetic. Here we only have two choices and we want to have the state with highest M and would have to be a linear combination of these two and also it has to be orthogonal to these two states and this is:

$$= \sqrt{\frac{j_1}{j_1+j_2}}\mid j_1j_2;j_1-1j_2\rangle - \sqrt{\frac{j_2}{j_1+j_2}}\mid j_1j_2;j_1j_2-1\rangle \tag{111}$$

and this tells us

$$\mid j_1+j_2+1j_1+j_2+1\rangle = \sqrt{\frac{j_1}{j_1+j_2}}\mid j_1j_2;j_1-1j_2\rangle - \sqrt{\frac{j_2}{j_1+j_2}}\mid j_1j_2;j_1j_2-1\rangle \tag{112}$$

So we constructed the next state by acting J_- on the highest M.
We can repeat this until we have all the states. All these has been summarized by the Clebsch-Gordan Coefficients.

Clebsch-Gordan Coefficients

We start with:

$$\mid j_1j_2;m_1m_2\rangle \Longrightarrow \mid JM\rangle \tag{113}$$

RHS and LHS of the above form an orthonormal bases.

$$\mid JM\rangle = \sum_{m_1=-j_1}^{j_1}\sum_{m_2=-j_2}^{j_2} a_{JMm_1m_2}\mid j_1j_2;m_1m_2\rangle \tag{114}$$

most of the coefficients (a) are 0 and if you multiply both sides by bra of the RHS we will have the coefficients:

$$a_{JMm_1m_2} = \langle j_1j_2;m_1m_2\mid JM\rangle \tag{115}$$

and these coefficients are all real (and remember that most of them are zero) and so if we take the complex conjugate we would have the same number:

$$= \langle JM \mid j_1 j_2; m_1 m_2 \rangle \tag{116}$$

and we know that:

$$M = m_1 + m_2 \tag{117}$$

otherwise the coefficient is zero and this reduces the number of coefficients and also we figure out:

$$|j_1 - j_2| \leq J \leq j_1 + j_2 \tag{118}$$

and that relation also reduces the number of coefficient to.
Example: We have

$$\langle j_1 j_2 + j_1 j_2 \;\; \mid j_1 + j_2; j_1 + j_2 \rangle = 1 \tag{119}$$

So here it should be 1 and if we have:

$$\langle j_1 j_2; j_1 - 1 j_2 \mid j_1 + j_2; j_1 + j_2 - 1 \rangle = \sqrt{\frac{j_1}{j_1 + j_2}} \tag{120}$$

the coefficient is $\sqrt{\frac{j_1}{j_1+j_2}}$ and also for:

$$\langle j_1 j_2; j_1 j_2 - 1 \mid j_1 + j_2; j_1 + j_2 - 1 \rangle = \sqrt{\frac{j_2}{j_1 + j_2}} \tag{121}$$

So these are the coefficients.

$$\sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} \mid j_1 j_2; m_1 m_2 \rangle \langle j_1 j_2; m_1 m_2 \mid = 1 \tag{122}$$

$$\sum a_{JMm_1m_2} a_{J'M'm_1m_2} = \delta_{JJ'} \delta_{MM'} \tag{123}$$

$$\sum_{J=|j_1-j_2|}^{j_1+j_2} \sum_{M=-J}^{J} \mid JM \rangle \langle JM \mid = 1 \tag{124}$$

$$\langle j_1 j_2 m_1 m_2 \mid \sum a_{JMm_1m_2} a_{JMm'_1m'_2} \rangle = \delta_{m_1 m'_1} \delta_{m_2 m'_2} \tag{125}$$

because a's are orthonormals to each other.
Last time we spoke of Clebsch-Gordan Coefficients. You obtain these from transforming basis.

$$|JM\rangle = \sum \; A_{JMj_1j_2m_1m_2} \, |j_1 j_2; m_1 m_2\rangle \tag{126}$$

where

$$A_{JMj_1j_2m_1m_2} = \langle j_1j_2; m_1m_2 \,|\, JM\rangle = \langle JM \,|\, j_1j_2; m_1m_2\rangle \tag{127}$$

$$|j_1j_2; m_1m_2\rangle = \sum_{J=|j_1-j_2|}^{j_1+j_2} \sum_{M=-J}^{J} A_{JMj_1j_2m_1m_2} \,|JM\rangle \tag{128}$$

and

$$\sum \sum |j_1j_2; m_1m_2\rangle \langle j_1j_2; m_1m_2| = II \tag{129}$$

$$\sum \sum |JM\rangle \langle JM| = II \tag{130}$$

Recurrence Relations

Act on equation (1.1) with the J_- operator.

$$\vec{J} = \vec{J_1} + \vec{J_2} \tag{131}$$

From last semester we know:

$$J_- \,|JM\rangle = \hbar\sqrt{J(J+1) - M(M-1)}\, |JM_{-1}\rangle \tag{132}$$

But now our state, $|JM\rangle$, is made up of two states. Introduce a sum to include the lowering operator acting on $m_1$and m_2.

$$\begin{aligned} J_- \,|JM\rangle \quad &= \sum A_{JMj_1j_2m_1m_2}[\hbar\sqrt{j_1(j_1+1) - m_1(m_1-1)}\, |j_1j_2; m_1-1m_2\rangle \\ &+\hbar\sqrt{j_2(j_2+1) - m_2(m_2-1)}\, |j_1j_2; m_1m_2-1\rangle] \end{aligned}$$

Take the inner product:

$$\left\langle j_1j_2; m_1^{'}m_2^{'} \,\middle|\, j_1j_2; m_1m_2-1 \right\rangle \tag{133}$$

Using equation (1.3) we obtain

$$\begin{aligned} (1.8) \quad &= \quad \hbar\sqrt{J(J+1) - M(M-1)}a_{JM-1j_1j_2m_1'm_2'} \\ &= \quad \sum a_{JMj_1j_2m_1m_2}\hbar\sqrt{j_1(j_1+1) - m_1(m_1-1)}\delta_{m_1-1m_1'}\delta_{m_2m_2'} \\ &+ \quad \hbar\sqrt{j_2(j_2+1) - m_2(m_2-1)}\delta_{m_1m_1'}\delta_{m_2-1m_2'} \\ &= \quad \hbar\sqrt{j_1(j_1+1) - m_1(m_1+1)}a_{JMj_1j_2m_1'+1m_2'} \\ &+ \quad \hbar\sqrt{j_2(j_2+1) - m_2(m_2+1)}a_{JMj_1j_2m_1'm_2'+1} \end{aligned} \tag{134}$$

Example 1: $j_1 = j_2$

(Remember we can rewrite $|lm\rangle$ as $Y_l^m(\theta, \psi)$)

If $j_1 = j_2 = 1$ and $m_1, m_2 = -1, 0, 1$, Then I'm interested in the state

$$|11; m_1 m_2\rangle \rightarrow Y_{l_1}^{m_1}(\theta, \psi) Y_{l_2}^{m_2}(\theta, \psi) \tag{135}$$

Where J can take on three values: $0, 1, 2$

First case: J = 2

Start with the highest state $|22\rangle = |11; 11\rangle$ and act on it with J_-.

$$J_- |22\rangle = \hbar\sqrt{2(2+1) - 2(2-1)}\,|21\rangle = 2\hbar\,|21\rangle \tag{136}$$

We can also write (1.11) as:

$$|21\rangle = A\,|11; 01\rangle + B\,|11; 10\rangle \tag{137}$$

By normalization we can determine the coefficients are $\sqrt{2}\hbar$. Therefore our normalized state is: $|21\rangle = \frac{1}{\sqrt{2}}[|11; 01\rangle + |11; 10\rangle]$

→ Repeat this process for $|21\rangle, |20\rangle$, and $|2-1\rangle$.

$$|20\rangle = \frac{1}{\sqrt{6}}[|11; 1-1\rangle + 2\,|11; 00\rangle + |11; -11\rangle] \tag{138}$$

$$|2-1\rangle = \frac{1}{\sqrt{2}}[|11; 0-1\rangle + |11; -10\rangle] \tag{139}$$

$$|2-2\rangle = |11; -1-1\rangle \tag{140}$$

Take time to notice that the $|2-1\rangle$ and $|2-2\rangle$ states are mirror images of the $|21\rangle$ and $|22\rangle$ states (with $m = -m$).

Second case: J = 1

From inspection we can deduce $|11\rangle = \frac{1}{\sqrt{2}}(|11; 10\rangle - |11; 01\rangle)$.
By applying the lowering operator J_- to $|11\rangle$ we see:

$$J_- |11\rangle = |10\rangle = \frac{1}{\sqrt{2}}(|11; 1-1\rangle - |11; -11\rangle - 0\,|11; 00\rangle) \tag{141}$$

Therefore,

$$|10\rangle = \frac{1}{\sqrt{2}}(|11; 1-1\rangle - |11; -11\rangle) \tag{142}$$

$$|1-1\rangle = \frac{1}{\sqrt{2}}(|11; 0-1\rangle - |11; 0-1\rangle -) \tag{143}$$

Third case: J = 0

$$|00\rangle = a\,|11;1-1\rangle + b\,|11;-11\rangle - c\,|11;00\rangle \tag{144}$$

We can deduce a, b, and c by exploiting orthogonality.

$$\begin{gathered}\langle 00\,|\,10\rangle = \tfrac{1}{\sqrt{2}}(a-b) = 0\\ \langle 00\,|\,20\rangle = \tfrac{1}{\sqrt{6}}(a+2c-b) = 0\\ a = b \rightarrow 2b+2c = 0 \rightarrow a = b = -c\\ \text{Normalize: } a^2+b^2+c^2 = 1 \rightarrow a = \tfrac{1}{\sqrt{3}}\end{gathered}$$

$$|00\rangle = \frac{1}{\sqrt{3}}(|11;1-1\rangle + |11;-11\rangle - |11;00\rangle) \tag{145}$$

Example 2: $j_1 = l_1$ **and** $j_2 = l_2$

$$|l_1 l_2; m_1 m_2\rangle \rightarrow Y_{l_1}^{m_1}(\theta_1,\psi_1) Y_{l_2}^{m_2}(\theta_2,\psi_2)$$

$$|LM\rangle \rightarrow \Phi(\theta_1,\psi_1;\theta_2,\psi_2) =$$

$$\sum\sum \langle l_1 l_2; m_1 m_2\,|\,LM\rangle\, Y_{l_1}^{m_1}(\theta_1,\psi_1) Y_{l_2}^{m_2}(\theta_2,\psi_2)$$

$$Y_{l_1}^{m_1}(\theta_1,\psi_1) Y_{l_2}^{m_2}(\theta_2,\psi_2) = \sum\sum \langle l_1 l_2; m_1 m_2\,|\,LM\rangle\, \Phi(\theta_1,\psi_1;\theta_2,\psi_2) \tag{146}$$

Two Coincident particles

$$\theta = \theta_1 = \theta_2 \text{ and } \psi = \psi_1 = \psi_2$$

$\Phi_{LM} = A(\theta,\psi)$ represents the probablity amplitude (wavefunction).

Where $|A|^2$ = probability of particles "coinciding" in a given direction.

Think of A as a single particle: $A_{LM} = \sum a_{lm} Y_l^m$
Apply L_z to A_{LM}:

$$L_z A_{LM}(\theta,\psi) = -i\hbar \frac{\partial}{\partial \psi} A_{LM} \tag{147}$$

$$-i\hbar \frac{\partial}{\partial \psi} A_{LM} = -i\hbar \frac{\partial}{\partial \psi_1} A_{LM} + -i\hbar \frac{\partial}{\partial \psi_2} A_{LM} \tag{148}$$

$$L_z A_{LM}(\theta,\psi) = (m_1\hbar + m_2\hbar) A_{LM} = M\hbar A_{LM} \tag{149}$$

This tells us that A_{LM} must be a **single** spherical harmonic and shares common eigenstates

Therefore A_{LM} is no longer a sum.

$$A_{LM} = a_{LM} Y_L^M \tag{150}$$

and

$$L_z A_{LM} = M\hbar A_{LM} \tag{151}$$

$$L^2 A_{LM} = \hbar(L+1) L A_{LM} \tag{152}$$

If we apply the lowering operator to A_{LM} we get

$$L_- A_{LM} = \hbar\sqrt{L(L+1) - M(M-1)} A_{LM-1} \tag{153}$$

Which is the same as when we apply the lowering operator to a spherical harmonic.

$$L_- A_{LM} = \hbar\sqrt{L(L+1) - M(M-1)} Y_L^{M-1} \tag{154}$$

From this we see a_{LM} is independent of M and we have this final expression:

$$A_L^M = a_L Y_L^M \tag{155}$$

Consider the forward direction. Set $\theta_1 = \theta_2 = 0$ or $\psi_l^m(0, \psi)$
The sum will collapse to:

$$\Phi_{LM}(0, \psi; 0, \psi) = \langle l_1 l_2 00 \,|\, L0 \rangle \, Y_{l_1}^0(0, \psi) Y_{l_2}^0(0, \psi) \tag{156}$$

$$\Phi_{LM}(0, \psi; 0, \psi) = A_L^0(0, \psi) = a_L Y_{l_1}^0(0, \psi) = a_L \sqrt{\frac{2L+1}{4\pi}} \tag{157}$$

$$a_L = \sqrt{\frac{(2l_1+1)(2l_2+1)}{4\pi(2L+1)}} \, \langle l_1 l_2 00 \,|\, L0 \rangle \tag{158}$$

Set $\theta_1 = \theta_2 = \theta$

$$Y_L^M(\theta, \psi) = \frac{1}{a_L} \sum \langle l_1 l_2; m_1 m_2 \,|\, LM \rangle \, Y_{l_1}^{m_1}(\theta, \psi) Y_{l_2}^{m_2}(\theta, \psi) \tag{159}$$

This is known as the spherical harmonic addition relation.
Take the inner product:

$$\int d^2\Omega Y_{l_1}^{m_1}(\Omega) Y_{l_2}^{m_2}(\Omega) Y_{l_3}^{m_3}(\Omega) = \tag{160}$$

$$\sum \langle l_1 l_2; m_1 m_2 \,|\, LM \rangle \, a_L \int Y_{l_3}^{m_3}(\Omega) Y_L^M d\Omega \tag{161}$$

Using the relation: $Y_l^m = (-1)^m Y_l^{-m}$. We see that only one term survives:

$$\int d^2\Omega Y_{l_1}^{m_1}(\Omega) Y_{l_2}^{m_2}(\Omega) Y_{l_3}^{m_3}(\Omega) = (-1)^m a_{l_3} \langle l_1 l_2; m_1 m_2 \,|\, l_3 - m_3 \rangle \tag{162}$$

$m_1 + m_2 = -m_3$ and $|l_1 - l_2| \leq l_3 \leq l_1 + l_2$
This relates to last semester when we studied the rotational eigenstates of the ammonia molecule.

$$\left\langle l_1 m_1 \left| Y_{l_2}^{m_2} \right| l_3 m_3 \right\rangle \tag{163}$$

Where the spherical harmonic represents the electric dipole moment and the m values represent the energy levels.

Wigner-Eckart Theorem

Scalars

What is the definition of an scalar? It is invariant under rotations or in other word it is simply one number. An example of common scalar operators are $\vec{r}^2$ and $\vec{p}^2$.

$$\vec{r} \cdot \vec{p} + \vec{r} \cdot \vec{p} \tag{164}$$

Total angular momentum always generates rotation and we have which is consists of Angular Momentum and Spin:

$$\vec{J} = \vec{L} + \vec{S} \tag{165}$$

To check to see if it is invariant under rotation we just need to check for an infinitesimal roation. We have a convenient check at hand, by definition of a QM scalar, if the commutator with J vanishes then we have a scalar. If the commutator is zero then no matter how complicated the matrix is it means that the quantity is scalar.

$$\left[A, \vec{J}\right] = 0 \tag{166}$$

Vectors

To see what is the definition of vector lets do the infinitesimal rotation again.

$$\vec{r} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}, \vec{p}, \vec{L}, \vec{S}, \vec{J} \tag{167}$$

If we do a very small roation around the Z-axis, then we would have for rotations with $\theta << 1$,:

$$\begin{aligned} x\prime &= x - \theta y \\ y\prime &= y + \theta x \\ z\prime &= z \\ \vec{r}\prime &= \vec{r} + \frac{1}{i\hbar}\theta \left[L_z, \vec{r}\right] \end{aligned} \tag{168}$$

$$[L_z, x] = [xp_y - yp_x, x] = i\hbar y \tag{169}$$

$$[L_z, y] = [xp_y - yp_x, y] = -i\hbar x \tag{170}$$

$$[L_z, z] = [xp_y - yp_x, z] = 0 \tag{171}$$

So in other words, the transformation of $\vec{r}$ is going to be the $[\vec{r}, L_z]$:

$$[L_z, \vec{r}] = [xp_y - yp_x, \vec{r}] = -i\hbar \begin{pmatrix} -y \\ x \\ 0 \end{pmatrix} \tag{172}$$

$$\vec{V} = \begin{pmatrix} V_x \\ V_y \\ V_z \end{pmatrix} \tag{173}$$

So if it is a vector the results of commuting with J should be like this.

$$[J_i, V_j] = i\hbar\varepsilon_{ijk}V_k \tag{174}$$

with

$$\varepsilon_{ijk} = \left(\begin{array}{l} 1 : cyclic \\ -1 : noncyclic \\ 0 : repeated \end{array} \right. \tag{175}$$

Through the cyclic permutations of the above commutator we are given 9 relations which define a vector. We know three and the other 6 can be found with them. Lets switch back to scalars, saying A is a scalar and we want to know the matrix elements of it. Eigenstates of A are given in the basis:

$$\mid jm\rangle \tag{176}$$

$$\langle j'm' \mid A \mid jm\rangle = a_{jm}\langle j'm' \mid jm\rangle \tag{177}$$

We know that: $[A, J_z] = 0$ and $\left[A, J^2\right] = 0$ and thus we see that A, J_z, J^2 form a C.S.C.O. We know that if two operators commute so they share the same common eigenstates.

$$A \mid jm\rangle = a_j \mid jm\rangle \tag{178}$$

The selection rules tell us a transition is only possible when $\langle j'm' \mid A \mid jm\rangle \neq 0$ only if $j' = j$ and $m' = m$.

$$\langle j'm' \mid [J_+, A] \mid jm\rangle = 0 \tag{179}$$

$$\begin{aligned} \langle j'm' \mid J_+A \mid jm\rangle = \langle j'm' \mid AJ+ \mid jm\rangle = \\ = \hbar\sqrt{j'(j'+1) - m'(m'-1)}a_{jm}\langle j'm'-1 \mid jm\rangle = \\ = \hbar\sqrt{j(j+1) - m(m-1)}a_{jm-1}\langle j'm' \mid jm+1\rangle = \end{aligned} \tag{180}$$

$m = m\prime - 1$
$a_{jm+1} = a_{jm} = a_{jm-1} = a_{jm-2} = a_j$
$j\prime = j$
When j is fixed then A is a matrix and we have $2j + 1$ states and we can think about A as $(2j + 1) * (2j + 1)$ matrix, $\mid jm\rangle$, where $m = -j \cdots j$. This matrix is symmetric and it is identity.

$$A = a_j II_{(2j+1)\times(2j+1)} \tag{181}$$

B is also a scalar:

$$B \mid jm\rangle = b_j \mid jm\rangle \tag{182}$$

$B = b_j II$
So we can see $A \propto B$ and it can be rewritten in the form of $\Rightarrow A = \lambda B$ where $\lambda = \frac{a_j}{b_j}$.

Vectors

By using our definition of vectors. Instead of A here we have V which has three separate components:

$$[V_z, J_z] = 0 \tag{183}$$

$$\langle j\prime m\prime \mid [V_z, J_z] \mid jm\rangle = 0 \tag{184}$$

$$\langle j\prime m\prime \mid V_z J_z \mid jm\rangle = \langle j\prime m\prime \mid J_z V_z \mid jm\rangle \tag{185}$$

$$\hbar m\langle j\prime m\prime \mid V_z \mid jm\rangle = \hbar m\prime\langle j\prime m\prime \mid V_z \mid jm\rangle \tag{186}$$

So $\langle j\prime m\prime \mid V_z \mid jm\rangle = 0$ or $m = m\prime$ Lets try for other components.

$$V_\pm = V_x \pm iV_y \tag{187}$$

$$[J_z, V_+] = \hbar V_+ \tag{188}$$

$$[J_z, V_-] = -\hbar V_- \tag{189}$$

Lets see what we can do for V_x:

$$\begin{aligned} \langle j\prime m\prime \mid [J_z, V_\pm] \mid jm\rangle &= \pm\hbar\langle j\prime m\prime \mid V_\pm \mid jm\rangle \\ &= \hbar m\langle j\prime m\prime \mid V_\pm \mid jm\rangle - \hbar m\prime\langle j\prime m\prime \mid V_\pm \mid jm\rangle \end{aligned} \tag{190}$$

So we can conclude that $\langle j\prime m\prime \mid V_\pm \mid jm\rangle = 0$ unless $m\prime = m + 1$. For V_- we have the same. So we have selection Rules which are:

$$\begin{aligned} V_z &: \triangle m = 0 \\ V_\pm &: \triangle m = \pm 1 \end{aligned} \tag{191}$$

Now if we fix j, what we can say about the matrices?

$$[J_+, V_+] = [J_x + iJ_y, V_x + iV_y] = i(i\hbar)V_z + i(-i\hbar)V_z = 0 \tag{192}$$

Now lets consider the matrix elements, we specialize it for simplicity of calculations:

$$\langle j\prime m\prime \mid J_+V_+ \mid jm\rangle = \langle j\prime m\prime \mid V_+J_+ \mid jm\rangle \tag{193}$$

$$\langle jm+2 \mid J_+V_+ \mid jm\rangle = \langle jm+2 \mid V_+J_+ \mid jm\rangle \tag{194}$$

with:

$$I = \sum \mid j\prime m\prime\rangle\langle j\prime m\prime \mid \tag{195}$$

So we only can get something from that summation when $m\prime = m+1$ contributes.

$$\begin{aligned} &\langle jm+2 \mid J_+ \mid jm+1\rangle\langle jm+1 \mid V_+ \mid jm\rangle \\ &= \langle jm+2 \mid V_+ \mid jm+1\rangle\langle jm+1 \mid J_+ \mid jm\rangle \end{aligned} \tag{196}$$

$$\frac{\langle jm+1 \mid V_+ \mid jm\rangle}{\langle jm+1 \mid J_+ \mid jm\rangle} = \frac{\langle jm+2 \mid V_+ \mid jm+1\rangle}{\langle jm+2 \mid J_+ \mid jm+1\rangle} = \alpha_+ \tag{197}$$

Notice, that this is indenpendent of m; thus the ratio is a constant and that is a very important conclusion. So we can say:

$$\begin{aligned} V_+ &= \alpha_+ J_+ \\ V_- &= \alpha_- J_- \\ V_z &= \alpha Jz \end{aligned} \tag{198}$$

We have to figure out all the three components.

$$[J_-, V_+] = i(i\hbar)V_z - i(-i\hbar)V_z = -2\hbar V_z \tag{199}$$

So:

$$\begin{aligned} \langle jm \mid (J_-V_+ - V_+J_-) \mid jm\rangle &= -2\hbar\langle jm \mid V_z \mid jm\rangle \\ = \hbar\sqrt{j(j+1) - m(m+1)}&\langle jm+1 \mid V_+ \mid jm\rangle \\ -\hbar\sqrt{j(j+1) - m(m-1)}&\langle jm \mid V_+ \mid jm+1\rangle \end{aligned} \tag{200}$$

We know everything except for α_{pm} so let us calculate them where:

$$\langle jm+1 \mid V_+ \mid jm\rangle = \alpha_+ J_+ = \alpha_+ \hbar\sqrt{j(j+1)-m(m+1)} \tag{201}$$

and

$$\langle jm \mid V_+ \mid jm+1\rangle = \alpha_+ J_+ = \alpha_+ \hbar\sqrt{j(j+1)-(m-1)m)} \tag{202}$$

This gives

$$\begin{aligned} &= \alpha_+\hbar^2[j(j+1)-m(m+1)-j(j+1)+m(m-1)] \\ &\qquad = -2m\alpha_+\hbar^2 = -2\hbar V_z \end{aligned} \tag{203}$$

Now we can say:

$$\langle jm \mid V_z \mid jm\rangle = m\hbar\alpha_+ = m\hbar\alpha_- \tag{204}$$

$\alpha_+ = \alpha_- = \alpha$

$$[J_+, V_-] = 2\hbar V_z \tag{205}$$

$$\langle jm \mid J_z \mid jm\rangle = m\hbar \tag{206}$$

$$V_z = \alpha J_z \tag{207}$$

This gives us a generalized result and a very powerful statement:

$$\vec{V} = \alpha\vec{J} \tag{208}$$

If we have: $\vec{W} = \beta\vec{J}$ and $\vec{V} \propto \vec{W}$, then when we fix j:

$$V_{\|} = \vec{V} \propto \vec{J} \tag{209}$$

So if we think of those as vectors we can write:

$$\vec{J}\cdot\vec{V} \propto \vec{J}^2 = \alpha j(j+1)\hbar^2 \tag{210}$$

and calculate coefficient α:

$$\langle\vec{J}\cdot\vec{V}\rangle = \alpha j(j+1)\hbar^2 \tag{211}$$

$$\alpha = \frac{\langle\vec{J}\cdot\vec{V}\rangle}{j(j+1)\hbar^2} = \frac{\langle\vec{J}\cdot\vec{V}\rangle}{\langle\vec{J}^2\rangle} \tag{212}$$

$$V_{\|} = V\cos(\theta) \tag{213}$$

$$\vec{J}\cdot\vec{V} = JV\cos(\theta) \tag{214}$$

So in this geometrical view we can conclude that:

$$V_{\|} = \frac{\vec{J}\cdot\vec{V}}{J} \tag{215}$$

$$\alpha = \frac{V_{\|}}{J} = \frac{\vec{J}\cdot\vec{V}}{J^2} \tag{216}$$

Recap from last class: Last time we spoke about vectors and found that for an arbitrary vector: $\vec{V}$ is proportional to $\vec{J}$ and more importantly for a fixed j value we have:

$$\vec{V} = \alpha\vec{J} \tag{217}$$

Today's Notes:

The Hydrogen Atom

Remember that we found the energy levels for the hydrogen atom before

$$E_n = -\frac{E_{ion}}{n^2} \tag{218}$$

and we can denote the energy levels as $|n, l, m\rangle$.
Say you have a complicated atom with a Hamiltonian like:

$$H_o = T_o + V_o + ... \tag{219}$$

Also this complicated atom has total angular momentum $\vec{L}$ and also $\vec{S}$. For all the constituents, the total angular momentum, $\vec{J}$, will be the sum of the spin and angular momentum components:

$$\vec{J} = \vec{L} + \vec{S} \tag{220}$$

Which is very important becuase this can generate rotation. And we know that $[H_o, \vec{J}] = 0$ even though we know nothing about the complicated atom. (H_o is a scalar and invariant under rotation)

We also know: $[H_o, \vec{L^2}] = [H_o, \vec{S^2}] = 0$ and $\{H_o, J^2, J_z, L^2, S^2\}$

In general our energy level can be written as: $|E_o, L, S, J, M\rangle$. If we fix J and E_o, the energy level with have a fixed J and $M = -J, ..., J$ with a degeneracy of at least $2J+1$ and in the case of hydrogen atom it is even more becuase it does not even depend on $\vec{J}$. To break down this degeneracy we will add a magnetic field.

Example 1:

Set $\vec{B} = B\hat{z}$.

$$H = H_o + H_1 \tag{221}$$

Where

$$H_1 = -\frac{q}{2m}[(\vec{B}\cdot\vec{L}) + 2\vec{B}\cdot\vec{S}] \tag{222}$$

Note: The coefficient 2 is due to relativistic effects.

$$H_1 = \omega_L(L_z + 2S_z) \tag{223}$$

In which:

$$\omega_L = \frac{-qB}{2m} \tag{224}$$

and as we know it is the Larmor frequency. By fixing L,S,J we will try to figure out what will happen to the energy level $|E_o, L, S, J, M\rangle$

$$\vec{L} = \frac{\left\langle \vec{L}\cdot\vec{J}\right\rangle}{J(J+1)\hbar^2}\vec{J} \tag{225}$$

$$\vec{S} = \frac{\left\langle \vec{S}\cdot\vec{J}\right\rangle}{J(J+1)\hbar^2}\vec{J} \tag{226}$$

and these are two operators we write based on $\vec{J}$. Now we have to calculate the expectation values:

$$\vec{L}\cdot\vec{J} = \vec{L}(\vec{L}+\vec{S}) = \vec{L^2} + (\vec{L}\cdot\vec{S}) \tag{227}$$

$$\vec{L}\cdot\vec{J} = \frac{1}{2}(\vec{J^2} - \vec{L^2} - \vec{S^2}) + \vec{L^2} = \frac{1}{2}(\vec{J^2} + \vec{L^2} - \vec{S^2}) \tag{228}$$

Therefore,

$$\vec{L} = \frac{[\frac{1}{2}(J(J+1) + L(L+1) - S(S+1)]}{J(J+1)}\vec{J} \tag{229}$$

and

$$\vec{S} = \frac{[\frac{1}{2}(J(J+1) - L(L+1) + S(S+1)]}{J(J+1)}\vec{J} \tag{230}$$

$$H_1 = \frac{\omega_L}{2J(J+1)}[3J(J+1) - L(L-1) + S(S+1)]J_z \tag{231}$$

By simplifying that we would have:

$$H_1 = \omega_L[\frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}]J_z \tag{232}$$

By acting this H_1 on our eigenstate we have:

$$H_1 \left|E_0, L, S, J, M\right\rangle = \omega_L g_J \hbar M \left|E_0, L, S, J, M\right\rangle \tag{233}$$

Here g_J is the Lande factor.

Spin-Spin Coupling: 2 magnetic moments

Even if we do not have an external magnetic field; since each spin has a magnetic moment so one magnetic moment will produce magnetic field and the other spin can see that magnetic field so they can interact. For example in the simplest case like a hydrogen atom we have an elctron with spin half and a proton with spin half. So electron can see the magnetic field due to proton spin and it generates very little splitting on electron's energy levels which is very small.

$$H_o = E_o I \tag{234}$$

$$H = H_o + a(\vec{S_1} \cdot \vec{S_2}) \tag{235}$$

The question is do we know the energy levels of this Hamiltonian? we define the total spin as:

$$\vec{S}^2 = \vec{S_1}^2 + \vec{S_2}^2 + 2(\vec{S_1} \cdot \vec{S_2}) \tag{236}$$

By acting it on our eigenstate we would have:

$$\vec{S}^2 \left|SM\right\rangle = (\frac{3}{4}\hbar^2 + \frac{3}{4}\hbar^2 + 2(\vec{S_1} \cdot \vec{S_2})) \left|SM\right\rangle \tag{237}$$

$$\vec{S}^2 \left|SM\right\rangle = S(S+1)\hbar^2 \left|SM\right\rangle \tag{238}$$

$$(\vec{S_1} \cdot \vec{S_2}) \left|SM\right\rangle = (\frac{S(S+1)}{2} - \frac{3}{4})\hbar^2 \left|SM\right\rangle \tag{239}$$

$$H \left|SM\right\rangle = [E_o + \frac{a\hbar^2}{2}(S(S+1) - \frac{3}{4})] \left|SM\right\rangle \tag{240}$$

and this is the new energy level, the new eigenvalue.

The system can transit between these two energy levels and when it transits, it emits a photon with frequency $\hbar\Omega$ which Ω is the Bohr frequency and as we can see from the above $\Omega = a\hbar$.
Here we want to understand the spin of electron and just the first spin $\vec{S_1}$ because usually one is going to do something and the other will not do anything. We want to see how its expectation value evolves in time:

$$\left\langle \vec{S_1} \right\rangle_t \tag{241}$$

That would tell us what kind of transition to expect and what kind of radiation we would observe. We have 4 states and we should have a 4 by 4 matrix:

$$|SM\rangle = [|1,1\rangle, |1,0\rangle, |1,-1\rangle, |0,0\rangle] \tag{242}$$

S_{1z} is the easist one to find so lets find it first:

$$S_{1z}|SM\rangle = \frac{\hbar}{2}\begin{pmatrix}1 & 0 & 0 & 0\\ 0 & 0 & 0 & 1\\ 0 & 0 & -1 & 0\\ 0 & 1 & 0 & 0\end{pmatrix} \tag{243}$$

We need two more components so:

$$S_{1+}|SM\rangle = \frac{\hbar}{\sqrt{2}}\begin{pmatrix}0 & 1 & 0 & -1\\ 0 & 0 & 1 & 0\\ 0 & 0 & 0 & 0\\ 0 & 0 & 1 & 0\end{pmatrix} \tag{244}$$

To find the S_{1-} we dont have to caculate it because we do know that:

$$S_{1-} = S_{1+}^T \tag{245}$$

So we can conclude that:

$$S_{1-}|SM\rangle = \frac{\hbar}{\sqrt{2}}\begin{pmatrix}0 & 0 & 0 & 0\\ 1 & 0 & 0 & 0\\ 0 & 1 & 0 & 1\\ -1 & 0 & 0 & 0\end{pmatrix} \tag{246}$$

As we can find out here:

$$\vec{S} = \frac{1}{2}\vec{J} \tag{247}$$

Which is the Wigner-Eckart theorem.
What information can we extract from:

$$|\psi(0)\rangle = \alpha|0,0\rangle + \beta_1|1,1\rangle\,\beta_0|1,0\rangle + \beta_{-1}|1,-1\rangle \tag{248}$$

Which is the wavefunction that the system can be determined with.
Apply the evolution operator.

$$|\psi(t)\rangle = \alpha e^{-i(E_0-\frac{3a\hbar^2}{4})\frac{t}{\hbar^2}}|0,0\rangle + e^{-i(E_0+\frac{3a\hbar^2}{4})\frac{t}{\hbar^2}}[\beta_1|1,1\rangle\,\beta_0|1,0\rangle + \beta_{-1}|1,-1\rangle] \tag{249}$$

This is the state of the system at time t and we can write it as:

$$|\psi(t)\rangle = e^{-i(E_0-\frac{3a\hbar^2}{4})\frac{t}{\hbar^2}}[\alpha|0,0\rangle + e^{-i\Omega t}[\beta_1|1,1\rangle\,\beta_0|1,0\rangle + \beta_{-1}|1,-1\rangle] \tag{250}$$

$$\langle S_{1z}\rangle = \frac{\hbar}{\sqrt{2}}[|\beta_1|^2 + e^{i\Omega t}\alpha\beta_0^* + e^{-i\Omega t}\alpha^*\beta_0 + |\beta_{-1}|^2] \tag{251}$$

$$\langle S_{1+}\rangle = \frac{\hbar}{\sqrt{2}}[\beta_1^*\beta_0 + \beta_0^*\beta_1 - e^{i\Omega t}\beta_1^*\alpha + e^{i\Omega t}\beta_{-11}\alpha^*] \tag{252}$$

$$\langle S_{1+}\rangle = \langle S_{1-}\rangle^* \tag{253}$$

Example: Consider the states $|1,0\rangle \rightarrow |0,0\rangle$ and here. Set $\beta_{-1} = \beta_1 = 0$ and suppose α is real so:

$$\langle S_{1z}\rangle = \frac{\hbar}{\sqrt{2}}[e^{i\Omega t}\alpha\beta_0^* + e^{-i\Omega t}\alpha^*\beta_0] \tag{254}$$

Where:

$$\beta_0 = |\beta_0|e^{i\psi_0} \tag{255}$$

$$\langle S_{1z}\rangle = \frac{\hbar}{2}\alpha|\beta_0|(e^{i(\Omega t-\psi_0)} + e^{-i(\Omega t-\psi_0)}) \tag{256}$$

$$\langle S_{1z}\rangle = \hbar\alpha|\beta_0|cos(\Omega t - \psi_0) \tag{257}$$

$$\langle S_{1+}\rangle = \langle S_{1-}\rangle = 0, \langle S_{1x}\rangle = \langle S_{1y}\rangle = 0 \tag{258}$$

So we can think of S as a vector and we have oscillation along the z-axis and get linearly polarized radiation in the z-direction because of the oscillation.
Example B(for other transition): $|1,1\rangle \rightarrow |0,0\rangle$

$$\beta_{-1} = \beta_1 = 0 \tag{259}$$

$$\langle S_{1z}\rangle = \frac{\hbar^2}{2}|\beta_1|^2 \tag{260}$$

$$\langle S_{1+}\rangle = -\frac{\hbar^2}{2}\alpha\beta_1^* e^{i\Omega t} \tag{261}$$

$$\beta_1 = |\beta_1|e^{i\psi_0} \tag{262}$$

$$\langle S_{1x}\rangle = -\frac{\hbar^2}{2}\alpha|\beta_1|cos(\Omega t - \varphi_1) \tag{263}$$

$$\langle S_{1y}\rangle = -\frac{\hbar^2}{2}\alpha|\beta_1|sin(\Omega t - \varphi_1) \tag{264}$$

Therefore it precesses in the x-y plane around the z-axis and radiate circularly polarized light which is right handed (counterclockwise).

UNIT 3

Stationary perturbation theory

Notes by L. Poudel, T. Papatheodore, and Y. Song

The Method

Perturbation theory applies to systems whose Hamiltonians may be expressed in the form

$$H = H_0 + W. \tag{1}$$

H_0 is called the unperturbed Hamiltonian and it is assumed to be time-independent. We already know the solution corresponding to H_0, which is to say that we already know its eigenvalues and eigenstates.

$$H_0 \mid E_{0,\ldots}\rangle = E_0 \mid E_{0,\ldots}\rangle \tag{2}$$

E_0 is degenerate in general and the 0,... allows for the possibility of other quantum numbers if there is degeneracy. W is called the "perturbation", which causes modifications to the energy levels and stationary states of the unperturbed Hamiltonian. W is assumed to be much smaller than H_0 and for *stationary* perturbation theory it is also time-independent. In order to quantify the "smallness" of W we assume that it is proportional to a real, dimensionless parameter λ which is much smaller than 1:

$$W = \lambda \hat{W}, \tag{3}$$

where $\lambda \ll 1$ and $\hat{W}$ is an operator whose matrix elements are comparable to those of H_0. Now, substitution of (3) into (1) yields

$$H = H_0 + \lambda \hat{W}. \tag{4}$$

From (4) we can see that as $\lambda \to 0, H(\lambda) \to H_0$, and we recover the unperturbed Hamiltonian.

Approximate Solution of the Eigenvalue Equation

We want to find a solution to the eigenvalue equation

$$H(\lambda) \mid \psi(\lambda)\rangle = E(\lambda) \mid \psi(\lambda)\rangle \tag{5}$$

In order to approximate the solutions $E(\lambda)$ and $\mid \psi(\lambda)\rangle$ we assume that they can be expanded in powers of λ:

$$E(\lambda) = E_0 + \lambda E_1 + \lambda^2 E_2 + ... \tag{6}$$

$$\mid \psi(\lambda)\rangle = \mid \psi_0\rangle + \lambda \mid \psi_1\rangle + \lambda^2 \mid \psi_2\rangle + ... \tag{7}$$

Substitution of (4), (6) and (7) into (5) yields

$$\begin{gathered}(H_0 + \lambda\hat{W})(\mid \psi_0\rangle + \lambda \mid \psi_1\rangle + \lambda^2 \mid \psi_2\rangle + ...) = \\ (E_0 + \lambda E_1 + \lambda^2 E_2 + ...)(\mid \psi_0\rangle + \lambda \mid \psi_1\rangle + \lambda^2 \mid \psi_2\rangle + ...)\end{gathered} \tag{8}$$

Multiply equation (8) out and collect like terms of λ. Now, since λ is arbitrary we must equate the coefficients of successive powers of λ on both sides of the equation.

0th Order Terms: λ^0

$$H_0 \mid \psi_0\rangle = E_0 \mid \psi_0\rangle \tag{9}$$

1st Order Terms: λ^1

$$H_0 \mid \psi_1\rangle + \hat{W} \mid \psi_0\rangle = E_0 \mid \psi_1\rangle + E_1 \mid \psi_0\rangle \tag{10}$$

2nd Order Terms: λ^2

$$H_0 \mid \psi_2\rangle + \hat{W} \mid \psi_1\rangle = E_0 \mid \psi_2\rangle + E_1 \mid \psi_1\rangle + E_2 \mid \psi_0\rangle \tag{11}$$

Since equation (5) defines $\mid \psi(\lambda)\rangle$ only to within a constant factor, we can choose its norm and phase. We assume $\mid \psi(\lambda)\rangle$ to be normalized and choose its phase so that $\langle\psi_0 \mid \psi(\lambda)\rangle$ is real.
Now, since $\langle\psi(\lambda) \mid \psi(\lambda)\rangle = 1$ we obtain the following:
To 0th Order $\mid \psi(\lambda)\rangle = \mid \psi_0\rangle$

$$\Longrightarrow \langle\psi(\lambda) \mid \psi(\lambda)\rangle = \langle\psi_0 \mid \psi_0\rangle = 1 \tag{12}$$

To 1st Order $\mid \psi(\lambda)\rangle = \mid \psi_0\rangle + \lambda \mid \psi_1\rangle$

$$\begin{gathered}\Longrightarrow \langle\psi(\lambda) \mid \psi(\lambda)\rangle = (\langle\psi_0 \mid + \lambda\langle\psi_1 \mid)(\mid \psi_0\rangle + \lambda \mid \psi_1\rangle) \\ = \langle\psi_0 \mid \psi_0\rangle + \lambda\langle\psi_0 \mid \psi_1\rangle + \lambda\langle\psi_1 \mid \psi_0\rangle + \lambda^2\langle\psi_1 \mid \psi_1\rangle = 1\end{gathered} \tag{13}$$

We can drop the last term involving λ^2 since we are only concerned with 1st order terms. Now we also know that $\langle\psi_0 \mid \psi_0\rangle = 1$ which then implies that $\langle\psi_0 \mid \psi_1\rangle + \langle\psi_1 \mid \psi_0\rangle = 0$. And, since $\langle\psi_0 \mid \psi_1\rangle$ is real we obtain

$$\langle\psi_0 \mid \psi_1\rangle = \langle\psi_1 \mid \psi_0\rangle = 0 \tag{14}$$

To 2nd Order $\mid \psi(\lambda)\rangle = \mid \psi_0\rangle + \lambda \mid \psi_1\rangle + \lambda^2 \mid \psi_2\rangle$
A similar argument for the 2nd order terms may be applied to obtain

$$\langle\psi_0 \mid \psi_2\rangle = \langle\psi_2 \mid \psi_0\rangle = -\frac{1}{2}\langle\psi_1 \mid \psi_1\rangle \tag{15}$$

Non-Degenerate Energy Level

We will now find the corrections to the energy levels and energy eigenstates of a non-degenerate level. Project the 1st order equation (10) onto the state $\mid \psi_0\rangle$:

$$\langle\psi_0 \mid H_0 \mid \psi_1\rangle + \langle\psi_0 \mid \hat{W} \mid \psi_0\rangle = \langle\psi_0 \mid E_0 \mid \psi_1\rangle + \langle\psi_0 \mid E_1 \mid \psi_0\rangle \tag{16}$$

Now let H_0 operate to the left on $\langle\psi_0 \mid$ in the first term and pull the constants out to obtain

$$E_0\langle\psi_0 \mid \psi_1\rangle + \langle\psi_0 \mid \hat{W} \mid \psi_0\rangle = E_0\langle\psi_0 \mid \psi_1\rangle + E_1\langle\psi_0 \mid \psi_0\rangle \tag{17}$$

From this equation we can see that since $\langle\psi_0 \mid \psi_0\rangle = 1$ from (12) and the first and third terms cancel we obtain the first order correction to the energy level:

$$E_1 = \langle\psi_0 \mid \hat{W} \mid \psi_0\rangle \tag{18}$$

Now we want to find the first order correction, $\mid \psi_1\rangle$, to the eigenstate. Project the first order equation (10) onto the state $\langle E_0' \mid$, where $\langle E_0' \mid$ is an eigenstate corresponding to any other energy level other than E_0. We obtain

$$E_0'\langle E_0' \mid \psi_1\rangle + \langle E_0' \mid \hat{W} \mid \psi_0\rangle = E_0\langle E_0' \mid \psi_1\rangle + E_1\langle E_0' \mid \psi_0\rangle \tag{19}$$

The last term, $\langle E_0' \mid \psi_0\rangle$, is equal to zero since the two terms of the inner product belong to different eigenvalues. Then we can solve for $\langle E_0' \mid \psi_1\rangle$ to obtain

$$\langle E_0' \mid \psi_1\rangle = \frac{\langle E_0' \mid \hat{W} \mid \psi_0\rangle}{E_0 - E_0'} \tag{20}$$

Now expanding the state $\mid \psi_1\rangle$ on the $\mid E_0'\rangle$ basis we conclude that the correction to the energy eigenstate is

$$\begin{aligned}\mid \psi_1\rangle &= \sum_{E_0'} \mid E_0'\rangle\langle E_0' \mid \psi_1\rangle \\ &= \sum_{E_0' \neq E_0} \mid E_0'\rangle \frac{\langle E_0' \mid \hat{W} \mid \psi_0\rangle}{E_0 - E_0'} + \mid E_0\rangle\langle E_0 \mid \psi_1\rangle \\ &= \sum_{E_0' \neq E_0} \mid E_0'\rangle \frac{\langle E_0' \mid \hat{W} \mid \psi_0\rangle}{E_0 - E_0'},\end{aligned} \tag{21}$$

where the last equation follows since $\langle E_0 \mid \psi_1\rangle = 0$ due to the fact that the two states of the inner product belong to different eigenvalues.

Now we follow the same procedure for the 2nd order equation. In order to find the 2nd order correction to the energy level we project the 2nd order equation (11) onto the state $\mid \psi_0\rangle$:

$$E_0\langle\psi_0 \mid \psi_2\rangle + \langle\psi_0 \mid \hat{W} \mid \psi_1\rangle = E_0\langle\psi_0 \mid \psi_2\rangle + E_1\langle\psi_0 \mid \psi_1\rangle + E_2\langle\psi_0 \mid \psi_0\rangle \tag{22}$$

Now, the first terms on each side of the equation cancel, the second term on the right side is zero since $\langle\psi_0 \mid \psi_1\rangle = 0$, and $\langle\psi_0 \mid \psi_0\rangle = 1$ which yields the conclusion

$$E_2 = \langle\psi_0 \mid \hat{W} \mid \psi_1\rangle \tag{23}$$

Now, plugging in equation (21) for $\mid \psi_1\rangle$ gives the 2nd order correction to the energy level:

$$E_2 = \sum_{E_0' \neq E_0} \langle\psi_0 \mid \hat{W} \mid E_0'\rangle \frac{\langle E_0' \mid \hat{W} \mid \psi_0\rangle}{E_0 - E_0'} = \sum_{E_0' \neq E_0} \frac{|\langle\psi_0 \mid \hat{W} \mid E_0'\rangle|^2}{E_0 - E_0'} \tag{24}$$

The second order correction to the energy level, $\mid \psi_2\rangle$ is to be found on your own at home following the same procedure as in the first order correction.

Degenerate Energy Level

Now we allow for the energy E_0 to be degenerate so that the corresponding states are denoted $\mid E_{0,a}\rangle$, where a is a quantum number. If we suppose that the degeneracy is 2, then a can take on two values: $a = 1, 2$.
We proceed in an analogous manner to the nondegenerate case except now we must project the first order equation onto both possible states $\mid E_{0,a}\rangle$. Doing so we see that

$$E_0\langle E_{0,a} \mid \psi_1\rangle + \langle E_{0,a} \mid W \mid \psi_0\rangle = E_0\langle E_{0,a} \mid \psi_1\rangle + E_1\langle E_{0,a} \mid \psi_0\rangle \tag{25}$$

Notice that the first term on each side of the equation cancels leaving us with two equations; one for each case $a = 1, 2$:

$$\langle E_{0,a} \mid W \mid \psi_0\rangle = E_1\langle E_{0,a} \mid \psi_0\rangle \tag{26}$$

For a = 1

$$\langle E_{0,1} \mid W \mid \psi_0\rangle = E_1\langle E_{0,1} \mid \psi_0\rangle \tag{27}$$

But generally $\mid \psi_0\rangle$ must be written as a linear combination of the states $\mid E_{0,a}\rangle$:

$$\mid \psi_0\rangle = \alpha_1 \mid E_{0,1}\rangle + \alpha_2 \mid E_{0,2}\rangle \tag{28}$$

Plugging equation (28) into (27) we obtain

$$\alpha_1\langle E_{0,1} \mid W \mid E_{0,1}\rangle + \alpha_2\langle E_{0,1} \mid W \mid E_{0,2}\rangle = E_1\alpha_1 \tag{29}$$

For a = 2

$$\langle E_{0,2} \mid W \mid \psi_0\rangle = E_1\langle E_{0,2} \mid \psi_0\rangle \tag{30}$$

Plugging equation (28) into (30) we obtain

$$\alpha_1\langle E_{0,2} \mid W \mid E_{0,1}\rangle + \alpha_2\langle E_{0,2} \mid W \mid E_{0,2}\rangle = E_1\alpha_2 \tag{31}$$

Now, the operator W may be written in matrix form in the $\mid E_{0,a}\rangle$ basis as

$$\begin{bmatrix} W_{11} & W_{12} \\ W_{21} & W_{22} \end{bmatrix}$$

so that equations (29) and (31) may be written as the matrix equation

$$W\begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix} = E_1\begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix}$$

The characteristic equation $det(W - E_1\mathbb{I}) = 0$ may then be solved in order to find the two eigenvalues and eigenstates.

Example: 1D Harmonic Oscillator

Here we can see the method in action by proceeding with an example that we already know the answer to and then checking to see if our results match. The Hamiltonian for the 1-D harmonic oscillator is given by

$$H_0 = \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2 \tag{32}$$

Now, if the particle has a charge q we can turn on an electric field $\vec{\varepsilon} = \varepsilon\hat{x}$ so that we introduce a perturbation $W = -q\varepsilon x$, and the total Hamiltonian then becomes

$$H = H_0 + W = \frac{p^2}{2m} + \frac{1}{2}m\omega^2x^2 - q\varepsilon x \tag{33}$$

Recall that we have already solved this problem exactly in compliment F_V where we showed that

$$E'_n = (n + \frac{1}{2})\hbar\omega - \frac{q^2\varepsilon^2}{2m\omega^2} \tag{34}$$

$$\varphi'(x) = \varphi(x - \frac{q\varepsilon}{m\omega^2}) \tag{35}$$

We will now find the same results using perturbation theory.

1st order correction to the energy

$$E_n^{(1)} = \langle n \mid W \mid n\rangle = -q\varepsilon\langle n \mid x \mid n\rangle = 0 \tag{36}$$

The last equality follows since $x = \sqrt{\frac{\hbar}{2m\omega}}(a^\dagger + a)$, and hence there is no shift in the energy level to first order correction.

2nd order correction to the energy

$$E_n^{(2)} = \sum_{n'\neq n} \frac{|\langle n' \mid W \mid n\rangle|^2}{E_n - E'_n} \tag{37}$$

$$\langle n' \mid W \mid n\rangle = -q\varepsilon\langle n' \mid x \mid n\rangle = -q\varepsilon\sqrt{\frac{\hbar}{2m\omega}}\langle n' \mid a^\dagger + a \mid n\rangle \tag{38}$$

$$= -q\varepsilon\sqrt{\frac{\hbar}{2m\omega}}(\sqrt{n+1}\langle n' \mid n+1\rangle + \sqrt{n}\langle n' \mid n-1\rangle \tag{39}$$

Therefore, the only nonzero contributions in equation (37) will come from $n' = n+1$ and $n' = n-1$, yielding a second order correction to the energy term

$$E_n^{(2)} = q^2\varepsilon^2\frac{\hbar}{2m\omega}(-\frac{n+1}{\hbar\omega} + \frac{n}{\hbar\omega}) = -\frac{q^2\varepsilon^2}{2m\omega^2} \tag{40}$$

Comparing equations (34) and (40) we notice that our second order correction to the energy level matches identically with the exact solution.
We now find the correction to the energy state:

$$\mid \psi_1\rangle = \sum_{n' \neq n}\frac{\langle n' \mid W \mid n\rangle}{E_n - E_{n'}} \mid n'\rangle \tag{41}$$

$$= -q\varepsilon\sqrt{\frac{\hbar}{2m\omega}}\frac{1}{\hbar\omega}(-\sqrt{n+1} \mid n+1\rangle + \sqrt{n} \mid n-1\rangle) \tag{42}$$

$$= -q\varepsilon\sqrt{\frac{\hbar}{2m\omega}}\frac{1}{\hbar\omega}(-a^\dagger + a) \mid n\rangle \tag{43}$$

$$= -\frac{iq\varepsilon}{m\hbar\omega^2}p \mid n\rangle \tag{44}$$

Equation (42) follows from (39), equation (43) follows from the definitions of the creation and annihilation operators, and equation (44) follows from the definition of momentum as $p = i\frac{m\hbar\omega}{2}(a^\dagger - a)$. We can now check to see if equation (44) matches with the exact solution (35).
Taylor expand equation (35):

$$\varphi_n(x - \frac{q\varepsilon}{m\omega^2}) = \varphi_n(x) - \frac{q\varepsilon}{m\omega^2}\frac{d\varphi}{dx} + ... \tag{45}$$

Now, since $p = -i\hbar\frac{d}{dx}$, we can see that equation (44) can be written as

$$\psi_1(x) = \langle x \mid \psi_1\rangle = -\frac{q\varepsilon}{m\omega^2}\frac{d\varphi}{dx}, \tag{46}$$

and we can verify that our first order correction to the eigenstate does match the known exact solution.

Ex-II: Harmonic oscillator with quadratic potential

Consider a harmonic oscillator with hamiltonian H_0, which is given by

$$H_0 = \frac{P^2}{2m} + \frac{1}{2}mw^2x^2 \tag{47}$$

Let us add a quadratic potential to above oscillator. So, the perturbation is given by

$$W = \frac{1}{2}\lambda m w^2 x^2 \tag{48}$$

We assume $\lambda \ll 1$. In practice, this can be done by adding very weak spring with small spring constant. Now, the hamiltonian becomes,

$$H = H_0 + W = \frac{P^2}{2m} + \frac{1}{2}(\lambda + 1) m w^2 x^2 \tag{49}$$

The hamiltonian given by equation (49) is also the equation of harmonic oscillator with frequency $\omega' = \omega\sqrt{1+\lambda}$, which can be solved exactly. So, the new energy levels is given by

$$E'_n = (n + \frac{1}{2})\hbar\omega' \tag{50}$$

Where,

$$\omega' = \omega\sqrt{(1+\lambda)} \tag{51}$$

Using taylor expansion, we get different order correction in energy level

$$E'_n = (n + \frac{1}{2})\hbar\omega(1 + \frac{\lambda}{2} - \frac{\lambda^2}{8} + ...) \tag{52}$$

But,this time we want to solve the problem using perturbation theory. First, we solve problem in H_0, the solution of which is

$$H_0 \mid n\rangle = E_n \mid n\rangle \tag{53}$$

Where

$$E_n = (n + \frac{1}{2})\hbar\omega \tag{54}$$

So, knowing that we can write expression for E', which is general expression for any perturbation

$$E'_n = E_n + \lambda\langle n|W|n\rangle + \lambda^2 \sum_{n' \neq n} \frac{|\langle n'|W|n\rangle|^2}{E_n - E'_n} + ... \tag{55}$$

The second term in equation (55) is average potential energy of harmonic oscillator, and therefore is exactly half of total energy of harmonic oscillator without perturbation. This is as expected from equation (52). We can also calculate it by using creation and annihilation operator.

$$\begin{aligned} \langle n|W|n\rangle &= \frac{1}{2} m\omega^2 \langle n|x^2|n\rangle \\ &= \frac{1}{2} E_N \end{aligned} \tag{56}$$

To calculate the third term let us first calculate $\langle n'|W|n\rangle$

$$\begin{aligned}\langle n'|W|n\rangle &= \frac{1}{2}m\omega^2\frac{\hbar}{2m\omega}\langle n'|(a^\dagger + a)^2|n\rangle \\ &= \frac{\hbar\omega}{4}\langle n'|a^{\dagger 2} + a^2 + a^\dagger a + aa^\dagger|n\rangle \\ &= \frac{\hbar\omega}{4}[\sqrt{(n+1)(n+2)}\delta_{n',n+2} + \sqrt{n(n-1)}\delta_{n',n-2} + (2n+1)\delta_{n',n}\end{aligned} \tag{57}$$

The first terms contributes when $n' = n+2$, second term contributes when $n' = n-2$. But third contributes only when $n' = n$, which is excluded in our relation

$$\begin{aligned}\sum_{n'\neq n}\frac{|\langle n'|W|n\rangle|^2}{\hbar\omega(n'-n)} &= \frac{\hbar\omega}{16}[-\frac{1}{2}(n+1)(n+2) + \frac{1}{2}n(n-1)] \\ &= -\frac{1}{8}\hbar\omega(n+\frac{1}{2})\end{aligned} \tag{58}$$

We get exactly same term as expected from equation (52). Similarly, we can calculate higher order terms.

EX-3: Harmonic oscillator with cubic potential

This time we add cubic potential to the same hamiltonian.

$$W = x^3 \tag{59}$$

In this case there is no way to solve the problem as we did previous example. So, we must use perturbation theory to solve this problem. Here, the first term in energy will be original energy without perturbation. The second term in energy is also straightforward (i.e. zero since x^3 is odd)

$$\langle n|x^3|n\rangle = 0 \tag{60}$$

The first correction in energy will be coefficient of λ^2. First we will evaluate $\langle n'|W|n\rangle$. Most of the terms of $\langle n'|W|n\rangle$ are zero. The non zero terms are,
(i) When $n' = n+3$

$$\langle n+3|W|n\rangle = (\frac{\hbar}{2m\omega})^{\frac{3}{2}}\langle n+3|(a^\dagger)^3|n\rangle \tag{61}$$

$$|\langle n+3|W|n\rangle|^2 = (\frac{\hbar}{2m\omega})^{\frac{3}{2}}(n+1)(n+2)(n+3) \tag{62}$$

(ii) When $n' = n-3$

$$|\langle n+3|W|n\rangle|^2 = (\frac{\hbar}{2m\omega})^{\frac{3}{2}}n(n-1)(n-2) \tag{63}$$

(iii) When $n' = n+1$

$$|\langle n+3|W|n\rangle|^2 = (\frac{\hbar}{2m\omega})^{\frac{3}{2}}9(n+1)^3 \tag{64}$$

(iv) When $n' = n-1$

$$|\langle n+3|W|n\rangle|^2 = (\frac{\hbar}{2m\omega})^{\frac{3}{2}}9n^3 \tag{65}$$

Combining contributions from all these terms, we get

$$\sum_{n'\neq n}\frac{|\langle n'|W|n\rangle|^2}{\hbar\omega(n'-n)} = (\frac{\hbar}{2m\omega})^{\frac{3}{2}}\frac{1}{\hbar\omega}[-\frac{1}{3}(n+1)(n+2)(n+3)+\frac{1}{3}n(n-1)(n-2)-9(n+1)^3+9n^3] \tag{66}$$

With little effort in algebra

$$= -\frac{1}{8}\frac{\hbar^2}{m^3\omega^4}[30(n+\frac{1}{2})^2]+\frac{7}{2}] \tag{67}$$

Finally, different between two successive energy level

$$E'_{n+1} - E'_n = \hbar\omega - \frac{15}{2}\frac{\lambda^2\hbar^2}{m^3\omega^4}(n+1) \tag{68}$$

In this case, separation in energy level is not equal but increases with increase in value of n. In realistic system, we never have only quadratic potential. Actually, if we expand potential around minimum, there will be higher order corrections. So, these cubic terms comes to play.

Diatomic Molecule

Consider a molecule which consists of two atoms. Let us pretend that we don't know much about the molecule. First, we guess that when the atoms are very far away the force between them must be attractive, otherwise no molecule could be formed. However, at closer distances, they repel each other, since they are restricted to be at finite distance from Heisenberg Uncertainty principle. Hence, there must be an equilibrium distance, which is also the size of molecule. The potential energy at this point is the dissociation energy of the molecule. Also, we have bound states due to this potential.

Expanding potential(Figure 1) around minimum value of potential energy,

$$V(r) = V(r_0)+V'(r_0)(r-r_0)+\frac{1}{2}V''(r_0)(r-r_0)^2+\frac{1}{6}V'''(r_0)(r-r_0)^3+\ldots\ldots \tag{69}$$

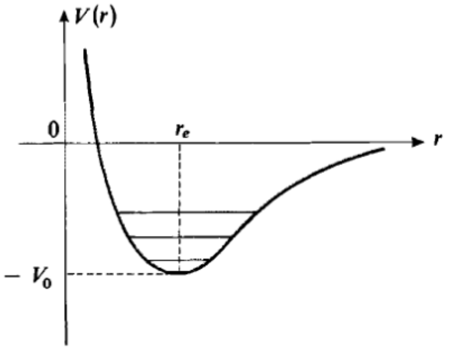


Figure 1: Potential of a diatomic moleculel

The higher order terms are less significant. $V'(r_0)$ will be zero, since potential is minimum at this point. If we call $r - r_0 = x$, then, the second order term correpsonds to a harmonic oscillator and $\frac{1}{6}V'''(r_0)$ is λ for a cubic potential in our formulation. Assume the system is in ground state, which is quite common at room temperature since thermal energy is much less than energy of harmonic oscillator($KT \ll \hbar\omega$) at room temperature. Now, we want to measure the possible transitions of the molecule by interacting with electromagnetic radiation. The dipole moment D couples to electromagnetic waves,thus for two states $|\phi\rangle$ and $|\psi\rangle$ to be able to transition from one to another the condition $\langle\phi|D|\psi\rangle \neq 0$ has to be satisfied.

When a system goes from first excited state $|\phi_1\rangle$ to ground state $|\phi_0\rangle$ so that energy of system changes.

$$|\phi_1\rangle \to |\phi_0\rangle + photon \tag{70}$$

the frequency of photon is given by $\omega_1 = \frac{E_1 - E_0}{\hbar} \approx \sqrt{\frac{V''(r_0)}{m}}$

This is what happens if we include only up till the second order term in the potential energy in equation (69). In this case the states $|\phi_n\rangle$ become the harmonic oscillator states $|n\rangle$. To be more accurate,we need to consider the third order term of the potential energy in equation (69). So, the general expression forthe ground state becomes

$$|\phi_0\rangle \to |0\rangle + \lambda|\psi\rangle + ... \tag{71}$$

where $|\psi\rangle$ is the first order correction

$$|\psi\rangle = \sum_{n\neq 0} \frac{\langle n|W|0\rangle|n\rangle}{n\hbar\omega} \tag{72}$$

So, the ground state becomes,

$$|\phi_0\rangle \to |0\rangle - \lambda\frac{\langle 1|W|0\rangle}{\hbar\omega}|1\rangle - \lambda\frac{\langle 3|W|0\rangle}{3\hbar\omega}|3\rangle \tag{73}$$

The ground state of the entire Hamiltonian is not only $|0\rangle$ but $|0\rangle$ with some higher order correction. We can think of higher states $|\phi_n\rangle$ to be approximtely states of the harmonic oscillator $|n\rangle$. So, to this approximation, we can see there can be transitions from $|\phi_4\rangle$,$|\phi_2\rangle$ and $|\phi_1\rangle$ to $|\phi_0\rangle$ because the correpsonding matrix elements $\langle\phi_n|D|\phi_0\rangle \neq 0$. When transition takes place from $|\phi_3\rangle \to |\phi_0\rangle$, frequency of photon is given as by applying our results for the cubic potential multiple times.

$$\omega_{3\to 0} = \frac{E'_3 - E'_0}{\hbar} \tag{74}$$

$$= 3\omega - \frac{90}{2}\lambda^2\frac{\hbar}{m^3\omega^4} \tag{75}$$

Spin-Spin Interaction

Two spins interact because they correspond to magnetic moments which create magnetic fields. Let us consider two spin half particle. Let us switch on magnetic field $\overrightarrow{B} = B\hat{z}$. So the Hamiltonian can be written as

$$H_0 = \omega_1 S_{1z} + \omega_2 S_{2z} \tag{76}$$

where ω_1 and ω_2 are given by equations

$$\omega_1 = -\gamma_1 B_0 \tag{77}$$

$$\omega_2 = -\gamma_2 B_0 \tag{78}$$

where γ is the gyromagnetic ratio. We know the eigenstates of Hamiltonian, which are

$$H_0|++\rangle = \frac{\hbar}{2}(\omega_1 + \omega_2)|++\rangle \tag{79}$$

$$H_0|+-\rangle = \frac{\hbar}{2}(\omega_1 - \omega_2)|+-\rangle \tag{80}$$

$$H_0|-+\rangle = \frac{\hbar}{2}(-\omega_1 + \omega_2)|-+\rangle \tag{81}$$

$$H_0|--\rangle = -\frac{\hbar}{2}(\omega_1+\omega_2)|--\rangle \tag{82}$$

we assume $\omega_1 > \omega_2$. In this way, we get four different energy levels. If we make transition from first energy level to second energy level, we get a photon of frequency ω_2. Similarly, if we make transition between second and fourth energy level, we get photon of frequency ω_1. Also, transition between first to third and third to fourth energy level gives photon of frequency ω_1 and ω_2 respectively.

We emphasize the transition with ω_1 and ω_2 since they are frequency they appear in the evolution of $\langle S_x\rangle$. Now, I am going to switch on small magnetic field B_1 in $\hat{x}$ direction. If We make this field oscillating with frequency ω then we can keep tuning it to one of ω_1 or ω_2 to get resonance. To do this, make B_1 time dependent $B_1 = B_1\hat{x}cos(\omega t)$. Then, we expect resonance when ω matches with ω_1 or ω_2.By tuning this $B1$ we can studying the transition of the system via resonanaces.

Consider two spin S_1 and S_2 at distance $R = R\hat{n}$. The magnetic moment corresponding to them will be $\mu_1 = \gamma_1 S_1$ and $\mu_2 = \gamma_2 S_2$. Their interaction between these magnetic moment gives perturbation to hamiltonian which is given by

$$W = \frac{\mu_0}{4\pi}\gamma_1\gamma_2[\frac{\overrightarrow{S_1}.\overrightarrow{S_2} - 3\hat{n}.\overrightarrow{S_1}\hat{n}.\overrightarrow{S_2}]}{R^3}] \tag{83}$$

If we take $\xi = -\frac{\mu_0\gamma_1\gamma_2}{4\pi R^3}$

In spherical coordinates, $\hat{n}$ can be written as

$$\hat{n} = \begin{pmatrix} sin\theta cos\phi \\ sin\theta sin\phi \\ cos\theta \end{pmatrix}$$

Finally,

$$\begin{aligned} W =& \xi[-S_{1z}S_{2z} - \frac{1}{2}S_{1+}S_{2-} - \frac{1}{2}S_{1-}S_{2+} \\ &+ 3(S_{1z}cos\theta + \frac{1}{2}e^{-i\phi}sin\theta S_{1+} + \frac{1}{2}e^{i\phi}sin\theta S_{1-}) \\ &(S_{2z}cos\theta + \frac{1}{2}e^{-i\phi}sin\theta S_{2+} + \frac{1}{2}e^{i\phi}sin\theta S_{2-})] \end{aligned}$$

Applying first order perturbation theory, we find the corrections to each of the enrgy levels.

$$\langle ++|W|++\rangle = \xi[-(\frac{\hbar}{2})^2 + 3(\frac{\hbar}{2}cos\theta)^2] = \xi\frac{\hbar^2}{4}[-1+3cos^2\theta] = \hbar\Omega \tag{84}$$

For perturbation theory to work, $\hbar\Omega \ll \hbar\omega_1, \hbar\omega_2$ has to be satisfied. Similarly we can determine the correction for the other states.

$$\langle -+|W|-+\rangle = -\hbar\Omega = \langle +-|W|+-\rangle, \langle --|W|--\rangle = \hbar\Omega \tag{85}$$

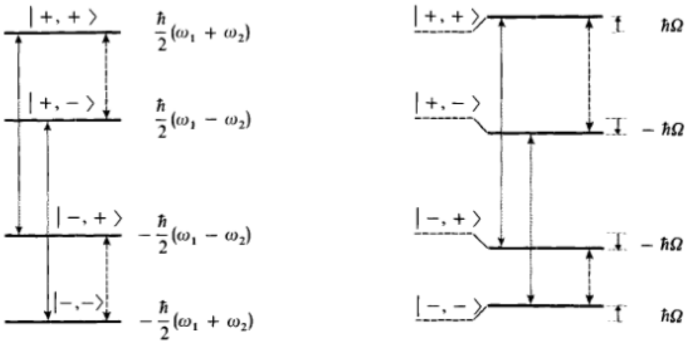


Figure 2: Energy corrections(non-degenerate)

From this correction we can find that the transition from $|++\rangle$ to $|-+\rangle$ now has an energy of $\hbar(\omega_1 + 2\Omega)$, the transition from $|++\rangle$ to $|+-\rangle$ has an energy of $\hbar(\omega_2 + 2\Omega)$, transition from $|+-\rangle$ to $|--\rangle$ now has an energy of $\hbar(\omega_1 - 2\Omega)$ and transition from $|-+\rangle$ to $|--\rangle$ now has an energy of $\hbar(\omega_2 - 2\Omega)$. We thus observe that the original two peaks in the spectrum split into two sets of twin peaks centered at ω_1 and ω_2 with the twin peaks separated by 4Ω(Figure 2 and Figure 3).

So far we considered $\omega_1 > \omega_2$, but as in some real materials such as gypsum($CaSO_4, 2H_2O$), $\omega_1 = \omega_2 = \omega$. In such cases we have to employ degenerate perturbation theory since the eigenvalues of H_0 for $|+-\rangle$ and $|-+\rangle$ are now the same.

We have already found $\langle +-|W|+-\rangle$ and $\langle -+|W|-+\rangle$, it turns out the the matrix elements $\langle +-|W|-+\rangle$ and $\langle -+W|-+\rangle$ are also $-\hbar\Omega$. Thus in the basis of $|+-\rangle$ and $|-+\rangle$ the perturbation can be written as

$$W = -\hbar\Omega \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \tag{86}$$

Solving for the eigenvalues and eigenvectors of this system, we obtain in the

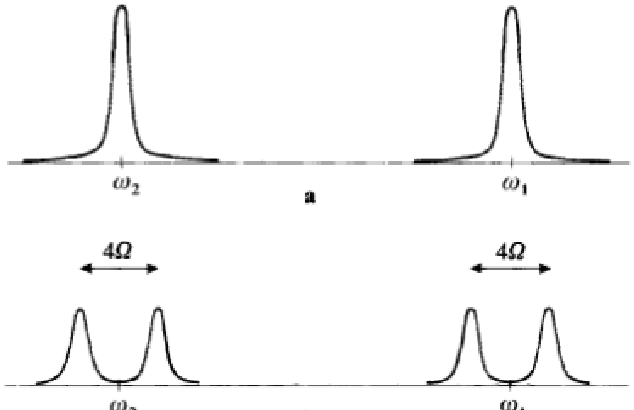


Figure 3: Split of resonance frequencies(non-degenerate)

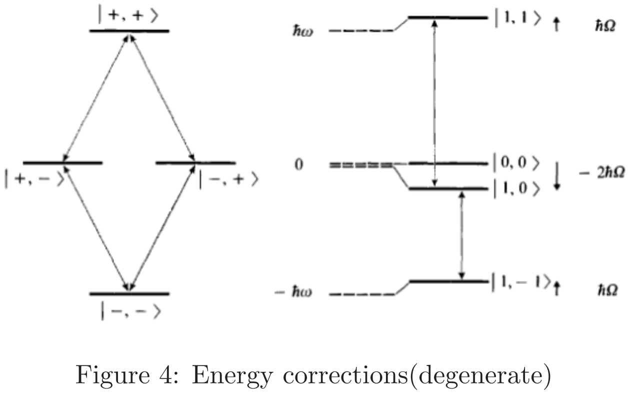


Figure 4: Energy corrections(degenerate)

Figure 5: Split of resonance frequencies(degenerate)

$|SM\rangle$ notation

$$|10\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} + \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}, |00\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix} - \frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix} \qquad (87)$$

The eigenvalues of W in the $|+-\rangle$ and $|-+\rangle$ basis are 0 and $-2\hbar\Omega$ corresponding to the states $|00\rangle$ and $|10\rangle$ in the $|SM\rangle$ notation. The other 2 nondegenerate states $|++\rangle$ and $|--\rangle$ corresponds to $|11\rangle$ and $|1-1\rangle$ in the $|SM\rangle$ notation. Transitions only occur between states with the same L. The frequency of transition after correction from $|11\rangle$ to $|10\rangle$ is $\omega + 3\hbar\Omega$ and the frequency for transition from $|10\rangle$ to $|1-1\rangle$ becomes $\omega - 3\hbar\Omega$. We can thus observe twin peaks centered at ω that are separated by 6Ω(Figure 4 and 5).

Volume Effect

In a hydrogen atom, we typically assume to have a potential of the form $V(r) = -\frac{e^2}{r}$, but with such an assumption we are treating the proton as a point which it really isn't. Thus this volume effect should show up in the spectrum of the atom. Assume the atom has a radius a_0 which is the Bohr radius and the proton has a radius of r_0, satisfying $r_0 \ll a_0$. Also assume the charge of the proton is uniformly distributed in the volume of the sphere, we ca find the potential for both inside and outside the proton

$$V(r) = \begin{cases} -\frac{e^2}{r} & , r > r_0 \\ \frac{3e^2}{r_0} - \frac{e^2}{2r_0^3}r^2 & , r < r_0 \end{cases} \tag{88}$$

Contrasting this potential with the original potential for which we known the energy levels, we obtain that our perturbation for this problem

$$W = \begin{cases} 0 & , r > r_0 \\ \frac{e^2}{2r_0}[(\frac{r}{r_0})^2 + 2\frac{r_0}{r} - 3] & , r < r_0 \end{cases} \tag{89}$$

With this correction the Hamiltonian of the hydrogen atom can be written as

$$H = H_0 + W \tag{90}$$

H_0 is the hamiltonian of the hydrogen atom treating the proton as fixed and as a point with $H_0|nlm\rangle = E_n|nlm\rangle$ and $E_n = -\frac{E_{ion}}{n^2}$. Where E_{ion} is the ionizing engergy. The engery levels $|nlm\rangle$ are degenerate which means we need to employ degenerate perturbation theory to solve this problem.
Consider the subspace for a fixed n and W in that subspace. The matrix elements in this basis are

$$\begin{aligned} \langle nlm|W|nl'm'\rangle &= \int d^3r\ \phi^*_{nlm}(\overrightarrow{r})W(r)\phi_{nl'm'}(\overrightarrow{r}) \\ &= \int d\Omega Y^*_{lm}Y_{l'm'} \int dr\ r^2 R^*_{nl}(r)W(r)R_{nl'}(r) \\ &= \delta_{ll'}\delta_{mm'} \int dr\ r^2 W(r)|R_{nl}(r)|^2 \end{aligned} \tag{91}$$

Thus W in this basis has only diagonal elements which simplifies everything. Also, W is non-zero only within r_0 thus within r_0 we can approximate $R_{nl}(r)$ by $R_{nl}(0)$. Thus the matrix elements are

$$\begin{aligned} \langle nlm|W|nlm\rangle &= \int dr\ r^2 W(r)|R_{nl}(r)|^2 \\ &\approx |R_{nl}(0)|^2 \int_0^{r_0} dr\ r^2 W(r) \\ &= |R_{nl}(0)|^2 \frac{e^2 r_0^2}{10} \end{aligned} \tag{92}$$

Thus we find the corrected energies are given by

$$E'_{nl} = E_n + |R_{nl}(0)|^2 \frac{e^2 r_0^2}{10} + ... \tag{93}$$

Note that $|R_{nl}(0)|^2$ is non-zero only when $l = 0$, thus only s-waves are affected by this effect(within this approximation) which can be verified by observation.

Variational Method

Suppose we are given a certain hamiltonian

$$H|\psi\rangle = E|\psi\rangle \tag{94}$$

The expectation of the hamiltonian is given by

$$\langle H\rangle = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \tag{95}$$

Now we introduce a perturbation to $|\psi\rangle$,

$$|\psi\rangle \rightarrow |\psi\rangle + \lambda|\delta\psi\rangle \tag{96}$$

Now $\langle H\rangle$ becomes, to the first order of λ,

$$\langle H\rangle \rightarrow \frac{\langle H\rangle + \lambda^*\langle\delta\psi|H|\psi\rangle + \lambda\langle\psi|H|\delta\psi\rangle + ...}{\langle\psi|\psi\rangle + \lambda^*\langle\delta\psi|\psi\rangle + \lambda\langle\psi|\delta\psi\rangle + ...} = \frac{N}{D} \tag{97}$$

Expand D^{-1} to first order of λ we obtain

$$D^{-1} = \langle\psi|\psi\rangle^{-1}[1 - \lambda^*\frac{\langle\delta\psi|\psi\rangle}{\langle\psi|\psi\rangle} - \lambda\frac{\langle\psi|\delta\psi\rangle}{\langle\psi|\psi\rangle} + ...] \tag{98}$$

Plug this into the expression for $\langle H\rangle$ we obtain

$$\langle H\rangle \rightarrow \frac{N}{D} = \langle H\rangle + \frac{1}{\langle\psi|\psi\rangle}\{\lambda\langle\psi|H|\delta\psi\rangle - \lambda\langle H\rangle\langle\psi|\delta\psi\rangle + C.C.\} + O(\lambda^2) \tag{99}$$

When the original wavefunction $|\psi\rangle$ is a eigenfunction of the Hamiltonian, $H|\psi\rangle = E|\psi\rangle$, the terms in curly brackets in the above equation becomes

$$\lambda E\langle\psi|\delta\psi\rangle - \lambda E\langle\psi|\delta\psi\rangle + C.C. = 0 \tag{100}$$

Thus in this case after introducing $|\delta\psi\rangle$ to $|\psi\rangle$, $\langle H\rangle \rightarrow \langle H\rangle + O(\lambda^2)$, which means any perturbation of first order to an eigenstate of the Hamiltonian will not change the expectation of the Hamiltonian to the first order.
Conversely, if $\langle H\rangle$ is not changed by any $|\delta\psi\rangle$ to first order, we can choose

$$|\delta\psi\rangle = \lambda^*(H - \langle H\rangle)|\psi\rangle \tag{101}$$

With this choice we plug it into the terms in culry brackets in Equation (99)

$$\begin{aligned} 0 &= \lambda\langle\psi|H|\delta\psi\rangle - \lambda\langle H\rangle\langle\psi|\delta\psi\rangle + C.C. && (102)\\ &= |\lambda|^2\langle\psi|(H - \langle H\rangle)(H - \langle H\rangle)|\psi\rangle + C.C. && (103)\\ &= 2\langle\delta\psi|\delta\psi\rangle && (104) \end{aligned}$$

From this result and the choice of $|\delta\psi\rangle$ we find that $H|\psi\rangle = \langle H\rangle|\psi\rangle$ which means $|\psi\rangle$ is an eigenvector. We see that the converse of our previous argument is also true.

Example: Harmonic Oscillator

Consider a Harmonic oscillator, the hamiltonian of which is given by

$$H = \frac{P^2}{2m} + \frac{1}{2}m\omega^2 x^2 \tag{105}$$

We want to figure out the ground state. We first want to guess the wave function. For the ground state, a good guess will be $\psi = e^{-\alpha x^2}$, where α is an arbitrary parameter. Now, we need to calculate H

First, the denominator

$$\langle\psi|\psi\rangle = \int_{-\infty}^{\infty} dx\ e^{-2\alpha x^2} \tag{106}$$

The numerator, i. e. average of hamiltonian is given by

$$\begin{aligned}\langle\psi|H|\psi\rangle &= \int_{-\infty}^{\infty} dx\ [\frac{\hbar^2}{2m}(\psi')^2 + \frac{1}{2}m\omega^2 x^2\psi^2] \\ &= \int_{-\infty}^{\infty} dx\ [\frac{\hbar^2}{2m}(2\alpha x)^2 e^{-2\alpha x^2}) + \frac{1}{2}m\omega^2 x^2 e^{-2\alpha x^2}] \\ &= (\frac{2\hbar^2\alpha^2}{m} + \frac{1}{2}m\omega^2)\int_{-\infty}^{\infty} dx\ x^2\ e^{-2\alpha x^2} \\ &= (\frac{2\hbar^2\alpha^2}{m} + \frac{1}{2}m\omega^2)[(-)\frac{x\ e^{-2\alpha x^2}}{4\alpha}|_{-\infty}^{\infty} + \frac{1}{4\alpha}\int_{-\infty}^{\infty} dx\ e^{-2\alpha x^2}]\end{aligned} \tag{107}$$

The first term goes to zero when $x \to \infty$ and only the second remains. Also, the integral inside the second term is exactly equal to $\langle\psi|\psi\rangle$ and get cancels with the denominator. So

$$\begin{aligned}\langle H\rangle &= [\frac{2\hbar^2\alpha^2}{m} + \frac{1}{2}m\omega^2]\frac{1}{4\alpha} \\ &= \frac{\hbar^2}{2m}\alpha + \frac{m\omega^2}{8\alpha}\end{aligned} \tag{108}$$

I have free parameter α which we haven't specified. So we find the extremum of $\langle H\rangle$ with respect to α. i.e,

$$\frac{d\langle H\rangle}{d\alpha} = \frac{\hbar^2}{2m} - \frac{m\omega^2}{8\alpha^2} = 0 \tag{109}$$

This equation fixes α, which is given by

$$\alpha = \frac{m\omega}{2\hbar} \tag{110}$$

For this α,

$$\begin{aligned}\langle H\rangle &= \frac{\hbar^2}{2m}\frac{m\omega}{2\hbar}+\frac{1}{8}m\omega^2\frac{2\hbar}{m\omega} \\ &= \frac{\hbar}{4}+\frac{\hbar}{4} \\ &= \frac{\hbar\omega}{2}\end{aligned}\tag{111}$$

Which is precisely the ground state energy. Now, we see ψ, which is the ground state wave function, is given by

$$\psi = e^{-\frac{m\omega}{2\hbar}x^2}\tag{112}$$

This is exactly the same wave function that we obtain by solving the Schrodinger equation.

Example II: Harmonic oscillator

Let us guess ψ which has peak at $x \to 0$ and goes to zero smoothly at $x \to \infty$, as ground state of harmonic oscillator. For that we choose $\psi = \frac{1}{(x^2+\alpha^2)}$. In the same way as before, we calculate the denominator.

$$\langle\psi|\psi\rangle = \int_{-\infty}^{\infty} dx\ \frac{1}{(x^2+\alpha^2)^2}\tag{113}$$

substitute $x = \alpha\ tan\theta$, we get,

$$\begin{aligned}\langle\psi|\psi\rangle &= \frac{2}{\alpha^3}\int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} d\theta\ \cos^2\theta \\ &= \frac{\pi}{2\alpha^3}\end{aligned}\tag{114}$$

Now, the numerator is

$$\langle\psi|H|\psi\rangle = \int_{-\infty}^{\infty} dx\ [\frac{\hbar^2}{2m}(\frac{1}{(x^2+\alpha^2)})'^2 + \frac{1}{2}m\omega^2x^2\frac{1}{(x^2+\alpha^2)^2}]\tag{115}$$

making substitution $x = \tan\theta$, we get,

$$\langle\psi|H|\psi\rangle = \frac{\pi\hbar^2}{8m\alpha^5}+\frac{\pi m\omega^2}{4\alpha}\tag{116}$$

Therefore,

$$\langle H\rangle = \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\hbar^2}{4m\alpha^2}+\frac{m\omega^2\alpha^2}{2}\tag{117}$$

Taking $\frac{d\langle H\rangle}{d\alpha} = 0$, we obtain

$$-\frac{\hbar^2}{2m\alpha^3}+m\omega^2\alpha = 0\tag{118}$$

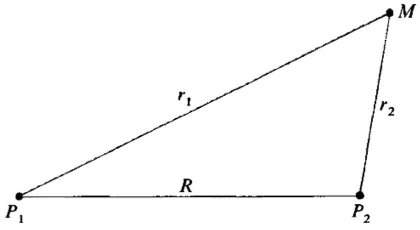


Figure 6: H_2^+ ion

or,

$$\alpha^4 = \frac{\hbar^2}{2m^2\omega^2} \tag{119}$$

Looking at energy

$$\begin{aligned} \langle H \rangle &= \frac{\hbar\omega}{\sqrt{2}} \\ &\approx 0.7\ \hbar\omega \end{aligned} \tag{120}$$

But, the correct answer is 0.5 $\hbar\omega$

Chemical Bond of H_2^+ Ion

In this section we will study the "real life" example of the chemical bond in a H_2^+ ion which consists of 2 protons which share an electron.
The geometry of the situation is shown in Figure 6 where $\vec{r_1}$ is the distance from proton 1 to the electron, $\vec{r_2}$ is the distance from proton 2 to the electron, and $\vec{R}$ is the distance from proton 1 to proton 2. The Hamiltonian for the system is given by

$$H = \frac{p^2}{2\mu} - \frac{e^2}{r_1} - \frac{e^2}{r_2} + \frac{e^2}{R} \tag{121}$$

where the last three terms in the Hamiltonian are the potential energies due to the particle interactions. Now consider the system when the electron is very close to proton 1. Referring to Figure 6 we see that $r_2 \approx R$ which implies that the last two terms in the Hamiltonian cancel leaving us with

$$H \approx \frac{p^2}{2\mu} - \frac{e^2}{r_1} \tag{122}$$

Recent work with the hydrogen atom allows us to recognize ground state solutions of the form

$$\varphi(\vec{r_1}) = Ae^{\frac{-r_1}{a_0}} = \frac{1}{\sqrt{\pi a_0^3}} e^{\frac{-r_1}{a_0}} \tag{123}$$

where the constant A was determined by normalization. We can make the same argument for the electron being very close to proton 2 which yields a solution

$$\varphi(\vec{r_2}) = \frac{1}{\sqrt{\pi a_0^3}} e^{\frac{-r_2}{a_0}} \tag{124}$$

The Variational Approach

Because the electron moves around in the real situation we cannot use these specific solutions to generally describe the motion. However, we may use a linear combination of the two solutions as our guess at the variational method

$$\psi = c_1\varphi(\vec{r_1}) + c_2\varphi(\vec{r_2}) \tag{125}$$

So we want to solve the equation

$$H\psi = E\psi \tag{126}$$

in order to find the eigenvalues and eigenfunctions. We use our guess and write the eigenvalue equation in the form

$$H \mid \psi\rangle = E \mid \psi\rangle \tag{127}$$

Projecting Equation (125) onto the state $\mid 1\rangle$ and using the expansion

$$\mid \psi\rangle = c_1 \mid 1\rangle + c_2 \mid 2\rangle \tag{128}$$

we obtain

$$c_1\langle 1 \mid H \mid 1\rangle + c_2\langle 1 \mid H \mid 2\rangle = Ec_1\langle 1 \mid 1\rangle + Ec_2\langle 1 \mid 2\rangle \tag{129}$$

Projecting Equation (125) onto the state $\mid 2\rangle$ and using Equation (126) we obtain

$$c_1\langle 2 \mid H \mid 1\rangle + c_2\langle 2 \mid H \mid 2\rangle = Ec_1\langle 2 \mid 1\rangle + Ec_2\langle 2 \mid 2\rangle \tag{130}$$

These two equations may be written in matrix form as

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \tag{131}$$

where

$$\langle i \mid H \mid j\rangle = H_{ij} \tag{132}$$

$$\langle i \mid j\rangle = S_{ij} \tag{133}$$

and i,j = 1,2. Our job now is to analyze the equation

$$det(H - ES) = 0 \tag{134}$$

We begin by constructing the matrix elements of H and S from Equation (131) **For the matrix S** we have

$$S_{11} = \langle 1 \mid 1\rangle \tag{135}$$

$$S_{12} = \langle 1 \mid 2\rangle \tag{136}$$

$$S_{21} = \langle 2 \mid 1\rangle \tag{137}$$

$$S_{22} = \langle 2 \mid 2\rangle \tag{138}$$

We can simplify this by noting that φ_1 and φ_2 are both normalized so that $S_{11} = S_{22} = 1$. We also notice that since our two states are real $S_{12} = S_{21} = s$. Then we see that

$$s = \langle 1 \mid 2\rangle = \langle 2 \mid 1\rangle = \int d^3r_1\varphi_1(r_1)\varphi_2(r_2) = \int d^3r_1\varphi_1(r_1)\varphi_2(r_1 - R) \tag{139}$$

where the last equality comes from the relation between positions $r_2 = r_1 - R$. We obtain

$$s = \frac{1}{\pi a_0^3}\int_0^\infty\int_0^\pi\int_0^{2\pi} r_1^2 cos\theta dr_1 d\theta d\phi e^{\frac{-r_1}{a_0}} e^{\frac{-|r_1-R|}{a_0}} \tag{140}$$

$$= e^{\frac{-R}{a_0}}[1 + \frac{R}{a_0} + \frac{1}{3}\frac{R^2}{a_0^2}] \tag{141}$$

For the matrix H we have

$$H_{11} = \langle 1 \mid H \mid 1\rangle = \langle 1 \mid \frac{p^2}{2\mu} - \frac{e^2}{r_1} - \frac{e^2}{r_2} + \frac{e^2}{R} \mid 1\rangle \tag{142}$$

The first two terms are simply the Hamiltonian corresponding to the hydrogen atom with $r = r_1$ where $H' \mid 1\rangle = E' \mid 1\rangle$. Since this is the familiar ionization energy we may rewrite the equation as

$$H_{11} = -E_{ion} - \langle 1 \mid \frac{e^2}{r_2} \mid 1\rangle + \frac{e^2}{R} \tag{143}$$

Now we determine $\langle 1 \mid \frac{e^2}{r_2} \mid 1\rangle$ as follows

$$\langle 1 \mid \frac{e^2}{r_2} \mid 1\rangle = \int d^3r_1\varphi^2(r_1)\frac{e^2}{\mid r_1 - R \mid} = \frac{1}{\pi a_0^3}\int d^3r_1 e^{\frac{-2r_1}{a_0}}\frac{e^2}{\mid r_1 - R \mid} \tag{144}$$

$$= E_{ion}\frac{2a_0}{R}[1 - e^{\frac{-2R}{a_0}}(1 + \frac{R}{a_0})] \tag{145}$$

The matrix element H_{12} is found in a similar manner to be

$$H_{12} = E_{ion}2e^{\frac{-R}{a_0}}(1 + \frac{R}{a_0}) \tag{146}$$

But $H_{11} = H_{22}$ since it does not matter whether you integrate over r_1 or r_2 and $H_{12} = H_{21}$ since H is Hermitian so we have constructed the two matrices S and H.

Solutions:

Now we find the determinant to obtain the eigenvalues.

$$det(H - ES) = (H_{11} - E)^2 - (H_{12} - E)^2 = 0 \tag{147}$$

which yields the two solutions

$$E_+ = \frac{H_{11} + H_{12}}{1 + S} \tag{148}$$

$$E_- = \frac{H_{11} - H_{12}}{1 - S} \tag{149}$$

If the protons fly away from each other ($R \rightarrow \infty$) what happens to these energies? Well, since both are dependent only on H_{11}, H_{12}, and S we can look at the behavior of these quantities as $R \rightarrow \infty$ to find out. Equations (143) and (145) imply that

$$\lim_{R\rightarrow\infty} H_{11} \rightarrow -E_{ion} \tag{150}$$

and equations (138) and (144) show that

$$\lim_{R\rightarrow\infty} S \rightarrow 0 \tag{151}$$

$$\lim_{R\rightarrow\infty} H_{12} \rightarrow 0 \tag{152}$$

Referring back to Equations (148) and (148) we see that

$$\lim_{R\rightarrow\infty} E_+ \rightarrow -E_{ion} \tag{153}$$

and

$$\lim_{R\rightarrow\infty} E_- \rightarrow -E_{ion} \tag{154}$$

So that the equations for E_+ and E_- come together asymptotically as shown in Figure 7.

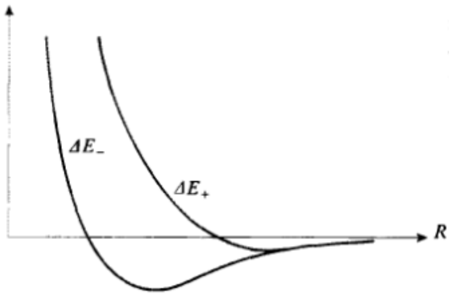


Figure 7: E_+ and E_- converges to $-E_{ion}$

UNIT 4

Fine and hyperfine structure of the hydrogen atom

Notes by N. Sirica and R. Van Wesep

Previously, we solved the time-independent Schödinger equation for the Hydrogen atom, described by the Hamiltonian

$$H = \frac{p^2}{2m} - \frac{e^2}{r} \tag{1}$$

Where e is the electron's charge in your favorite units. However, this is not really the Hamiltonian for the Hydrogen atom. It is non-relativistic and it does not contain spin. In order to completely describe the Hydrogen we would need to use the Dirac equation. We will not introduce that equation here, but we will say a few words about the most important energy level of the relativistic Hydrogen atom, namely the rest mass energy.

$$E = mc^2 \approx 0.5\text{MeV} \tag{2}$$

We can compare this to the ground state (ionization) energy we found for the Hamiltonian in 1.

$$E = -E_{ion} \approx 13.6\text{eV} \ll mc^2 \tag{3}$$

Even though the rest mass energy is so much larger, it appears constant in the non-relativistic regime. Since differences in energy are important, we could ignore it before. The rest mass energy may be large, but it does not enter the world of everyday experience. Regardless, it is fruitful to investigate the relative size of the ionization energy to the rest mass energy.

$$\frac{E_{ion}}{mc^2} = \frac{me^4}{2\hbar^2}\frac{1}{mc^2} = \frac{e^4}{2c^2\hbar^2} = \frac{\alpha^2}{2} \tag{4}$$

Where $\alpha = \frac{e^2}{\hbar c} = \frac{1}{137}$ is a fundamental constant of nature. No one understands it, but it is important that it is small. This means that calculations, such as those in perturbation theory, are possible and gives the orders successive corrections. Let us move to these corrections in the case of the Hydrogen atom.

Relativistic Energy Correction

We begin with the relativistically correct expression for the energy.

$$\begin{aligned} E &= \sqrt{p^2c^2 + m^2c^4} = mc^2\sqrt{1 + \frac{p^2}{m^2c^2}} \\ &= mc^2\left(1 + \frac{p^2}{2m^2c^2} - \frac{p^4}{8m^4c^4} + \dots\right) \\ &= mc^2 + \frac{p^2}{2m} - \frac{p^4}{8m^3c^4} + \dots \end{aligned} \tag{5}$$

The second term is the non-relativistic kinetic energy that we are familiar with in everyday life. The third term is the first relativistic correction to the energy. We shall define this as the first perturbation to the Hamiltonian $W_1 = -p^4/8m^3c^4$. Let us investigate the relative strength of this perturbation. First we recognize that $\frac{p^2}{2m} \sim E_{ion}$ so $\frac{p^4}{m^2} \sim E_{ion}^2$. Thus,

$$W_1 \sim \frac{E_{ion}^2}{mc^2} \tag{6}$$

$$\frac{W_1}{E_{ion}} \sim \frac{E_{ion}}{mc^2} \sim \alpha^2 \tag{7}$$

So once again we see the the fine structure constant. We expect to see a correction in the spectrum that is $\sim \alpha^2$. This number is small enough that we can use perturbation theory.

Spin-Orbit Coupling

From relativity, a particle moving in an electric field feels a small magnetic field in its reference frame. For a particle with velocity $\vec{v} = \vec{p}/m$ moving in an electric field $\vec{E}$ this magnetic field is given by:

$$\vec{B} = -\frac{1}{c^2}\vec{v} \times \vec{E} + \mathcal{O}(v^2/c^2) \tag{8}$$

In the Hydrogen we have an electric field due to the Coulomb potential.

$$\vec{E} = \nabla\frac{e}{r} = -e\frac{\vec{r}}{r^3} \tag{9}$$

We shall define our next perturbation as the energy of a dipole moment in a magnetic field.

$$W_2 = -\vec{\mu}\cdot\vec{B} \tag{10}$$

In this case the magnetic dipole moment is related to the electron spin.

$$\vec{\mu} = \frac{e}{m}\vec{S} \tag{11}$$

Putting this, the magnetic field given in 8 and the electric field given in 9 into 10 we obtain

$$\begin{aligned} W_2 &= \frac{e}{m^2c^2}\vec{S}\cdot\left(\vec{p}\times\vec{E}\right) \\ &= -\frac{e^2}{m^2c^2}\vec{S}\cdot\left(\vec{p}\times\frac{\vec{r}}{r^3}\right) \end{aligned} \tag{12}$$

Since the angular momentum is given by $\vec{L} = \vec{r}\times\vec{p}$ we can write the spin-orbit term as

$$W_2 = \frac{e^2}{m^2c^2}\frac{1}{r^3}\vec{S}\cdot\vec{L} \tag{13}$$

Unfortunately, this answer is wrong. If we had performed a completely relativistic calculation we would have found the correct expression, one describing Thomas precession.

$$W_2 = \frac{e^2}{2m^2c^2}\frac{1}{r^3}\vec{S}\cdot\vec{L} \tag{14}$$

As we did for the previous correction, let us look at the relative order of the spin-orbit coupling energy. Recognizing that $r \sim a_0 = \hbar^2/me^2$, $\vec{S} \sim \hbar$, $\vec{L} \sim \hbar$ we find

$$\begin{aligned} \frac{W_2}{E_{ion}} &\sim \frac{e^2\hbar^2}{m^2c^2}\frac{m^3e^6}{\hbar^6}\frac{\hbar^2}{me^4} \\ &\sim \frac{e^4}{c^2\hbar^2} = \alpha^2 \end{aligned} \tag{15}$$

Once again, the order of this correction is related to the fine structure constant.

Darwin Term

The next correction is a bit more subtle than the previous two. It has to do with the relativistic effects that arise from the Schrödinger equation being an approximation of the Dirac equation. The order of these relative effects is governed by the ratio $v/c = p/mc$ which defines an upper limit to the electron momentum mc. This ratio is often written λ/λ_0 where the deBroglie wavelength is given by $p = h/\lambda$ and the Compton wavelength is given by $mc = h/\lambda_0$. Since the Compton wavelength is the minimum wavelength that the electron can have, measurements of the position of the electron can only be accurate up to $\sim \lambda_0$. So, rather than being able to exactly determine the electron position, we can only determine a fuzzy ball about the size of λ_0. This is illustrated in Figure 1.

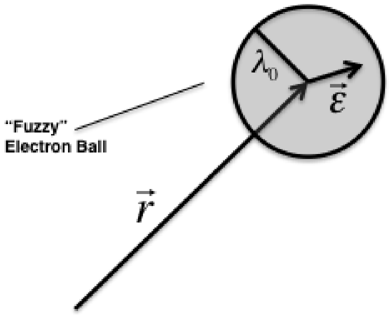


Figure 1: Setup of the Darwin correction

In order to quantify this correction we shall define an effective potential that is the average of the potential over the fuzzy ball.

$$V_{eff} = \frac{1}{\text{Volume}} \int V\left(\vec{r} + \vec{\epsilon}\right) d^3\epsilon \tag{16}$$

The effective potential is almost the Coulomb potential because the sphere we shall use for the integration is very small: $|\vec{\epsilon}| \leq \lambda_0$. We shall perform the integration over a sphere of Volume $= \frac{4}{3}\pi\left(\frac{\hbar}{mc}\right)^3$ where we have used $\hbar$ instead of h in the Compton wavelength for convenience. Since $\vec{\epsilon}$ is small we shall Taylor expand:

$$V\left(\vec{r} + \vec{\epsilon}\right) = V\left(\vec{r}\right) + \vec{\epsilon} \cdot \nabla V + \sum_{i,j=1}^{3} \frac{1}{2} \epsilon_i \epsilon_j \frac{\partial}{\partial x_i} \frac{\partial}{\partial x_j} V + \cdots \tag{17}$$

Let us perform the integration term by term for clarity.

$$\int V\left(\vec{r}\right) d^3\epsilon = V\left(\vec{r}\right) \times \text{Volume} \tag{18}$$

$$\int \vec{\epsilon} \cdot \nabla V d^3\epsilon = \nabla V \cdot \int \vec{\epsilon} d^3\epsilon = 0 \tag{19}$$

Since there is no preferred direction and we are integrating over all directions. This is also the reason why

$$\int \epsilon_i \epsilon_j d^3\epsilon = A\delta_{ij} \tag{20}$$

Where A is an undetermined constant. In order to find A we shall perform the integration

$$\begin{aligned}\int \left(\epsilon_x^2 + \epsilon_y^2 + \epsilon_z^2\right) d^3\epsilon &= 3A \\ 4\pi \int_0^{\lambda_0} \epsilon^4 d\epsilon &= \frac{4\pi}{5}\lambda_0^5 \\ A &= \frac{4\pi}{15}\lambda_0^5 \end{aligned} \tag{21}$$

Putting 20 and 21 into the average of the third term in 17 we obtain

$$\begin{aligned}\frac{3m^3c^3}{4\pi\hbar^3} \int \epsilon_i \epsilon_j \frac{\partial}{\partial x_i}\frac{\partial}{\partial x_j} V d^3\epsilon &= \frac{1}{2}\frac{4\pi}{15}\lambda_0^5 \frac{3m^3c^3}{4\pi\hbar^3}\nabla^2 V \\ &= \frac{1}{10}\left(\frac{\hbar}{mc}\right)^2 \nabla^2 V \end{aligned} \tag{22}$$

So in the end we have obtained an expression for the effective potential.

$$V_{eff} = V\left(\vec{r}\right) + \frac{1}{10}\left(\frac{\hbar}{mc}\right)^2 \nabla^2 V + \cdots \tag{23}$$

Unfortunately, once again we are slightly off. A full relativistic calculation gives us our third perturbation to the Hamiltonian in 1.

$$W_3 = \frac{1}{8}\left(\frac{\hbar}{mc}\right)^2 \nabla^2 V \tag{24}$$

Let us once again examine the relative strength of this term for the Hydrogen atom. In this case

$$\nabla^2 V = \nabla^2 \frac{e^2}{r} = -4\pi e^2 \delta^3\left(\vec{r}\right) \tag{25}$$

In order to compare this W_3 to the ionization energy, we must specify the state and take an expectation value. Let us use the ground state.

$$\varphi = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} \tag{26}$$

Then the order of the expectation value of W_3 can be obtained.

$$\begin{aligned}\langle W_3\rangle &\sim \frac{\hbar^2}{m^2c^2}\frac{e^2}{\pi a_0^3}\int e^{-r/a_0}\delta^3\left(\vec{r}\right)d^3r\\ &\sim \frac{\hbar^2}{m^2c^2}\frac{e^8m^3}{\hbar^6}\end{aligned}\tag{27}$$

From this we can find the relative order of the Darwin correction.

$$\frac{\langle W_3\rangle}{E_{ion}}\sim\frac{e^8m}{c^2\hbar^4}\frac{\hbar^2}{me^4}=\frac{e^4}{\hbar^2c^2}=\alpha^2\tag{28}$$

Not surprisingly the correction is again $\sim\alpha^2$.

Fine Structure: $n=2$ Level

The $n=2$ level of the Hydrogen is the first level that will exhibit significant changes, so we shall examine the effects of the above perturbations in this level. The $n=2$ level admits angular momentum numbers $l=0,1$ These momentum states are termed 2s and 2p respectively. When we consider the spin degree of freedom the degeneracy of the 2s and 2p states is 2 and 8 respectively. Luckily, each term in the perturbation $W=W_1+W_2+W_3$ is rotationally invariant (they only involve the operators $\vec{L}$, p^2, r and $\vec{S}$), so $\left[W,L^2\right]=0$. Hence, the perturbation will not mix the 2s and 2p subsets and we can treat them separately.

2s State

In the 2s state the electron eigenfunction is given by $\langle\vec{r}|200\rangle=\varphi\left(\vec{r}\right)=R_{20}(r)Y_{00}(\Omega)$ where

$$R_{20}=\frac{2}{\left(2a_0\right)^{3/2}}\left(1-\frac{r}{2a_0}\right)e^{-r/2a_0}\tag{29}$$

In addition to the orbital wave equation, we much include the spin degree of freedom, so our eigenstates are $|200\pm\rangle$. In order to find the first order correction to the $n=2$ energy level, we must find the matrix elements of W between these eigenstates.

$$\delta E_1=\langle 200\pm|W_1|200\pm\rangle=-\frac{1}{8m^3c^2}\langle 200|p^4|200\rangle\langle\pm|\pm\rangle\tag{30}$$

Since $\langle\pm|\pm\rangle$ yields the elements of the identity matrix, we only have to worry about the inner product $\langle 200|p^4|200\rangle$. We can rewrite W_1 into a more convenient form.

$$H_0=\frac{p^2}{2m}-\frac{e^2}{r}\implies p^2=2m\left(H_0+\frac{e^2}{r}\right)\tag{31}$$

$$W_1 = -\frac{1}{8m^3c^2}4m^2\left(H_0 + \frac{e^2}{r}\right)^2 = -\frac{1}{2mc^2}\left(H_0 + \frac{e^2}{r}\right)^2 \tag{32}$$

Using this form and recognizing that $|200\rangle$ is an eigenstate of H_0 makes taking the necessary inner product easier.

$$\begin{aligned}\delta E_1 &= -\frac{1}{2mc^2}\langle 200|\left(H_0 + \frac{e^2}{r}\right)^2|200\rangle \\ &= -\frac{1}{2mc^2}\left(E_2^2 + 2E_2\left\langle\frac{e^2}{r}\right\rangle + \left\langle\frac{e^4}{r^2}\right\rangle\right) \\ &= -\frac{13}{128}mc^2\alpha^4 \qquad (33)\end{aligned}$$

Since $\vec{L}$ only has to do with the angles and φ_{200} has no angular dependence it is easy to see that $\langle 200|\vec{L}|200\rangle = 0$. This means that
Since $\nabla^2\frac{1}{r} = -4\pi\delta^3(\vec{r})$ the change in energy level due to the Darwin correction is simple to compute.

$$\begin{aligned}\delta E_3 = \langle W_3\rangle &= \frac{\hbar^2}{8m^2c^2}4\pi e^2\left|\varphi_{200}(\vec{0})\right|^2 \\ &= \frac{\hbar^2 e^2}{16m^2c^2a_0^3} = \frac{1}{16}mc^2\alpha^4 \qquad (34)\end{aligned}$$

Combining 33 and 34, we obtain the first order energy correction to the 2s state.

$$\delta E = \langle W\rangle = -\frac{5}{128}mc^2\alpha^4 \tag{35}$$

This is a precise number that we can compare to experiment.

Fine Structure of the 2p State

Last time, using the framework of time independent perturbation theory, we had discussed the three corrective terms to the hydrogen atom Hamiltonian. Using this, a first order energy correction to the $|200\rangle$ state was then constructed. However, if instead of considering this non-degenerate first excited state, we turn our attention to the degenerate $2p$ subshell. Computing first the matrix elements due to the relativistic correction of the Hamiltonian.

$$\langle 21m_l|W_1|21m_{l'}\rangle = \langle 21m_l| - \frac{P^4}{8m^3c^2}|21m_{l'}\rangle \tag{36}$$

Writing P^4 in terms of the unperturbed Hamiltonian of the hydrogen atom, $H_0 = \frac{P^2}{2m} - \frac{e^2}{r}$, one then notices for $|21m_l\rangle$ being an eigenstate of H_0 with eigenvalue E_2 that the matrix elements may be written separately in terms of their angular and radial components. In doing so,

$$
\begin{aligned}
&-\frac{1}{2mc^2}\langle 21m_l|(H_0+\frac{e^2}{r})^2|21m_{l'}\rangle && (37)\\
&=\langle 1m_l|1m_{l'}\rangle\int_0^\infty drr^2|R_{21}(r)|^2[-\frac{1}{2mc^2}(E_2+\frac{e^2}{r})^2] && (38)
\end{aligned}
$$

where as we know $R_{21}=\frac{\frac{r}{a_0}}{\sqrt{3}(2a_0)^{3/2}}\exp(-\frac{r}{2a_0})$. To evaluate this integral, begin first with considering each term independently, namely,

$$
\begin{aligned}
&-\frac{1}{2mc^2}\delta_{1,1}\delta m_l, m_{l'}[E_2^2\int_0^\infty drr^2|R_{21}(r)|^2\\
&+2E_2e^2\int_0^\infty drr|R_{21}(r)|^2+e^4\int_0^\infty dr|R_{21}(r)|^2] && (39)
\end{aligned}
$$

After computing these integrals, the diagonal matrix elements of W_1 are given by

$$
\begin{aligned}
&-\frac{1}{2mc^2}\delta_{m_l,m_{l'}}[E_2^2+2E_2\frac{e^2}{4a_0}+\frac{e^4}{12a_0^2}]\\
&=-\frac{7}{384}\delta_{m_l,m_{l'}}mc^2\alpha^4 && (40)
\end{aligned}
$$

To account then for the additional corrective terms, let's consider first the Darwin term, $W_3=\frac{\hbar^2}{10m^2c^2}\nabla^2V$. Now, in the case of a Coulomb potential, $\nabla^2V=-\nabla\cdot\nabla\frac{e^2}{r}=e^2\delta(r)$. Thus in evaluating the matrix element, it follows

$$
\langle 21m_l|W_3|21m_{l'}\rangle\propto\int drr^2|R_{21}|^2\delta(r)=0 \qquad (41)
$$

Meaning the Darwin term makes no contribution to the fine structure of the $2p$ state. Thus, in lastly accounting for spin orbit coupling, we consider from the basis common to the C.S.C.O. H_0, L^2, S^2, L_z, S_Z the eigenstate $|21m_lm_s\rangle$. Here, just as with W_1, we may separate the angular from the radial part in computing the matrix elements.

$$
\begin{aligned}
&\langle 21m_lm_s|W_2|21m_{l'}m_{s'}\rangle\\
&=\frac{e^2}{2m^2c^2}\langle 21m_lm_s|\frac{1}{r^3}L\cdot S|21m_{l'}m_{s'}\rangle && (42)\\
&=\frac{e^2}{2m^2c^2}\int_0^\infty dr\frac{1}{r}|R_{21}(r)|^2\langle 1m_lm_s|L\cdot S|1m_{l'}m_{s'}\rangle
\end{aligned}
$$

Where the integral then solves to $\frac{1}{3(2a_0)^3}$. To evaluate the angular expression, it is best to perform a change of basis to a common eigenstate of H_0, J^2, J_z, L^2, L^z where J of course denotes the total angular momentum $J=L+S$. In working then in the $|Jm_j\rangle$ basis one defines through the triangle rule, $|l-s| \leq J \leq l+s$, $j = 3/2$, with a degeneracy of 4 and $j = 1/2$ with a degeneracy 2. The benefit of this change of basis stems from the fact that $\langle L \cdot S\rangle$ may be expressed as $\langle \frac{1}{2}(J^2 - L^2 - S^2)\rangle$. Hence, for $l = 1$ and $s = 1/2$ the expectation value of $\langle L \cdot S\rangle$ becomes $\frac{\hbar^2}{2}(j(j+1) - 2 - \frac{3}{4})$. Thus the first order energy correction due to spin-orbit coupling within the $2p$ state is given as

$$\begin{aligned}\langle W_2\rangle =& \frac{\hbar^2 e^2}{96 m^2 c^2 a_0^3}(j(j+1) - \frac{11}{4}) \\ =& -\frac{1}{48} mc^2\alpha^4 \quad if \;\; j = \frac{1}{2} \qquad (43) \\ =& \frac{1}{96} mc^2\alpha^4 \quad if \;\; j = \frac{3}{4} \qquad (44)\end{aligned}$$

where α denotes the fine structure constant $\frac{e^2}{\hbar c}$. From these two expressions we see the degeneracy of the $2p$ state is partially lifted. Namely, the six eigenstates of the $|21 m_l m_s\rangle$ are separated into the four upper $|2\frac{3}{4}m_j\rangle$ and two lower $|2\frac{1}{2}m_j\rangle$ states.

The Zeeman effect

As seen on a number of occasions, perhaps one of the most apparent ways in which one may remove the degeneracy of a state is through switching on a magnetic field, say for instance, $\vec{B} = B\hat{z}$. By modelling an electron as an ideal magnetic dipole, this field will exert a torque on it. Associated with this torque is an energy given then by $H = -\vec{\mu}\cdot\vec{B}$. As previously found, the magnetic dipole of the electron is given by the sum of the dipole due to the orbital angular momentum and intrinsic spin. Provided $\vec{B} = B\hat{z}$ to be small, we may treat it as a perturbation defined by

$$W_z = -\vec{\mu} \cdot \vec{B} = \omega_L(L_z + 2S_z) \qquad (45)$$

with ω_L denoting the Larmor frequency. In considering once again the $2s$ state, by acting with W_z,

$$W_z\,|200\pm\rangle = \pm\hbar\omega_L\,|200\pm\rangle \qquad (46)$$

Hence, for the doubly degenerate eigenstate of the Hamiltonian $H_0 + W_{fs}$ the inclusion of W_z serves to lift the degeneracy, separating these states by $\hbar\omega_L$. Having sufficiently warmed up now, let us move on now to the more complicated $2p$ state. As one may recall, the degeneracy of the six $2p$ states was partially lifted through the effect of spin-orbit coupling. However, there is a problem with the operation of W_z on the $2p$ states, as such states were diagonalized within an eigenstate common to H_0, L^2, S^2, J^2, J_z not L_z and S_z. Thus, in considering the fact that W_{fs} was diagonalized in the $|Jm_j\rangle$ basis for the $2p$ state, we must perform a change basis to the $|m_l m_s\rangle$ basis, operate with W_z and then revert back to $|Jm_j\rangle$. Namely, as found using a table of clebsch-gordan coefficients

$$\begin{aligned}
&|\frac{3}{2}\frac{3}{2}\rangle = |1\frac{1}{2}\rangle \\
&|\frac{3}{2}\frac{1}{2}\rangle = \frac{1}{\sqrt{3}}\,|1-\frac{1}{2}\rangle + \sqrt{\frac{2}{3}}\,|0\frac{1}{2}\rangle \\
&|\frac{3}{2}-\frac{1}{2}\rangle = \sqrt{\frac{2}{3}}\,|0-\frac{1}{2}\rangle + \sqrt{\frac{1}{3}}\,|{-1}\frac{1}{2}\rangle \\
&|\frac{3}{2}-\frac{3}{2}\rangle = |{-1}-\frac{1}{2}\rangle \\
&|\frac{1}{2}\frac{1}{2}\rangle = -\frac{1}{\sqrt{3}}\,|0\frac{1}{2}\rangle + \sqrt{\frac{2}{3}}\,|1-\frac{1}{2}\rangle \\
&|\frac{1}{2}-\frac{1}{2}\rangle = -\sqrt{\frac{2}{3}}\,|{-1}\frac{1}{2}\rangle + \frac{1}{\sqrt{3}}\,|0-\frac{1}{2}\rangle
\end{aligned} \tag{47}$$

Acting with W_z on these states then entails

$$\begin{aligned}
&W_z\,|\frac{3}{2}\frac{3}{2}\rangle = W_z\,|1\frac{1}{2}\rangle = 2\hbar\omega_L\,|\frac{3}{2}\frac{3}{2}\rangle \\
&W_z\,|\frac{3}{2}\frac{1}{2}\rangle = \sqrt{\frac{2}{3}}\hbar\omega_L\,|0\frac{1}{2}\rangle = \hbar\omega_L[\frac{2}{3}\,|\frac{3}{2}\frac{1}{2}\rangle - \frac{\sqrt{2}}{3}\,|\frac{1}{2}\frac{1}{2}\rangle] \\
&W_z\,|\frac{3}{2}-\frac{1}{2}\rangle = -\sqrt{\frac{2}{3}}\hbar\omega_L\,|0-\frac{1}{2}\rangle = -\hbar\omega_L[\frac{2}{3}\,|\frac{3}{2}-\frac{1}{2}\rangle + \frac{\sqrt{2}}{3}\,|\frac{1}{2}-\frac{1}{2}\rangle] \\
&W_z\,|\frac{3}{2}-\frac{3}{2}\rangle = -2\hbar\omega_L\,|\frac{3}{2}-\frac{3}{2}\rangle \\
&W_z\,|\frac{1}{2}\frac{1}{2}\rangle = -\hbar\omega_L[\frac{\sqrt{2}}{3}\,|\frac{3}{2}\frac{1}{2}\rangle - \frac{1}{3}\,|\frac{1}{2}\frac{1}{2}\rangle] \\
&W_z\,|\frac{1}{2}-\frac{1}{2}\rangle = -\hbar\omega_L[\frac{\sqrt{2}}{3}\,|\frac{3}{2}-\frac{1}{2}\rangle + \frac{1}{3}\,|\frac{1}{2}-\frac{1}{2}\rangle]
\end{aligned} \tag{48}$$

Writing then a sub-matrix for $J = 3/2$,

$$\hbar\omega_L \begin{pmatrix} 2 & 0 & 0 & 0 \\ 0 & 2/3 & 0 & 0 \\ 0 & 0 & -2/3 & 0 \\ 0 & 0 & 0 & -2 \end{pmatrix} = \frac{4}{3}\hbar\omega_L \begin{pmatrix} 3/2 & 0 & 0 & 0 \\ 0 & 1/2 & 0 & 0 \\ 0 & 0 & -1/2 & 0 \\ 0 & 0 & 0 & -3/2 \end{pmatrix} \tag{49}$$

Which as one may recognize is $\frac{4}{3}\hbar\omega_L J_Z$. While the result obtained in (14) by all means correct, the calculation proved to be somewhat lengthy. Fortunately there exists a more expedient means to obtain this same result through the exploitation of the Wigner-Eckert Theorem. According to this theorem, for a fixed J, one may express any vector in terms of its projection along $\vec{J}$. That is, the quantity $\vec{L} \cdot 2\vec{S}$ is proportional to $\vec{J}$ by the constant of proportionality g_j

defined by

$$g_j \;=\; \frac{\langle \vec{L}\cdot\vec{J}\rangle}{|J|^2} + 2\frac{\langle \vec{S}\cdot\vec{J}\rangle}{|J|^2} \tag{50}$$

Thus for any fixed J we may then express

$$W_z = g_j \omega_L J_z \tag{51}$$

As a final note, one may recall that the results in this section are based upon the magnetic field being sufficiently weak such that it may be treated as a time independent perturbation. If the magnetic field is sufficiently strong then the above analysis does not hold. Rather one must revert back to the $|2lm_l ms\rangle$ basis, where the action of W_z gives

$$W_z\,|2lm_lm_s\rangle = \hbar\omega_L(m_l + 2m_s)\,|2lm_lm_s\rangle \tag{52}$$

Stark Effect

In the next application of perturbation theory to the Hydrogen atom, we will switch on an electric field $\vec{\mathcal{E}} = \mathcal{E}\hat{z}$. The dipole moment of a proton and electron separated by a vector $\vec{R}$ is $\vec{p} = q\vec{R}$. Our perturbation will be the energy of this dipole in the above electric field.

$$W_s = -\vec{p}\cdot\vec{\mathcal{E}} = -q\vec{\mathcal{E}}\cdot\vec{R} \tag{53}$$

In order to apply perturbation theory, it must be true that $W_s \ll H_0$ where H_0 is the Hamiltonian of the unperturbed atom. In practice, unlike the magnetic field, the electric field is almost never strong enough for this condition not to hold. Furthermore, we shall assume that we are in a strong field regime so that $W_s \gg W_1 + W_2 + W_3$ where the perturbations on the right hand side are the fine structure corrections.

Stark Effect: $n = 1$

We shall start by considering the $n = 1$ level. In this case $l = 0$ and $m = 0$ and the zeroth order eigenstate is $|100\rangle$. In this case the first order correction to the energy is given by $\Delta E = \langle 100\,|W_s|\,100\rangle$. This can be seen to vanish without calculation by observing that $|100\rangle$ has even parity while W_s depends linearly on $\vec{R}$ and so has odd parity.
Since the first order correction is zero, we must move on to the second order correction given by

$$\Delta E = \sum_{\substack{nlm\\ n\neq 1}} \frac{|\langle 100|W_s|nlm\rangle|^2}{E_1 - E_n} \tag{54}$$

Before calculating we know that $\Delta E \propto \mathcal{E}^2$ since $W_s \propto \mathcal{E}$. Also, we know that $\Delta E < 0$ since $E_1, E_n < 0$ and $|E_1| > |E_n|$. So, there is an energy shift, but the question is: where does the dipole moment come from? We know that

$$\langle\vec{p}\rangle = q\langle\vec{R}\rangle = q\langle 100|\vec{R}|100\rangle = 0 \tag{55}$$

Since symmetry dictates that $\vec{R}$ cannot choose a direction in which to point. So at first glance, there doesn't seem to be a dipole moment. The answer lies in the change of state due to the perturbation.

$$|100\rangle \rightarrow |100\rangle + \sum_{\substack{nlm \\ n\neq 1}} \frac{\langle nlm|W_s|100\rangle}{E_1 - E_n}|nlm\rangle \tag{56}$$

So the dipole moment is given approximately by

$$\langle\vec{p}\rangle = \sum_{\substack{nlm \\ n\neq 1}} \frac{\langle nlm|W_s|100\rangle}{E_1 - E_n}\langle nlm|\vec{p}|100\rangle + c.c. \tag{57}$$

Before calculating anything we notice that $\langle\vec{p}\rangle \propto \vec{\mathcal{E}}$ since the electric field is the only thing in the problem that defines a direction in which the dipole moment can point. This implies that $\langle p_x\rangle = \langle p_y\rangle = 0$. So, we only have to calculate $\langle p_z\rangle = q\langle z\rangle$.

In order to do this we shall use that

$$z = r\cos\theta = \sqrt{\frac{4\pi}{3}}rY_{10} \tag{58}$$

Where Y_{10} is a spherical harmonic. This will greatly simplify the integral.

$$\langle 100|z|nlm\rangle = \sqrt{\frac{4\pi}{3}}\int_0^\infty drr^2rR_{10}R_{nl}\int d\Omega Y_{00}^*Y_{10}Y_{lm} \tag{59}$$

Since $Y_{00}^* = 1/\sqrt{4\pi} = const.$ the angular integral simply gives $\delta_{l1}\delta_{m0}$. Since $W_s = -p_z\mathcal{E}$, the dipole moment is given by

$$\langle p_z\rangle = -2\mathcal{E}q^2\sum_{n=2}^{\infty}\frac{|\langle 100|z|n10\rangle|^2}{E_1 - E_n} = \chi\mathcal{E} \tag{60}$$

Where χ is the electric susceptibility.

Stark Effect: $n = 2$

Now $l = 1, 0$ where the degeneracy is 3 and 1 respectively. So, we must consider 4 states: $|21m\rangle$ and $|200\rangle$ where $m = 0, \pm 1$. We can see without calculation that $\langle 200\,|W_s|\,200\rangle = 0$ by the same parity argument we used in the $n = 1$ case. By a similar argument $\langle 21m\,|W_s|\,21m'\rangle = 0$ because W_s and the states $|21m\rangle$ all have odd parity. So the only non-vanishing matrix elements are given by

$$\langle 21m\,|W_s|\,200\rangle = -\sqrt{\frac{4\pi}{3}}\int_0^\infty drr^2q\mathcal{E}rR_{20}R_{21}\int d\Omega Y_{00}Y_{10}Y_{1m}^* \tag{61}$$

The angular integral yields a δ_{m0}, so there are two non-vanishing matrix elements given by $\langle 210\,|W_s|\,200\rangle = \gamma\mathcal{E}$ where γ is real and can be calculated from the radial integral. The matrix representation of W_s can be constructed by setting

$$|211\rangle = \begin{pmatrix}1\\0\\0\\0\end{pmatrix}, |210\rangle = \begin{pmatrix}0\\1\\0\\0\end{pmatrix}, |21{-1}\rangle = \begin{pmatrix}0\\0\\1\\0\end{pmatrix}, |200\rangle = \begin{pmatrix}0\\0\\0\\1\end{pmatrix} \tag{62}$$

Then the matrix representation of the perturbation becomes

$$W_s = \begin{pmatrix}0 & 0 & 0 & 0\\ 0 & 0 & 0 & \gamma\mathcal{E}\\ 0 & 0 & 0 & 0\\ 0 & \gamma\mathcal{E} & 0 & 0\end{pmatrix} \tag{63}$$

From this matrix we can instantly see that $|211\rangle$ and $|21{-1}\rangle$ have eigenvalue zero, i.e. there is no shift associated with them. This leaves the submatrix

$$\begin{pmatrix}0 & \gamma\mathcal{E}\\ \gamma\mathcal{E} & 0\end{pmatrix} \tag{64}$$

Diagonalizing yields the energy shifts $\Delta E = \pm\gamma\mathcal{E}$ and the zeroth order eigenstates

$$|+\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix}, |-\rangle = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix} \tag{65}$$

UNIT 5

Time-dependent perturbation theory

Notes by S. Kyle, A. Sunghoon, and T. Weisong

Introduction and Method

In the former chapter, we talked about the Time-independent Perturbation Theory. In this chapter, we will work on a more complicated problem, the Time-dependent Perturbation Theory. Now let's consider the same problem as we did in the chapter three: a system whose Hamiltonian can be expressed in the form

$$H_0|n>= E_n|n>, \tag{1}$$

H_0 is the unperturbed Hamiltonian like what we did before. However, the perturbation in this case is $\lambda W_{(t)}$, which depends on time. So if we want to solve the Schrodinger equation, we will have the equation:

$$H = H_0 + \lambda W_{(t)} \tag{2}$$

If we want to find the eigenvalue of H, which is time dependent, we need to solve time-depended Schrodinger equation:

$$H|\psi(t)>= i\hbar\frac{d}{dt}|\psi(t)> \tag{3}$$

In this case, we have the initial condition $t = 0$, and we have the eigenstate of the original Hamiltonian:

$$|\psi(0)>= |i> \tag{4}$$

where i is some values of n. After we measure the system at time $t > 0$, the system will be in a different state of Hamiltonian $|f>$, where the f is another number of n. If we are given the initial state $|i>$, the probability of the transition to $|f>$ is:

$$P_{if}(t) = |<f|\psi(t)>|^2 \tag{5}$$

So, Let's calculate the probability and solve the Schrodinger equation. First we need to split the function ψ into some states, which is the eigenstate of the Hamiltonian. Therefore we can have

$$|\psi(t)>=\sum_n c_n(t)|n> \tag{6}$$

where we have the coefficients c_n are:

$$C_n(t)=<n|\psi(t)> \tag{7}$$

Then we go back tho the Schrodinger equation, and split the Hamiltonian H. We will have:

$$H_0|\psi>+\lambda w|\psi>=i\hbar\frac{d}{dt}|\psi> \tag{8}$$

Since the equation 6 defined the $|\psi>$ before, so can we have

$$\sum_n c_n E_n(t)|n>+\lambda\sum_n c_n w|n>=i\hbar\sum_n\frac{dc_n}{dt}|n> \tag{9}$$

Next, we can select one state of n, which we can write as $|k>$, to multiply the equation 9, so we can have:

$$C_k E_k+\lambda\sum_n c_n<k|w|n>=i\hbar\frac{dc_n}{dt} \tag{10}$$

In this case, the w is a matrix which we can write as $w_k n.$ let' s simplified the complex equation. Firstly, let assume $\lambda=0$, which means there is no perturbation, so we have:

$$i\hbar\frac{dc_k}{dt}=E_k c_k \tag{11}$$

We can solve this equation seriately. Then we have:

$$C_k(t)=C_k(0)e^{-i\frac{E_k}{\hbar}t} \tag{12}$$

Next, we calculate the condition that $\lambda\neq 0$. Then we have

$$C_k(t)=b_k(t)e^{-i\frac{E_k}{\hbar}t} \tag{13}$$

In this case, we got a complex function. However, we can separate the complex function to two parts. The first part is $b_k(t)$, which we don't know, while the second part $e^{-i\frac{E_k}{\hbar}t}$ that we have already talked about in former chapters. We substitute the equation 13 into 10, then we can get:

$$C_k(t)=b_k(t)e^{-i\frac{E_k}{\hbar}t}E_k+\lambda\sum_n W_{kn}b_n e^{-i\frac{E_k}{\hbar}t} \tag{14}$$

which equals to

$$i\hbar[\frac{d_b k}{dt}e^{-i\frac{E_k}{\hbar}t}+b_k(-i\frac{iE_k}{\hbar})e^{-i\frac{E_k}{\hbar}t} \tag{15}$$

and then we can get

$$b_k E_k + \lambda \sum_n W_{kn} b_n e^{-i\frac{E_n - E_k}{\hbar}t} = i\hbar[\frac{db_k}{dt} - \frac{i}{\hbar} E_k b_k] \tag{16}$$

so we can get:

$$\frac{db_k}{dt} = \frac{\lambda}{i\hbar} \sum_n W_{kn} e^{-i\frac{E_k - E_n}{\hbar}t} b_n \tag{17}$$

This is the exact equation which we didn't use any approximation, and this equation is equivalent to the Schrodinger equation. In addition, if we write $\frac{E_k - E_n}{\hbar} = \omega_{kn}$, then we can have the frequency $\omega_k n$, which we get from the transition between state k to state n. We call the ω_{kn} Born Frequency.

Approximate Solution Using Perturbation Theory

In last section, we calculate the exact solution of the Schrodinger equation for a time-dependent perturbation question. However, the equation is very complicated and we can not solve it in many cases. In this section, we find the approximation solution through perturbation theory. Firstly, under the perturbation theory, we will writer the equation $b_n(t)$ in the form:

$$b_n(t) = b_n^0(t) + \lambda b_n^1(t) + \lambda^2 b_n^2(t)... \tag{18}$$

First, we have to look the terms in the equation when there is no λ, then we can have the λ^0, which means the 0_{th} order, term:

$$\frac{db_k^0}{dt} = 0 \tag{19}$$

Then we know that b_k^0 is a constant. In this case, there is only one term which we write as b_i^0 equal to 1. Other b_k^0 where $k \neq i$ will be 0. So if we write equation of ψ at $t = 0$, then we have:

$$|\psi(0)>= \sum_n b_n^0 |n>= |i> \tag{20}$$

Now we consider the first order, we can get:

$$\lambda^1 = i\hbar \frac{db_k^1}{dt} = e^{iW_{ki}t} W_{ki} \tag{21}$$

Form the former equation, we can integrate the $b_k^1(t)$ as

$$b_k^1(t) = \frac{1}{i\hbar} \int_0^t dt' e^{iW_{ki}t'} W_{ki}(t') \tag{22}$$

Somehow, in this case, when $t = 0$, we have $b_k^1(t) = 0$. Because b_i^0 equal to 1, Other b_k^0 where $k \neq i$ will be 0. That is also the reason why all the other coefficients will be vanish at $t = 0$. Since we have get the b_n, then we can calculate the c_n and function $|\psi >$.

$$|\psi(t) >= \Sigma_n b_n(t) e^{-\frac{iE_n t}{\hbar}} |n > \tag{23}$$

Then we can substitute the λ^0 and λ^1 we get before into this equation, we will have:

$$|\psi(t) >= e^{-\frac{iE_n t}{\hbar}} |i > + \lambda \Sigma_n b_n^1(t) e^{-\frac{iE_n t}{\hbar}} |n > ... \tag{24}$$

So, if we measure the system at $t > 0$, I will find the system will stay at the state $|f >$. Then we have probability of the transition from $|i >$ to $|f >$ is $P_{if}(t) = | < f|\psi(t) > |^2|$, and it equals to

$$P_{if}(t) = \lambda^2 |\Sigma_n b_n^1(t) e^{-\frac{iE_n t}{\hbar}} < f|n > |^2 = \lambda^2 |b_f^1(t) e^{-\frac{iE_f t}{\hbar}}|^2 \tag{25}$$

As what we did for the Born frequency, we can write the probability as:

$$P_{if}(t) = \frac{\lambda^2}{\hbar^2} \int_0^t dt' e^{iW_{if}t'} W_{if}(t') \tag{26}$$

where we have $W_{fi} = \frac{E_f - E_i}{\hbar}$. That is the probability for the first order. Now we will work on some examples.

Example 1:$W(t) = A\sin(\omega t)$

In this case, we will have the probability of $P_{if}(t)$ as:

$$\begin{aligned} P_{fi}(t) &= \frac{|A|^2}{\hbar^2} | \int_0^t dt' e^{iW_{if}t'} sin(\omega t')|^2 \\ &= \frac{|A|^2}{\hbar^2} |[\frac{e^{i(\omega+\omega_{fi})t}}{2(\omega+\omega_{fi})} + \frac{e^{-i(\omega-\omega_{fi})t}}{2(\omega-\omega_{fi})}]|^2 \\ &= \frac{|A|^2}{4\hbar^2} |[\frac{e^{i(\omega+\omega_{fi})t} - 1}{\omega+\omega_{fi}} - \frac{e^{-i(\omega-\omega_{fi})t} - 1}{\omega-\omega_{fi}}]|^2 \end{aligned} \tag{27}$$

Example 2:$W(t) = A\cos(\omega t)$

This example is very familiar with the example 1, so we will have:

$$P_{fi}(t) = \frac{|A|^2}{4\hbar^2} |[\frac{e^{i(\omega+\omega_{fi})t} - 1}{\omega+\omega_{fi}} + \frac{e^{i(\omega-\omega_{fi})t} - 1}{\omega+\omega_{fi}}]|^2 \tag{28}$$

Example 3:$W(t) = A$

In this case, the perturbation term equals to a constant. We will have:

$$P_{fi}(t) = \frac{|A|^2}{4\hbar^2} |[\frac{e^{i\omega_{fi}t} - 1}{\omega_{fi}} + \frac{e^{i\omega_{fi}t} - 1}{\omega_{fi}}]|^2 = \frac{|A|^2}{\hbar^2} |[\frac{e^{i\omega_{fi}t} - 1}{\omega_{fi}}|^2 = \frac{|A|^2}{\hbar^2} |[\frac{e^{\frac{i\omega_{fi}t}{2}} - e^{-\frac{i\omega_{fi}t}{2}}}{\omega_{fi}}]|^2 \tag{29}$$

so we can have $P_{if} = \frac{4|A|^2}{\hbar^2}\frac{\sin^2(\frac{\omega_{fi}t}{2})}{\omega_{fi}^2}$

In the example 2, we have the probability of the transition is $P_{fi}(t) = \frac{|A|^2}{4\hbar^2}|[\frac{e^{i(\omega+\omega_{fi})t}-1}{\omega+\omega_{fi}} + \frac{e^{i(\omega-\omega_{fi})t}-1}{\omega+\omega_{fi}}]|^2$ which we can write as $P_{fi} = \frac{|A|^2}{4\hbar^2}|A_+ + A_-|^2$

So if we ignore the second term (A_-), we can calculate the rest part through the same way we used in the example 3. Then we can get:

$$P_+ = \frac{|A|^2}{4\hbar^2}|A_+|^2 = \frac{|A|^2}{4\hbar^2}|\frac{e^{i(\omega+\omega_{fi})t}-1}{\omega+\omega_{fi}}|^2 = \frac{|A|^2}{4\hbar^2}\frac{\sin^2\frac{\omega_{fi}+\omega}{2}}{(\omega_{fi}+\omega)^2} \tag{30}$$

Next, if we ignore the fist term A_+, then we will have

$$P_- = \frac{|A|^2}{4\hbar^2}|A_-|^2 = \frac{|A|^2}{4\hbar^2}\frac{\sin^2\frac{\omega_{fi}-\omega}{2}}{(\omega_{fi}-\omega)^2} \tag{31}$$

In this case, if we assume the state is near resonance, which means the distance from the resonance is much smaller than the resonance, we will have $|\omega-\omega_{fi}| \ll \omega_{fi}$, then we get $P_+ \approx 0$ and $P_{if} = P_-$. The width $\Delta\omega = \frac{4\pi}{t} \ll 2\omega_{fi}$, so we have $t \gg \frac{2\pi}{\omega_{fi}} \approx \frac{1}{\omega}$. This means we need to wait long enough, which is much longer than a couple of oscillations, to the resonance. However, on the other hand, I can not wait too long, for the probability can not bigger than 1. So we have $P_{if} \ll 1$, and because $\frac{|A|t}{2\hbar} \ll 1$, then we can get $t \ll \frac{\hbar}{|A|}$. At last, we can get $\frac{1}{\omega_{fi}} \ll t \ll \frac{\hbar}{|A|}$. If we write it in difference of energy levels, we will have $E_f - E_i = \hbar\omega_{fi} \gg |A|$.

Secular Approximation

In last section, we discussed the situation near the resonance, which means $t \ll \frac{\hbar}{|A|}$. On the other hand, if we have $t \gg \frac{\hbar}{|A|}$, the schrodinger equation will be:

$$i\hbar\frac{db_k}{dt} = \sum_n e^{iW_{kn}t}W_{kn}b_n \tag{32}$$

in this case, we assume $\lambda = 1$ in the equation. Then we the example we did in last section again. We assume $W = A\sin(\omega t)$, then $W_{kn} = A_{kn}\sin(\omega t)$, in which $A_{kn} =< k|A|n >$. If we go near the resonance, we will have the condition $\omega \approx \omega_{fi}$. We assume the initial and final state as $|i>$ and $|f>$, and we only consider the situation when the system in these two states. Then we will have:

$$i\hbar\frac{db_i}{dt} = A_{ii}b_i\sin(\omega t) + e^{-iW_{fi}t}A_{if}b_f\sin(\omega t) \tag{33}$$

Another equation is:

$$i\hbar\frac{db_f}{dt} = e^{i\omega_{fi}t}A_{fi}b_i\sin(\omega t) + A_{ff}b_f\sin(\omega t) \tag{34}$$

Because we have $\sin(\omega t) = \frac{e^{i\omega t} - e^{-i\omega t}}{2i}$, so we can have equations:

$$i\hbar \frac{db_i}{dt} = \frac{1}{2i} e^{-i(\omega f i - \omega)t} A_{if} b_f \tag{35}$$

$$i\hbar \frac{db_f}{dt} = -\frac{1}{2i} e^{i(\omega_{fi} - \omega)t} A_{fi} b_i \tag{36}$$

If we calculate the second derivative, then we can get:

$$\begin{aligned} i\hbar \frac{d^2 b_f}{dt^2} &= \frac{1}{2}(\omega_{fi} - \omega) e^{i(\omega_{fi} - \omega)t} A_{fi} b_i - \frac{1}{2i} e^{i(\omega_{fi} - \omega)t} A_{fi} \frac{db_i}{dt} \\ &= \hbar(\omega_{fi} - \omega) \frac{db_f}{dt} - \frac{1}{4\hbar} |A_{fi}|^2 b_f \end{aligned} \tag{37}$$

so we can transform the equation to:

$$\frac{d^2 b_f}{dt^2} + i(\omega_{fi} - \omega)t \frac{db_f}{dt} + \frac{1}{4\hbar^2} |A_{fi}|^2 b_f = 0 \tag{38}$$

If we assume $b_f = e^{\lambda t}$, and we plug it into the former equation, then we have:

$$\lambda^2 - i(\omega_{fi} - \omega)\lambda + \frac{|\lambda_{if}|^2}{4\hbar^2} = 0 \tag{39}$$

Then we can solve the equation to get the λ is:

$$\lambda = \lambda_{\pm} = \frac{1}{2}[i(\omega_{fi} - \omega) \pm i\sqrt{(\omega_{fi} - \omega)^2 + \frac{|A_{fi}|^2}{\hbar^2}}] \tag{40}$$

It is important to note that λ is pure imaginary, so that there is no damping. We have also seen that

$$b_f = e^{\lambda_{\pm} t} \tag{41}$$

so the most general solution will be a linear combination of the two.

$$b_f(t) = A e^{\lambda_+ t} + B e^{\lambda_- t} \tag{42}$$

To fix the coefficients A and B we look at the initial conditions, $t = 0$. At $t = 0$ the initial state is the state $|i>$ so that $b_i(0) = 1$ and $b_f(0) = 0$. The condition that $b_f(0) = 0$ tells us that $A = -B$. The condition $b_i(0) = 1$ is useful if we know $b_i(0)$. From our equations above

$$i\hbar \frac{db_i}{dt} = \frac{1}{2i} e^{i(\omega - \omega_{fi})t} A_{if} b_f \tag{43}$$

and using (42) we can show that

$$b_i(0) = \frac{2\hbar}{A_{fi}} (A\lambda_+ + B\lambda_-) = 1 \tag{44}$$

and

$$A = \frac{A_{fi}}{2\hbar(\lambda_+ - \lambda_-)} = \frac{A_{fi}}{2i\hbar\sqrt{(\omega-\omega_{fi})^2 + \frac{|A_{if}|^2}{\hbar^2}}} \tag{45}$$

This allows us to calculate the probability of a transition from the state $|i>$ to the state $|f>$. It is given by

$$\begin{aligned} P_{if}(t) &= |b_f(t)|^2 = |A|^2 |e^{\lambda_+ t} - e^{\lambda_- t}|^2 \\ &= \frac{|A_{if}|^2}{\hbar^2(\omega-\omega_{fi})^2 + |A_{if}|^2} sin^2(\frac{\sqrt{(\omega-\omega_{fi})^2 + \frac{|A_{if}|^2}{\hbar^2}}t}{2}) \end{aligned} \tag{46}$$

Since we are near the resonance the terms $(\omega - \omega_{fi}) \approx 0$ so we can ignore them. This gives

$$P_{if}(t) = sin^2(\frac{|A_{if}|}{2\hbar}t) \tag{47}$$

This is Rabi's formula, which we studied last semester.

Interaction of an atom with light

When considering the interaction between an atom and an electromagnetic wave, we first choose a gauge. It is always possible to choose a gauge such that

$$\phi = A_0 = 0, \tag{48}$$

The vector potential is

$$\overrightarrow{A}(\overrightarrow{r}, t) = \overrightarrow{A_z} sin(\overrightarrow{k}.\overrightarrow{r} - \omega t) \tag{49}$$

$$\omega = c|\overrightarrow{k}| \tag{50}$$

$$\overrightarrow{A_z} = A_z\hat{z} \tag{51}$$

$$\overrightarrow{k} = k\hat{y} \tag{52}$$

The electric field is given by

$$\overrightarrow{E} = -\overrightarrow{\nabla}\phi - \frac{d\overrightarrow{A}}{dt} = \omega A_z cos(ky - \omega t)\hat{z} = E_0 cos(ky - \omega t)\hat{z} \tag{53}$$

and the magnetic field by

$$\overrightarrow{B} = \overrightarrow{\nabla} * \overrightarrow{A} = kA_z cos(ky - \omega t)\hat{x} = B_0 cos(ky - \omega t)\hat{x} \tag{54}$$

so that

$$\frac{E_0}{B_0} = \frac{\omega}{k} = c \tag{55}$$

The time averaged Poynting vector is given by

$$< \overrightarrow{S} >= \frac{c\epsilon_0 E_0^2}{2}\hat{y} \tag{56}$$

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Interaction with an Hydrogen Atom: Low-Intensity Limit

The hamiltonian for the electron in a Hydrogen atom interacting with an electromagnetic wave is:

$$H = \frac{(\overrightarrow{p} - q\overrightarrow{A})^2}{2m} + V(r) - \frac{q}{m}\overrightarrow{S}.\overrightarrow{B} - q\phi \tag{66}$$

This can be rewritten as

$$H = H_0 - \frac{q}{m}p_z A_z - \frac{q}{m}S_x B_0 + \frac{q^2 A_z^2}{2m} \tag{67}$$

where H_0 is the atomic hamiltonian and

$$W(t) = W_1 + W_2 + W_3 = -\frac{q}{m}p_z A_z + \frac{q^2 A_z^2}{2m} - \frac{q}{m}S_x B_0 \tag{68}$$

is the perturbation. We will consider W_1 here since W_1 is much larger than W_3 or W_2. This can be seen by considering the order of the ratio

$$\frac{W_3}{W_1} \approx \frac{\hbar k}{p} \approx \frac{1}{1000} \tag{69}$$

for everyday light, and noting that at low intensity the quadratic terms of A_z are insignificant. So,

$$H \approx H_0 + W_1 \approx H_0 - \frac{q}{m} \overrightarrow{p} . \overrightarrow{A} \tag{70}$$

The Electric Dipole Hamiltonian

Now let us consider a gauge transformation given by

$$\overrightarrow{A}' = \overrightarrow{A} + \overrightarrow{\nabla}\chi \tag{71}$$

$$\phi' = \phi - \frac{d\chi}{dt} \tag{72}$$

If we let

$$\chi = zA_0 sin(\omega t) \tag{73}$$

then

$$\phi' = -zA_0 \omega cos(\omega t) \tag{74}$$

$$A'_x = A'_y = 0 \tag{75}$$

$$A'_z = A_0 sin(ky - \omega t) + A_0 sin(\omega t) \tag{76}$$

In the electric dipole approximation we have $ky \approx 0$ so that

$$A_z \approx 0 \tag{77}$$

In this case the interaction hamiltonian is

$$H = H_0 - q\phi' = H_0 - qE_0 z cos(\omega t) = H_0 - \overrightarrow{d} . \overrightarrow{E} - \frac{q}{m} \overrightarrow{S} . \overrightarrow{B} \tag{78}$$

Again, as before, we ignore the last term because its contribution is insignificant and we have

$$W_1 = -\overrightarrow{d} . \overrightarrow{E} \tag{79}$$

W_1 is called the electric dipole hamiltonian. The gauge transformation used here illustrates that the W_1 we found before((70)) is, in fact, the electric dipole hamiltonian.

The Matrix Elements of the Electric Dipole Hamiltonian

In order to describe a transition from some initial state, i, to some final state, f,

$$|i> -- > |f> \tag{80}$$

we need to calculate the matrix elements

$$< f|W_1|i >= \frac{qE_0}{m\omega} sin(\omega t) < f|p_z|i > \tag{81}$$

In order to calculate the matrix elements we first consider the commutator between H_0 and Z. Using

$$H_0 = \frac{p_z^2}{2m} + V(r) \tag{82}$$

$$[z, p_z^2] = p_z[z, p_z] + [z, p_z]p_z = 2i\hbar p_z \tag{83}$$

we get

$$[Z, H_0] = i\hbar \frac{p_z}{m} \tag{84}$$

On the other hand,

$$< f|[z, H_0]|i >=< f|zH_0|i > - < f|H_0 z|i >= -(E_f - E_i) < f|z|i > \tag{85}$$

Therefore

$$< f|W_1|i >= iq\frac{\omega_{fi}}{\omega} E_0 sin(\omega t) < f|z|i > \tag{86}$$

$$\omega_{fi} = (E_f - E_i)/\hbar \tag{87}$$

We see that the matrix elements of the electric dipole hamiltonian are proportional to those of z.

Electric Dipole Selection Rules

Now let us consider transitions in an hydrogen atom. The wavefunctions will be

$$\phi_{nlm}(\overrightarrow{r}) = R_{n_l}(r) Y_{l^m}(\theta, \phi) \tag{88}$$

The matrix elements can then be represented in integral form as

$$< f|z|i >= I \int d\Omega Y_{l_f}^{m_f} * (\theta, \phi) Y_1^0(\theta, \phi) Y_{l_i}^{m_i}(\theta, \phi) \tag{89}$$

where

$$I = \sqrt{\frac{4\pi}{3}} \int_0^\infty drr^2 R_{n_{f l_f}}(r) r R_{n_{i l_i}}(r) \tag{90}$$

The angular integral, which was calculated in our discussion of "Addition of Spherical Harmonics"(see Cohen-Tannoudji C_x), is nonzero if and only if

$$\Delta l = l_f - l_i = \pm 1 \tag{91}$$

$$m_f = m_i \tag{92}$$

The equations (91) (92) are the selection rules for the elecric dipole transition. We can also consider the case where the polarization of the elecric field is in the x-direction. In this case, the matrix elements are proportional to the integral

$$\int d\Omega Y_{l_f}^{m_f} * (\theta,\phi)[Y_1^1(\theta,\phi) - Y_1^{-1}(\theta,\phi)]Y_{l_i}^{m_i}(\theta,\phi) \tag{93}$$

and the selection rules are

$$\Delta l = l_f - l_i = \pm 1 \tag{94}$$

$$\Delta m = m_f - m_i = \pm 1 \tag{95}$$

We can generalize this to any direction of polarization. In this case the direction will be some linear combination of x,y, and z. Our angular integral will then have some combination of the corresponding spherical harmonics. Evaluation of this integral will give us, as was shown previously, the selection rules for electric dipole transitions

Transition Probability Associated with Natural Light

Let us now consider an hydrogen atom placed in an electromagnetic field with a spectrum of angular frequencies corresponding to natural light. In this case our expression for E_0 is a function of ω. If we consider the Poynting vector

$$< \overrightarrow{S} >= \frac{c\epsilon_0 E_0^2}{2} \tag{96}$$

$$< \overrightarrow{S} >= I(\omega)\Delta\omega \tag{97}$$

This gives us a relation between E_0 and $I(\omega)$, explicitly

$$E_0^2 = \frac{2I(\omega)\Delta\omega}{c\epsilon_0} \tag{98}$$

The probability of a transition, corresponding to emission or absorption, is given by

$$P_{if} = \frac{q^2}{\hbar^2}(\frac{\omega_{fi}}{\omega})^2 E_0^2 | < f|Z|i > |^2 \frac{sin[(\frac{\omega_{fi}-\omega}{2}t)}{(\omega_{fi}-\omega)^2} \tag{99}$$

For natural light we replace E_0^2 using equation 42 and get

$$P_{if} = \int_0^\infty \frac{q^2}{\hbar^2}(\frac{\omega_{fi}}{\omega})^2\frac{2I(\omega)\delta\omega}{c\epsilon_0}| < f|Z|i > |^2\frac{sin[(\frac{\omega_{fi}-\omega}{2}t)}{(\omega_{fi}-\omega)^2} \tag{100}$$

To solve this integral we first cast it in the form

$$P_{if} = \frac{2q^2}{c\epsilon_0\hbar^2}| < f|Z|i > |^2\int_0^\infty \delta\omega(\frac{\omega_{fi}}{\omega})^2 I(\omega)f(\omega) \tag{101}$$

$$f(\omega) = \frac{sin^2[(\frac{\omega_{fi}-\omega}{2}t)]}{(\omega_{fi}-\omega)^2} \tag{102}$$

If we plot$I(\omega)$ and $f(\omega)$ against ω we see that the largest contribution to the product $I(\omega)f(\omega)$ comes from $\omega \approx \omega_{fi}$. Replacing $I(\omega)$ with $I(\omega_{fi})$ and $(\frac{\omega_{fi}}{\omega})$ with 1 and noting that integrating from $-\infty$ to 0 adds alomst nothing to the integral, we can express the transition probability as

$$P_{if} \approx \frac{2q^2}{c\epsilon_0\hbar^2}| < f|z|i > |^2 I(\omega_{fi})\int_\infty^{-\infty} \delta\omega f(\omega) \tag{103}$$

Using substitution and an integral table or solving with a computer we find

$$P_{if} = \frac{\pi q^2 t}{c\epsilon_0\hbar^2}| < f|z|i > |^2 I(\omega_{fi}) \tag{104}$$

or

$$\frac{P_{if}}{t} = \frac{\pi q^2}{c\epsilon_0\hbar^2}| < f|z|i > |^2 I(\omega_{fi}) \tag{105}$$

When considering natural light we also need to average over all polarizations. Our electric dipole matrix elements are then given by

$$< W_1 >= \frac{1}{3}(| < f|x|i > |^2 + | < f|y|i > |^2 + | < f|z|i > |^2) = \frac{1}{3}| < f|\overrightarrow{r}|i > |^2 \tag{106}$$

giving

$$\frac{P_{if}}{t} = \frac{\pi q^2}{c\epsilon_0\hbar^2}| < f|\overrightarrow{r}|i > |^2 I(\omega_{fi}) = B \tag{107}$$

This is known as Einstein's B coefficient, it is the probability per unit time for a transition corresponding to absorption or induced emission.

Einstein's A and B coefficients

For spontaneous emission Einstein calculated his A coefficient using a rather clever thought experiment. He considered a volume in which a finite number of atoms are confined. He assumed that if the rate of absorption is given byN_iB, the rate of induced emission by N_fB, and the rate of spontaneous emission by

$N_f A$, where N_i and N_f are the number of particles in the initial or final state resectively, then the followng equality must hold

$$N_f B + N_f A = N_i B \tag{108}$$

which gives

$$A = (\frac{N_i}{N_f} - 1)B = (e^{\frac{E_f - E_i}{kT}} - 1)B \tag{109}$$

In this case, we can get the rate of absorption can be written as

$$rate\ of\ absorption = (\begin{matrix} induced\ or \\ stimulated \end{matrix})\ emmision$$

Einstein's A and B coefficients are defined by

$$A = \left(e^{\frac{\hbar\omega_k}{kT}} - 1\right) B \tag{110}$$

$$B = \frac{\pi q^2}{3\epsilon_0 c\hbar^2} |\langle f \mid \vec{r} \mid i\rangle|^2 I\left(\omega_{fi}\right) \tag{111}$$

In case of black body radiation, we have the intensity of the photons $I\left(\omega\right)$ as

$$I\left(\omega\right) = \frac{\hbar^2\omega^3}{\pi^2 c^2\left(e^{\frac{\hbar\omega}{kT}} - 1\right)} \tag{112}$$

Thus, we get

$$\begin{aligned} A &= \frac{\pi q^2}{3\epsilon_0 c\hbar^2} \frac{\hbar^2\omega_{fi}^3}{\pi^2 c^2} |\langle f \mid \vec{r} \mid i\rangle|^2 \\ &= \frac{q^2\omega_{fi}^3}{3\pi\epsilon_0 c^3\hbar} |\langle f \mid \vec{r} \mid i\rangle|^2 \end{aligned} \tag{113}$$

Let's look at asymptotic behavior of $I\left(\omega\right)$ in detail. For small ω, we can expand the exponential term as

$$e^{\frac{\hbar\omega}{kT}} - 1 = 1 + \frac{\hbar\omega}{kT}. \tag{114}$$

So, we get $I\left(\omega\right)$ as

$$I\left(\omega\right) \approx \frac{\hbar\omega^3}{\pi^2 c^2\left(\frac{\hbar\omega}{kT}\right)} = \frac{\omega^2}{\pi^2 c^2} kT \tag{115}$$

This result is well known from Maxwell equation.
However, if the radiation comes in "packet" (such as photons with $\hbar\omega$), we must identify how many photons are in a certain E. We know that

$$N\left(nE\right) \approx e^{-\frac{nE}{kT}}, P\left(n\right) = P_n = \frac{e^{-\frac{nE}{kT}}}{Z} \tag{116}$$

, where

$$\begin{aligned} Z &= \sum_{n=0}^{\infty} e^{-\frac{nE}{kT}} \\ &= \frac{1}{1-e^{-\frac{nE}{kT}}} \end{aligned}$$

Thus, we find $\langle n\rangle$ as

$$\langle n\rangle = \sum nP\left(n\right) = \frac{1}{Z}\sum_{n=0}^{\infty} ne^{-\frac{nE}{kT}} \tag{117}$$

Let's define α as $\alpha = e^{-\frac{E}{kT}}$. Then, we get $Z = \sum_{n=0}^{\infty}\alpha^n$. Hence, we can rewrite $\langle n\rangle$ as

$$\langle n\rangle = \frac{1}{Z}\sum_{n=0}^{\infty} n\alpha^n \tag{118}$$

,as well as

$$\begin{aligned} \frac{dZ}{d\alpha} &= \sum_{n=0}^{\infty} n\alpha^{n-1} \\ \Longrightarrow \alpha\frac{dZ}{d\alpha} &= \sum_{n=0}^{\infty} n\alpha^{n} \\ \Longrightarrow \quad \langle n\rangle &= \frac{\alpha}{Z}\frac{dZ}{d\alpha} \\ &= \alpha\left(1-\alpha\right)\frac{1}{\left(1-\alpha\right)^2} \\ &= \frac{\alpha}{1-\alpha} \\ &= \frac{1}{e^{\frac{E}{kT}}-1} \end{aligned} \tag{119}$$

Average # of photons with $\vec{k} = 2\left\langle n\right\rangle \frac{d^3k}{(2\pi)^3}$,whose 2 is the number of polarization.

Thus, the average # of photons with ω can be written as

$$\begin{aligned} \int 2\langle n\rangle\frac{d^3k}{\left(2\pi\right)^3} &= \int 2\langle n\rangle\frac{dkk^2d\Omega}{\left(2\pi\right)^3} \\ &= \frac{8\pi}{\left(2\pi\right)^3}\langle n\rangle dkk^2 \\ &= \frac{1}{\pi^2}\langle n\rangle dkk^2 \\ &= \frac{1}{c^3\pi^2}\langle n\rangle d\omega\omega^2,\ from\ \omega = ck \end{aligned} \tag{120}$$

Finally, we get the total energy E_{total} as

$$\begin{aligned}E_{total} &= E\frac{1}{c^3\pi^2}\langle n\rangle d\omega\omega^2\\ &= I\left(\omega\right)d\omega = cE_{total}\end{aligned}$$

Also, we get $I\left(\omega\right)d\omega$ as

$$\begin{aligned}\Longrightarrow I\left(\omega\right)d\omega &= E\frac{1}{c^2\pi^2}\langle n\rangle\omega^2 d\omega\\ \Longrightarrow I\left(\omega\right)d\omega &= \hbar\omega\frac{1}{c^2\pi^2}\frac{1}{e^{\frac{\hbar\omega}{kT}}-1}\omega^2\\ &= \frac{\hbar\omega^3}{c^2\pi^2}\frac{1}{e^{\frac{\hbar\omega}{kT}}-1}\end{aligned}$$

Dipole moment

Let's consider an electron subject to a restoring force directed towards the origin and proportiional to the displacement. $\mid\Psi\left(0\right)\rangle$ can be written as

$$\mid\Psi\left(0\right)\rangle=\mid i\rangle=\mid 0\rangle\ \ (ground\ state)$$

and we have $\mid\Psi\left(t\right)\rangle$ as

$$\mid\Psi\left(t\right)\rangle = e^{-\frac{iE_0t}{\hbar}}\mid 0\rangle+\lambda\sum_{n\neq 0}b_n^{(1)}e^{-\frac{iE_nt}{\hbar}}\mid n\rangle+\cdots$$

,where

$$\begin{aligned}\lambda b_n^{(1)}\left(t\right) &= \frac{W_{f0}}{\hbar}\int_0^t dt'e^{i\omega_{f0}t'}sin\left(\omega t'\right)\\ &= \frac{W_{n0}}{2i\hbar}\left[\frac{e^{i(\omega_{n0}+\omega)t}-1}{\omega_{n0}+\omega}-\frac{e^{i(\omega_{n0}-\omega)t}-1}{\omega_{n0}-\omega}\right]\end{aligned}$$

and

$$\begin{aligned}W_{n0} &= \frac{q\mathcal{E}_0}{m\omega}\langle n\mid p_z\mid 0\rangle\\ &= iq\mathcal{E}_0\frac{\omega_{n0}}{\omega}\langle n\mid z\mid 0\rangle\end{aligned}$$

Hence, we can rewrite $\mid\Psi\left(t\right)\rangle$ as

$$\mid\Psi\left(t\right)\rangle = e^{-\frac{iE_0t}{\hbar}}\left[\mid 0\rangle+\lambda\sum_{n\neq 0}b_n^{(1)}e^{-i\omega_{n0}t}\mid n\rangle+\cdots\right] \tag{121}$$

,where

$$\omega_{n0} = \frac{E_n - E_0}{\hbar}$$

However, we know that $e^{-i\omega_{n0}t}$ goes to zero in nature due to the damping factor $e^{-\Gamma t}$, in such that

$$e^{-i\omega_{n0}t} = e^{-i(\omega_{n0}-i\Gamma)t} = e^{-\Gamma t}e^{-i\omega_{n0}t} \rightarrow 0, \quad as\ t \rightarrow \infty \tag{122}$$

Thus, we get

$$\mid \Psi(t)\rangle = e^{-\frac{iE_0t}{\hbar}}\left[\mid 0\rangle + \sum_{n\neq 0}\frac{q\mathcal{E}_0}{2\hbar}\frac{\omega_{n0}}{\omega}\langle n \mid z \mid 0\rangle \mid n\rangle\left[\frac{e^{i\omega t}}{\omega_{n0}+\omega} - \frac{e^{-i\omega t}}{\omega_{n0}-\omega}\right]\right] \tag{123}$$

Therefore, the projection of the dipole moment $\vec{D}\,(=q\vec{z})$ becomes

$$\begin{aligned} D_z(t) &= \langle \Psi(t) \mid qz \mid \Psi(t)\rangle \\ &= \langle 0 \mid qz \mid 0\rangle + \sum_{n\neq 0}\frac{q\mathcal{E}_0}{2\hbar}\frac{\omega_{n0}}{\omega}\langle n \mid z \mid 0\rangle\left[\frac{e^{i\omega t}}{\omega_{n0}+\omega} - \frac{e^{-i\omega t}}{\omega_{n0}-\omega}\right]\langle 0 \mid qz \mid n\rangle + C.C. \end{aligned}$$

The first term becomes zero due to $\int even * odd * even$, and we get

$$\begin{aligned} D_z(t) &= \sum_{n\neq 0}\frac{q^2\mathcal{E}_0}{2\hbar}\frac{\omega_{n0}}{\omega}\mid\langle n \mid z \mid 0\rangle\mid^2\left[\frac{e^{i\omega t}}{\omega_{n0}+\omega} - \frac{e^{-i\omega t}}{\omega_{n0}-\omega}\right] + C.C. \\ &= \sum_{n\neq 0}\frac{q^2\mathcal{E}_0}{2\hbar}\frac{\omega_{n0}}{\omega}\mid\langle n \mid z \mid 0\rangle\mid^2\left[\frac{1}{\omega_{n0}+\omega} - \frac{1}{\omega_{n0}-\omega}\right]cos(\omega t) \\ &= \sum_{n\neq 0}\frac{q^2\mathcal{E}_0}{2\hbar}\frac{\omega_{n0}}{\omega}\mid\langle n \mid z \mid 0\rangle\mid^2\left[-\frac{2\omega}{\omega_{n0}^2-\omega^2}\right]cos(\omega t) \\ &= \sum_{n\neq 0}\frac{q^2\mathcal{E}_0}{2\hbar}\omega_{n0}\mid\langle n \mid z \mid 0\rangle\mid^2\left[-\frac{2\omega}{\omega_{n0}^2-\omega^2}\right]cos(\omega t) \end{aligned} \tag{124}$$

Finally, we find the electric susceptibility $\mathcal{X}_e$ as,

$$\mathcal{X}_e = -\sum_{n\neq 0}\frac{2q^2\omega_{n0}}{\hbar}\frac{\mid\langle n \mid z \mid 0\rangle\mid^2}{\omega_{n0}^2-\omega^2} \tag{125}$$

Spring Problem

For the spring problem, the differential equation can be written as

$$m\frac{d^2z}{dt^2} = -m\omega_0^2 z + q\mathcal{E}_0 cos(\omega t)\,. \tag{126}$$

And, the ansatz of this equation can be written as

$$z = Acos\left(\omega t\right) \tag{127}$$

By inserting this ansatz to find the coefficient A, we get

$$\begin{aligned} -m\omega^2 A &= -m\omega_0^2 A + q\mathcal{E}_0 \\ \Rightarrow A &= \frac{q\mathcal{E}_0}{m\left(\omega_0^2 - \omega^2\right)} \end{aligned} \tag{128}$$

Hence, we find the projection of the dipole moment $d_z \left(= qz\right)$ as

$$d_z = \frac{q^2\mathcal{E}_0}{m\left(\omega_0^2 - \omega^2\right)} cos\left(\omega t\right) \tag{129}$$

Also, we find $\mathcal{X}_e$ as

$$\mathcal{X}_e = \frac{q^2}{m\left(\omega_0^2 - \omega^2\right)} \tag{130}$$

Let's compare two results. We found two $\mathcal{X}_e$ as

$$\begin{aligned} \mathcal{X}_e &= -\sum_{n\neq 0} \frac{2q^2\omega_{n0}}{\hbar} \frac{\mid \langle n \mid z \mid 0\rangle \mid^2}{\omega_{n0}^2 - \omega^2} \\ \mathcal{X}_e &= \frac{q^2}{m\left(\omega_0^2 - \omega^2\right)} \\ \Rightarrow \mathcal{X}_e &= \sum_{n\neq 0} \frac{2m\omega_{n0} \mid \langle n \mid z \mid 0\rangle \mid^2}{\hbar} \frac{q^2}{m\left(\omega_{n0}^2 - \omega^2\right)} \\ &= \sum_{n\neq 0} f_{n0} \frac{q^2}{m\left(\omega_{n0}^2 - \omega^2\right)} \end{aligned} \tag{131}$$

,where

$$f_{n0} = \frac{2m\omega_{n0} \mid \langle n \mid z \mid 0\rangle \mid^2}{\hbar}$$

It turns out $\sum f_{n0} = 1$, which means the sum of the probability is equal to 1. Let's prove it.
Since we find that

$$\begin{aligned} \omega_{n0}\langle n \mid z \mid 0\rangle &= \frac{1}{\hbar}\langle n \mid [H_0, z] \mid 0\rangle \\ &= -\frac{i}{m}\langle n \mid p_z \mid 0\rangle, \end{aligned}$$

We can calculate $\sum f_{n0}$ as

$$\sum f_{n0} = \frac{2m}{\hbar}\sum -\frac{i}{m}\langle n \mid p_z \mid 0\rangle\langle 0 \mid z \mid n\rangle \tag{132}$$

Since we know $C = \frac{1}{2}\left(C + C^*\right)$ when C is a complex number,

$$\begin{aligned}\sum f_{n0} &= \frac{2m}{\hbar}\sum -\frac{i}{2m}\langle n \mid p_z \mid 0\rangle\langle 0 \mid z \mid n\rangle + C.C.\\ &= -\frac{i}{\hbar}\sum\left[\langle 0 \mid z \mid n\rangle\langle n \mid p_z \mid 0\rangle - \langle 0 \mid p_z \mid n\rangle\langle n \mid z \mid 0\rangle\right]\\ &= -\frac{i}{\hbar}\langle 0 \mid [z, p_z] \mid 0\rangle\\ &= 1 \; (q.e.d.)\end{aligned} \tag{133}$$

Blackbody Radiation

In case of the blackbody radiation, we have $\langle n\left(E\right)\rangle$ of the photon as

$$\langle n\left(E\right)\rangle = \frac{1}{e^{\frac{E}{kT}}e^{E/kT} - 1} \tag{134}$$

The average number with $\vec{k}$ is, then,

$$\langle n\left(E\right)\rangle * \frac{d^3k}{\left(2\pi\right)^3} \tag{135}$$

Since we can write $\vec{k}$ as

$$\vec{k} = (k_x, k_y, k_z)$$

and using periodic conditions of the boundary condition, we find

$$\Psi(\vec{k}, \vec{r}) = e^{ik_x x}e^{ik_y y}e^{ik_z z} \tag{136}$$

and

$$\begin{aligned} e^{ik_x L} &= 1\\ \Rightarrow k_x L &= 2\pi L\\ \Rightarrow \quad k_x &= \frac{2\pi}{L}n\\ \Rightarrow \Delta k_x &= \frac{2\pi}{L}\end{aligned} \tag{137}$$

Thus, we get

$$\langle n\left(E\right)\rangle(\frac{L}{2\pi}\Delta k_x)(\frac{L}{2\pi}\Delta k_y)(\frac{L}{2\pi}\Delta k_z) = \frac{L^3}{\left(2\pi\right)^3}d^3k \tag{138}$$

So, the energy E can be found by

$$\begin{aligned} E &= \hbar\omega\int\langle n(E)\rangle\frac{L^3}{(2\pi)^3}d^3k\\ &= \frac{V\hbar\omega^3 d\omega}{\pi^2 c^3(e^{\hbar\omega/kT} - 1)}\end{aligned} \tag{139}$$

And, we find the energy density $du(=E/V)$ by

$$du = \frac{\hbar\omega^3 d\omega}{\pi^2 c^3 (e^{\hbar\omega/kT} - 1)} \tag{140}$$

Therefore, we find $I(\omega)$ as

$$I(\omega) = c\frac{du}{d\omega} = \frac{\hbar\omega^3}{\pi^2 c^2 (e^{\hbar\omega/kT} - 1)} \tag{141}$$

Continuous Spectrum: $\mid i\rangle \rightarrow \mid f\rangle$

We will consider the case that has a transition from discrete states to continuous states. Let's say the energy of the final states can be written as

$$E_f = \frac{p_f^2}{2m}. \tag{142}$$

In case of continuous spectrum, we may write the probability of the transition as $P_i(E_f)$ instead of P_{if}, where $E_f \ < \ E \ < \ E_f + \Delta E_f$. Also, the probability can be written as

$$Probability = P_i(E_f)\ \Delta E_f\ \rho(E_f) \tag{143}$$

, where the density of states $\rho(E)$ is

$$\rho(E) = \frac{\#\ of\ states}{\Delta E}$$

In order to find $\rho(E)$, we will introduce a projection operator $\mid \vec{p}\rangle\langle\vec{p}\mid$.
In the range of $E_f \ < \ E(=\frac{p^2}{2m}) \ < \ E_f + \Delta E_f$, we find

$$\begin{aligned}
\int d^3p \mid \vec{p}\rangle\langle\vec{p}\mid &= \int dp p^2 \int d\Omega \mid \vec{p}\rangle\langle\vec{p}\mid \\
&= \int \frac{m}{\sqrt{2}} \frac{dE}{mE} 2mE \int d\Omega \mid \vec{p}\rangle\langle\vec{p}\mid \\
&= \int dE \int d\Omega\ m\sqrt{2mE} \mid \vec{p}\rangle\langle\vec{p}\mid \\
&= \int dE \int d\Omega\ \rho(E,\Omega) \mid \vec{p}\rangle\langle\vec{p}\mid
\end{aligned} \tag{144}$$

,where

$$\rho(E,\Omega) = \frac{\#\ of\ states}{\Delta E \Delta\Omega}.$$

We know that

$$\mid f\rangle = \mid \vec{p}\rangle = \mid E,\Omega\rangle \tag{145}$$

So,

$$P_i(E_f) = \mid \langle\Psi(t) \mid f\rangle \mid^2 = \mid \langle\Psi(t) \mid E,\Omega\rangle \mid^2 \tag{146}$$

Let's look at examples.

Example 0⟩ To measure the energy of electrons.
Assuming E = 10eV, with $\sigma_E = 1eV$, we have the probability as

$$Probability = \int P(E,\Omega)\rho(E,\Omega)d\lambda dE \tag{147}$$

Example 1⟩ Constant perburbation.

$$\begin{aligned} P(E,\Omega) &=\mid \langle E,\Omega \mid \Psi(t)\rangle \mid^2 = \mid b_E^{(1)}(t) \mid^2 \\ &= \frac{1}{\hbar^2} \mid \int_0^t dt' e^{i\frac{E-E_i}{\hbar}t'} \mid \langle E,\Omega \mid W \mid i\rangle \mid^2 \\ &= \frac{\mid \langle E,\Omega \mid W \mid i\rangle \mid^2}{\hbar^2} \frac{sin^2 \frac{E-E_i}{2\hbar}t}{(\frac{E-E_i}{2\hbar})^2} \end{aligned} \tag{148}$$

Since we know

$$\frac{Probability}{\Delta\Omega} = \int dE\rho(E,\Omega)P(E,\Omega)$$

,and by assuming $\rho(E,\Omega)$ is approximately constant, which is $\rho(E_i,\Omega)$, we find

$$\begin{aligned} \frac{Probability}{\Delta\Omega} &\simeq \rho(E_i,\Omega) \int_0^\infty dE \frac{\mid \langle E,\Omega \mid W \mid i\rangle \mid^2}{\hbar^2} \frac{sin^2 \frac{E-E_i}{2\hbar}t}{(\frac{E-E_i}{2\hbar})^2} \\ &= \rho(E_i,\Omega) \frac{\mid \langle E,\Omega \mid W \mid i\rangle \mid^2}{\hbar^2} \int_0^\infty dE \frac{sin^2 \frac{E-E_i}{2\hbar}t}{(\frac{E-E_i}{2\hbar})^2} \end{aligned} \tag{149}$$

For E < 0, the integral is very small($\Rightarrow 0 \rightarrow -\infty$.) By defining a new variable u as

$$u \equiv \frac{E-E_i}{2\hbar}t,\ du = \frac{dE}{2\hbar}t,$$

we find

$$\begin{aligned} \frac{Probability}{\Delta\Omega} &= \rho(E_i,\Omega) \frac{\mid \langle E,\Omega \mid W \mid i\rangle \mid^2}{\hbar^2} \int_{-\infty}^\infty du \frac{2\hbar}{t} \frac{sin^2 ut^2}{u^2} \\ &= \frac{2\pi t}{\hbar} \rho(E_i,\Omega) \mid \langle E_i,\Omega \mid W \mid i\rangle \mid^2 \end{aligned} \tag{150}$$

Hence, we get w as

$$w \equiv \frac{Probability}{\Delta\Omega\Delta t} = \frac{2\pi}{\hbar}\rho(E_i,\Omega) \mid \langle E_i,\Omega \mid W \mid i\rangle \mid^2 = constant!! \tag{151}$$

This result, $w = constant$, is so called "Fermi's Golden Rule."

Now, let's consider the scattering theory to describe with the time perturbation theory. We have an electron e^- for incoming particle having a mass m and a momentum $\vec{p_i}$, as well as a heavy target having a potential V. Due to this potential V, the momentum of the electron is deflected to $\vec{p_f}$. From this situation, we get

$$E_i = \frac{p_i^2}{2m},\ E_f = \frac{p_f^2}{2m},\ E_i = E_f,\ p_i^2 = p_f^2 \tag{152}$$

The hamiltonian H can be written as

$$H = \frac{p^2}{2m} + V = H_0 + W \tag{153}$$

, where

$$H_0 = \frac{p^2}{2m},\ W = V.$$

We define an initial state and a final state as

$$\mid i\rangle = \mid \vec{p_i}\rangle,\ \mid f\rangle = \mid \vec{p_f}\rangle = \mid E_i, \Omega\rangle \tag{154}$$

Then, w becomes

$$w = \frac{2\pi}{\hbar} m\sqrt{2mE} \mid \langle \vec{p_f} \mid V \mid \vec{p_i}\rangle \mid^2 \tag{155}$$

We need to find the form of $\mid \vec{p_i}\rangle$. Since we know that

$$\mid \vec{p}\rangle = C\ e^{i\vec{p}\cdot\vec{r}/\hbar} \quad and \quad \langle \vec{p} \mid \vec{p'}\rangle \propto \delta^3(\vec{p} - \vec{p'}),$$

we need to find the coefficient C. Let's work on it.
We have an inner product $\langle \vec{p} \mid \vec{p'}\rangle$ as

$$\begin{aligned}
\langle \vec{p} \mid \vec{p'}\rangle &= C^2 \int d^3r e^{i(\vec{p'}-\vec{p})\cdot\vec{r}/\hbar} \\
&= \int_{-\infty}^{\infty} dx e^{i(p'_x - p_x)x/\hbar} \\
&= \int_{0}^{\infty} dx e^{i(p'_x - p_x)x/\hbar} + \int_{-\infty}^{0} dx e^{i(p'_x - p_x)x/\hbar} \\
&= \int_{0}^{\infty} dx e^{i(p'_x - p_x)x/\hbar} + \int_{0}^{\infty} dx e^{-i(p'_x - p_x)x/\hbar}
\end{aligned} \tag{156}$$

By multiplying $e^{-\epsilon x}$ with $\epsilon > 0$ but $\epsilon \sim 0$, we get

$$\begin{aligned}
\langle \vec{p} \mid \vec{p'}\rangle &= \frac{1}{\frac{\epsilon}{\hbar} - i\frac{(p'_x - p_x)}{\hbar}} + \frac{1}{\frac{\epsilon}{\hbar} + i\frac{(p'_x - p_x)}{\hbar}} \\
&= \frac{2\epsilon\hbar}{\epsilon^2 + (p'_x - p_x)^2}
\end{aligned} \tag{157}$$

Let's define $f(q)$ as

$$f(q) = \frac{2\epsilon\hbar}{\epsilon^2 + q^2} \tag{158}$$

When $\epsilon \rightarrow 0$, $f(q)$ behaves in such that

$$f(q) \rightarrow 0,\ if\ q \neq 0 \tag{159}$$

$$f(q) \rightarrow \infty,\ if\ q = 0 \tag{160}$$

Thus, we find that

$$\int_{-\infty}^{\infty} f(q)dq = \int_{-\infty}^{\infty} \frac{2\epsilon\hbar}{\epsilon^2 + q^2} dq \tag{161}$$

Let $q = \epsilon tan\theta$. Then, $dq = \frac{\epsilon}{cos^2\theta} d\theta$. So, we get

$$\begin{aligned} \int_{-\infty}^{\infty} f(q)dq &= \int_{-\infty}^{\infty} \frac{2\epsilon\hbar}{\epsilon^2} cos^2\theta \frac{\epsilon}{cos^2\theta} d\theta \\ &= 2\hbar \int_{-\pi/2}^{\pi/2} d\theta = 2\pi\hbar \end{aligned} \tag{162}$$

Thus, we find $f(q)$ as

$$f(q) = 2\pi\hbar\delta(q) \tag{163}$$

And, we get

$$\begin{aligned} &\int_{-\infty}^{\infty} dx e^{i(p'_x - p_x)x/\hbar} = 2\pi\hbar\delta(p'_x - p_x) \\ \Longrightarrow &\int_{-\infty}^{\infty} d^3r\ e^{i(\vec{p'} - \vec{p})\cdot\vec{r}/\hbar} = (2\pi\hbar)^3\ \delta^3(\vec{p'} - \vec{p}) \end{aligned} \tag{164}$$

By recalling the result of $\langle \vec{p} \mid \vec{p'} \rangle$, we finally find C as

$$\begin{aligned} \langle \vec{p} \mid \vec{p'} \rangle &= C^2 (2\pi\hbar)^3\ \delta^3(\vec{p'} - \vec{p}) \\ \Longrightarrow C &= \frac{1}{(2\pi\hbar)^{3/2}} \end{aligned} \tag{165}$$

Therefore, we find $w(\vec{p_i}, \vec{p_f})$ as

$$w(\vec{p_i}, \vec{p_f}) = \frac{2\pi}{\hbar} m\sqrt{2mE} \frac{1}{(2\pi\hbar)^6} \mid \int d^3r\ V(r) e^{i(\vec{p_i} - \vec{p_f})\cdot\vec{r}/\hbar} \mid^2 \tag{166}$$

We can write the probability current density J_i as

$$\begin{aligned} J_i &= \frac{\hbar}{2mi} (\Psi^* \partial_z \Psi - C.C.) \\ &= \frac{p_i}{m} \frac{1}{(2\pi\hbar)^3} \end{aligned} \tag{167}$$

,where

$$\Psi = \frac{1}{(2\pi\hbar)^{3/2}} e^{ip_i z/\hbar}$$

Hence, the differential cross section $d\sigma/d\Omega$ can be found

$$\begin{aligned}\frac{d\sigma}{d\Omega} = \frac{w}{J_i} &= \frac{2\pi}{\hbar} m\sqrt{2mE}\frac{m}{p_i} \mid \int d^3r\ V(r)e^{i(\vec{p_i}-\vec{p_f})\boldsymbol{\cdot}\vec{r}/\hbar} \mid^2 \frac{1}{(w\pi\hbar)^3} \\ &= \frac{m^2}{4\pi^2\hbar^4} \mid \int d^3r\ V(r)e^{i(\vec{p_i}-\vec{p_f})\boldsymbol{\cdot}\vec{r}/\hbar} \mid^2 \qquad (168) \\ &= \ \mathit{same\ as\ Born\ cross\ section}!!\end{aligned}$$

Example 2⟩ Sinusoidal Perturbation.
We can state the transition probability $P_{if}(t,\omega)$ as

$$P_{if}(t,\omega) = \mid \langle E,\Omega \mid \Psi(t)\rangle \mid^2 = \frac{\mid w_{fi} \mid^2}{4\hbar^2} = \frac{sin^2\{\frac{(E-E_i-\hbar\omega)}{2\hbar}t\}}{(\frac{(E-E_i-\hbar\omega)}{2\hbar})^2} \qquad (169)$$

Since we have a condition in such that

$$E \sim E_i + \hbar\omega,$$

we get w as

$$w = \frac{\pi}{2\hbar} \mid \langle E_i+\hbar\omega,\Omega \mid W \mid i\rangle \mid^2 \rho(\Omega, E_i+\hbar\omega). \qquad (170)$$

Example 3⟩ Decay; *nucleus* $\rightarrow$ α + *nucleus*′.
Again, in this problem we also have a transition from a discrete state(*nucleus*, $\mid i\rangle$) to two continuous states(α and *nucleus*′, $\mid E,\Omega\rangle$). We will talk about the decay rate Γ at this time, which is defined as

$$\mathit{decay\ rate}\ \Gamma \ \equiv\ \mathit{probability/time} = \int d\Omega w(\Omega). \qquad (171)$$

We also define the probability of no decay P_{ii} as

$$P_{ii} = 1 - \Gamma t. \qquad (172)$$

In order to make it true, we must have a condition in such that

$$\Gamma t \ll 1 \ \Rightarrow\ t \ll \frac{1}{\Gamma}. \qquad (173)$$

Also, if you look at this Γ as a function of E, then

$$\Gamma(E) = \frac{2\pi}{\hbar} \mid \langle E,\Omega \mid W \mid i\rangle \mid^2 \rho(\Omega, E) \qquad (174)$$

Since we have a majority of $\Gamma(E)$ in the range of the small width centered by a peak, we have another condition in such that

$$t \ \gg \frac{1}{\Delta\Gamma} \qquad (175)$$

Therefore, we have a condition,

$$\frac{1}{\Delta\Gamma} \ll t \ll \frac{1}{\Gamma} \tag{176}$$

Example 4⟩ Beyond perturbation theory; $t \geq 1/\Gamma$.
We can consider a Schrodinger equation, in such that

$$i\hbar\frac{db_k}{dt} = \sum_n e^{i\omega_{kn}t}W_{kn}b_n \tag{177}$$

, where

$$\omega_{kn} = \frac{E_i - E}{\hbar}$$
$$and \;\; W_{kn} = \langle i \mid W \mid E, \Omega\rangle$$

In the case of the continuous state and $k = i$, we can rewrite this equation as

$$i\hbar\frac{db_i}{dt} = \int d\Omega dE\rho(\Omega, E)e^{i\frac{(E_i-E)}{\hbar}t}\langle i \mid W \mid E, \Omega\rangle b(\Omega, E) \tag{178}$$

When $k = k(\Omega, E)$, it becomes

$$i\hbar\frac{db(\Omega, E)}{dt} = e^{i\frac{(E_i-E)}{\hbar}t}\langle E, \Omega \mid W \mid i\rangle b_i \tag{179}$$

At $t = 0$, $b_i = 0$ and $b(\Omega, E) = 0$. So,

$$\begin{aligned}\frac{db_i}{dt} &= -\frac{1}{\hbar^2}\int d\Omega dE\rho(\Omega, E)e^{i\frac{(E_i-E)}{\hbar}t}\langle i \mid W \mid E, \Omega\rangle \\ &\quad \times \int_0^t dt' e^{i\frac{(E-E_i)}{\hbar}t'}\langle \Omega, E \mid W \mid i\rangle b_i(t') \\ &= -\frac{1}{\hbar^2}\int d\Omega dE\rho(\Omega, E)\int_0^t dt' \mid \langle i \mid W \mid E, \Omega\rangle \mid^2 e^{i\frac{(E_i-E)}{\hbar}(t-t')}b_i(t') \\ &= -\frac{1}{\hbar^2}\frac{\hbar}{2\pi}\int dE\Gamma(E)\int_0^t dt' e^{i\frac{(E_i-E)}{\hbar}(t-t')}b_i(t')\end{aligned} \tag{180}$$

When $(t - t')$ is very large, we get

$$\begin{aligned}\int dE\Gamma(E)e^{i\frac{(E_i-E)}{\hbar}(t-t')} &\propto sin\frac{E(t-t')}{\hbar} \\ &\Rightarrow \frac{E(t-t')}{\hbar} = \pi \\ &\Rightarrow E = \frac{\pi\hbar}{(t-t')}\end{aligned} \tag{181}$$

Thus, we have a rapid oscillation and it leads to

$$\int_0^t dt' \cdots = 0!! \tag{182}$$

When $(t-t')$ is very small, we get

$$\int_0^t dt' \cdots \neq 0, \tag{183}$$

compared to $\frac{1}{\Delta\Gamma}$.
For $(t-t')$, we have a condition that

$$\begin{aligned} large: t-t' &\gg \frac{1}{\Delta\Gamma} \\ small: t-t' &\leq \frac{1}{\Delta\Gamma} \\ \Longrightarrow (t-\frac{1}{\Delta\Gamma}) &< t' < t \ only\ for\ a\ reasonable\ contribution. \\ \Longrightarrow b_i(t') &\sim b_i(t) \sim b_i \end{aligned}$$

Finally, we find

$$\begin{aligned} \frac{db_i}{dt} &= -\left[\frac{1}{2\pi\hbar}\int dE \int_0^t dt'\Gamma(E)e^{i\frac{(E_i-E)}{\hbar}(t-t')}\right]b_i \\ &= -\left[\frac{1}{2\pi\hbar}\int dE\ \Gamma(E)\frac{e^{i\frac{(E_i-E)}{\hbar}t}-1}{i\frac{E_i-E}{\hbar}}\right]b_i \\ &= -\left[\frac{1}{2\pi\hbar}\int dE\ \Gamma(E)f(E)\right]b_i \end{aligned} \tag{184}$$

, where

$$f(E) = \frac{e^{i\frac{(E_i-E)}{\hbar}t}-1}{i\frac{E_i-E}{\hbar}}$$

Note that $\mid f(E)\mid^2$ becomes

$$\mid f(E)\mid^2 = \frac{sin^2\frac{E_i-E}{2\hbar}t}{(\frac{E_i-E}{\hbar})^2}. \tag{185}$$

Since $\Gamma(E)$ is approximately constant, we can rewrite db_i/dt as

$$\frac{db_i}{dt} = -\left[\frac{1}{2\pi\hbar}\Gamma(E_i)\int dE\ f(E)\right]b_i \tag{186}$$

In addition, we want to look at $\int dE\ f(E)$ in detail.

For the real part of $\int dE\ f(E)$, we find

$$\begin{aligned}\int dE\frac{1}{2}\left[f(E)+F^*(E)\right] &= \frac{1}{2}\int dE\frac{e^{i\frac{(E_i-E)}{\hbar}t}-e^{-i\frac{(E_i-E)}{\hbar}t}}{i\frac{E_i-E}{\hbar}} \\ &= \int_{-\infty}^{\infty}dE\frac{sin\frac{E_i-E}{\hbar}t}{\frac{E_i-E}{\hbar}}\end{aligned}\tag{187}$$

Let's define u as $u=\frac{E-E_i}{\hbar}t$ to solve this integral.

$$\begin{aligned}\int dE\frac{1}{2}\left[f(E)+F^*(E)\right] &= \hbar\int_{-\infty}^{\infty}du\frac{sinu}{u} \\ &= \pi\hbar\end{aligned}\tag{188}$$

On the other hand, for the imaginary part of $\int dEf(E)$, we find

$$\int dE\frac{1}{2i}\left[f(E)-F^*(E)\right]=constant\sim\delta E.\tag{189}$$

Thus, we find

$$\begin{aligned}\frac{db_i}{dt} &= -\left[\frac{1}{2}\Gamma(E_i)+i\frac{\delta E}{\hbar}\right]b_i \\ \Longrightarrow b_i(t) &= e^{-(\frac{\Gamma}{2}+i\frac{\delta E}{\hbar})t}\end{aligned}\tag{190}$$

In case of no decay, we have

$$P_{ii}=\mid b_i(t)\mid^2=e^{-\Gamma t}=1-\Gamma t+\cdots\tag{191}$$

In the time dependent perburbation theory, we had

$$P_{ii}=1-\Gamma t\tag{192}$$

Thus, we can see good agreement between the exact solution and the perturbation theory.
For the decay probability, we have

$$\begin{aligned}b(\Omega,E) &= \frac{1}{i\hbar}\int_0^t dt'e^{i\frac{E-E_i}{\hbar}t'}\langle\Omega E\mid W\mid i\rangle b_i(t') \\ &= \frac{1}{i\hbar}\langle\Omega E\mid W\mid i\rangle\int_0^t dt'e^{-\frac{\Gamma t}{2}}e^{i\frac{E-E_i-\delta E}{\hbar}t'} \\ &= \langle\Omega E\mid W\mid i\rangle\frac{1-e^{-\frac{\Gamma t}{2}}e^{i\frac{E-E_i-\delta E}{\hbar}t}}{E-E_i-\delta E+i\hbar\frac{\Gamma}{2}}\end{aligned}\tag{193}$$

Since the probability density is defined by $\mid b\mid^2$, we finally get

$$\mid b\mid^2\sim\frac{1}{(E-E_i-\delta E)^2+\hbar^2\frac{\Gamma^2}{4}}\tag{194}$$

We can find the uncertainty principle, in such that

$$\Delta E\geq\hbar\Gamma=\frac{\hbar}{\tau}\quad\Rightarrow\quad\tau\ \Delta E\geq\hbar.\tag{195}$$

UNIT 6

Identical particles