Quantum Mechanics II

Ray Romero

Quantum Mechanics Notes

Physics
FIU

Contents

Chapter 1
Classical Mechanics

1 Introduction

Like in quantum mechanics I, we will begin by considering a classical problem and then using these results to compare its quantum mechanics counterpart. We ended quantum mechanics I with the one dimensional harmonic oscillator, and because of the importance of the harmonic oscillator in nature, (since oscillations near an equilibrium point can be modeled as such) it will be of interest to consider how the problem changes as we move to higher dimensions.

2 Simple Harmonic Oscillator

To begin we will first consider 2 dimensions, the harmonic oscillator in 2 dimensions is defined by

$$V(\rho) = \frac{1}{2}k\rho^2 \tag{1}$$

Where $\rho^2 = x^2 + y^2$. Notice how this is a central-force problem similar to the one considered in quantum mechanics I, as such angular momentum, L will be conserved. This is because,

$$\vec{\tau} = \vec{r} \times \vec{F} = \frac{\mathrm{d}\vec{L}}{\mathrm{d}t} \tag{2}$$

$$\vec{\tau} = 0 \tag{3}$$

$$\vec{L} = Constant \tag{4}$$

Now r is defined as $\vec{r} = \rho\hat{\rho}$ and $\vec{L} = \vec{r} \times \vec{p}$ so we can write the angular momentum as

$$\vec{L} = m\rho\hat{\rho} \times \left(\dot{\rho}\hat{\rho} + \rho\dot{\phi}\hat{\phi}\right) = m\rho^2\dot{\phi}\hat{z} = constant \tag{5}$$

Now since $\vec{L}$ is constant we can fix both the direction and magnitude. We will pick the $\hat{z}$ for L and the plane perpendicular to L to be defined in polar coordinates.

This problem may also be worked out in Cartesian coordinates and the benefit there lies in the fact that $\delta\hat{x} = 0$ same for the y coordinate. This allows the problem to be separates into the two coordinates where each coordinate acts like a one-dimensional harmonic oscillator. However since we will not gain any new information from this since we have already solved the one-dimensional harmonic oscillator we will consider how polar coordinates changes the problem.

Since the potential is of the form $V(\rho)$, the force is conserved and energy is conserved. So let us consider the energy equation

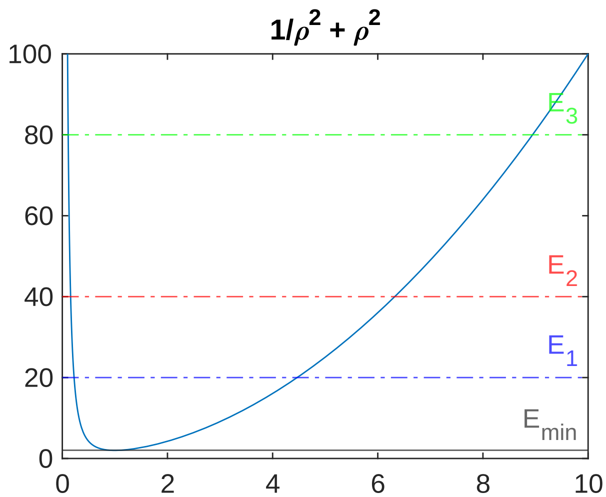
$$E = constant = \frac{1}{2}m\vec{v} \cdot \vec{v} + V(\rho) \tag{6}$$

$$E = \frac{1}{2}m(\dot{\rho}^2 + \rho^2\dot{\phi}^2) + \frac{1}{2}k\rho^2 \tag{7}$$

$$E = \frac{1}{2}m\dot{\rho}^2 + \frac{L^2}{2m\rho^2} + \frac{1}{2}k\rho^2 \tag{8}$$

Where equation (8) just takes into account the effect of the angular momentum. Now $\dot{\rho}^2 \geq 0$ so it is useful to look at the plot of $\frac{L^2}{2m\rho^2} + \frac{1}{2}k\rho^2$ as a function of ρ and see what types of solutions will be allowed.

Fig. 1 Here we can see that the allowed energies are all $E \geq E_{min}$



In figure 1 we can see that E = 0 is not allowed, however this is only in the case that $L \neq 0$. When $L = 0$ we have the case of a simple harmonic oscillator in one dimension along $\hat{\rho}$, where $\delta\hat{\rho} = 0$. So we will be interested in the case where $L \neq 0$. From figure 1 we can also see that the motion of the particle is bounded so we should be able to find ρ_{min}, ρ_{max}.

Now let us go about solving for the equations of motions. Again consider the energy equation

$$E = \frac{1}{2}m\dot{\rho}^2 + \frac{L^2}{2m\rho^2} + \frac{1}{2}k\rho^2 \tag{9}$$

We can solve for $\dot{\rho}$ to obtain the following expression

$$\dot{\rho} = \frac{\omega}{\rho}\sqrt{\frac{1}{m^2\omega^4}\left(E^2 - L^2\omega^2\right) - \left(\rho^2 - \frac{E}{m\omega^2}\right)^2} \tag{10}$$

Where we used the angular frequency of the harmonic oscillator is $\omega^2 = \frac{k}{m}$, this can be seen from the quadratic term in E as well as the equations of Force.

Now since we have terms of the order ρ^4 it might be useful to consider ρ^2 and for this reason we will let $u = \rho^2$ so $\frac{\mathrm{d}u}{\mathrm{d}t} = 2\rho\frac{\mathrm{d}\rho}{\mathrm{d}t}$. As for the intuition behind this substitution we are considering $u = \vec{r} \cdot \vec{r} = \rho^2$ as opposed to $\vec{r}$ because u is invariant making it an important quantity to consider. Now we also want to consider natural units, in such a way that will make our problem dimensionless. In this case since angular momentum is conserved and ω as well as mass are constant, we may use these quantities to come up with units that make our problem dimensionless. Now the left term in the square root in equation (10) suggests that $E = \alpha L\omega$, let us check the units of $L\omega$

$$[L\omega] = \frac{kgm^2}{s}\frac{1}{s} = J = [E] \tag{11}$$

so it seems like the natural units of Energy are $L\omega$, now let us consider what units we should use for u again let us look at our equation (10), and notice that the right term in the square root is $u - \frac{E}{m\omega^2}$, so it seems natural to say $u = \beta\frac{L\omega}{m\omega^2} = \beta\frac{L}{m\omega}$ again it must be checked that $\frac{L}{m\omega}$ has the appropriate units, in this case we want units of m^2. Dimensional analysis shows that $[\frac{L}{m\omega}] = m^2$. After incorporating the appropriate substitutions we obtain the equation

$$\frac{1}{2\omega}\dot{\beta} = \sqrt{\left(\alpha^2 - 1\right) - (\beta - \alpha)^2} \tag{12}$$

Which is unit-less as we wanted when choosing natural units. Now another substitution we will do to simplify the algebra will be $\tau = 2\omega t$ so we obtain the following result

$$\frac{\mathrm{d}\beta}{\mathrm{d}\tau} = \sqrt{\left(\alpha^2 - 1\right) - (\beta - \alpha)^2} \tag{13}$$

This equation may be solved explicitly however it would make more sense to consider $\beta(\phi)$ instead of $\beta(\tau)$ since we want to have a clear relation between the angle and the position of the particle which seems to be in closed orbit. Therefore we need one more relation specifically $\frac{\mathrm{d}\phi}{\mathrm{d}\tau}$. However, we already know this relation from the angular momentum, $L = \rho^2\dot{\phi}$. So let us put this expression in our natural units

$$L = mu\frac{\mathrm{d}\phi}{\mathrm{d}t} = \beta m\frac{L}{m\omega}\frac{\mathrm{d}\phi}{\mathrm{d}\tau}2\omega \tag{14}$$

$$\frac{\mathrm{d}\phi}{\mathrm{d}\tau} = \frac{1}{2\beta} \tag{15}$$

so we obtain the following expression for $\beta(\phi)$

$$\frac{\mathrm{d}\beta}{\mathrm{d}\phi} = 2\beta\sqrt{\left(\alpha^2 - 1\right) - (\beta - \alpha)^2} \tag{16}$$

An elegant equation due to the use of appropriate natural units, had we left everything in terms of E and L we would not see the simple underlying structure of our equation of motion. From this it is clear the effect that α and β have and it is clear that $\alpha \geq 0$ so that $E_{min} = L\omega$.

Now we will solve equation (16)

$$\int \frac{1}{\beta\sqrt{\left(\alpha^2 - 1\right) - (\beta - \alpha)^2}}\, d\beta = 2\int\, d\phi \tag{17}$$

The solution of the right hand side is clear so we will focus on the left hand side. To solve this integral we will use a clear substitution, letting $b = \frac{1}{\beta}$ so $db = -\frac{1}{\beta^2}d\beta$, I found this substitution to lead to a nice simple result which I found to be elegant, there are other ways to solve such an integral, however my other approaches did not lead to such nice equations. So to continue solving the R.H.S. of equation (17)

$$-\int \frac{1}{b\sqrt{\left(\alpha^2 - 1\right) - \left(\frac{1}{b} - \alpha\right)^2}}\, db \tag{18}$$

$$= -\int \frac{1}{\sqrt{-b^2 - 1 + 2\alpha b}}\, db \tag{19}$$

$$= -\int \frac{1}{\sqrt{\left(\alpha^2 - 1\right) - (b - \alpha)^2}}\, db \tag{20}$$

This integral is already easily solvable but to make the integral clear let us use another substitution $y = b - \alpha$ so that $dy = db$

$$= -\int \frac{1}{\sqrt{(\alpha^2 - 1) - y^2}} dy \tag{21}$$

This integral is $-sin^{-1}(\frac{y}{\sqrt{\alpha^2-1}})$ This can be easily shown by using the substitution $y = \sqrt{\alpha^2 - 1} sin\theta$. Now using this result we get the expression

$$\beta = \left(\alpha - \sqrt{\alpha^2 - 1} sin[2(\phi + \phi_0)]\right)^{-1} \tag{22}$$

But we are interested in u, so we can use $u = \beta\frac{L}{m\omega}$ to find u and $u = \rho^2$ to find $\rho(\phi)$. Giving us our equation of motion which is elliptical. This can be shown by showing that you can get to the form $\frac{x^2}{a^2} + \frac{y^2}{b^2} = 1$. To show this I suggest using $\rho^2(\phi)$ and using $\rho^2 = x^2 + y^2$ and then diagonalizing the equation so that we only have quadratic terms and all the cross terms disappear. As a hint this can be done by doing a rotation so that

$$\begin{bmatrix} x \\ y \end{bmatrix} = R(\theta) \begin{bmatrix} x' \\ y' \end{bmatrix} \tag{23}$$

Chapter 2
Quantum Mechanics

Now we will begin to consider how to deal with these types of problems in quantum mechanics. First we begin by writing the Schrodinger wave equation

$$i\hbar\frac{\partial\Psi(x,t)}{\partial t} = \frac{-\hbar^2}{2m}\left(\frac{\partial^2\Psi(x,y,t)}{\partial x^2} + \frac{\partial^2\Psi(x,y,t)}{\partial y^2}\right) + V(x,y)\Psi(x,y,t) \quad (1)$$

Now we will assume solutions of the form $\Psi(x,y,t) = T(t)\phi(x,y)$ so then $T(t) = e^{-i\frac{E}{\hbar}t}$. This was shown in quantum mechanics I. So we have in general $\Psi(x,y,t) = e^{-i\frac{E}{\hbar}t}\phi(x,y)$ when energy is conserved. Substituting this solution into the wave equation lets us separate the spacial and time coordinate giving us

$$-\frac{\hbar^2}{2m}\left(\frac{\mathrm{d}^2\phi(x,y)}{\mathrm{d}x^2} + \frac{\mathrm{d}^2\phi(x,y)}{\mathrm{d}y^2}\right) + V(x,y)\phi(x,y) = E\phi(x,y) \quad (2)$$

Now let us consider the case of a harmonic oscillator potential.

1 Cartesian Coordinates

First we will consider the harmonic oscillator in Cartesian coordinates but we will later consider the problem in polar coordinates and see the benefit to each parameterization.

In Cartesian coordinates the wave equation is equation (2), where $V(x, y) = \frac{1}{2}k(x^2 + y^2)$ giving us

$$-\frac{\hbar^2}{2m}\left(\frac{d^2\phi(x,y)}{dx^2} + \frac{d^2\phi(x,y)}{dy^2}\right) + \frac{1}{2}k(x^2 + y^2)\phi(x,y) = E\phi(x,y) \tag{3}$$

Now we will consider the natural units of the problem. Let $x = bu$ and $y = bv$ so let $\psi(u, v) = \phi(x = bu, y = bv)$ substituting these into equation (3) give us

$$-\frac{\hbar^2}{2mb^2}\left(\frac{d^2\psi(u,v)}{du^2} + \frac{d^2\psi(u,v)}{dv^2}\right) + \frac{1}{2}b^2k(u^2 + v^2)\psi(u,v) = E\psi(u,v) \tag{4}$$

Now let $b^2 = \frac{\hbar}{m\omega}$

$$-\frac{1}{2}\hbar\omega\left(\frac{d^2\psi(u,v)}{du^2} + \frac{d^2\psi(u,v)}{dv^2}\right) + \frac{1}{2}\hbar\omega(u^2 + v^2)\psi(u,v) = E\psi(u,v) \tag{5}$$

So it seems natural for Energy to be $E = \alpha\hbar\omega$. If you refer back to the classical case this is the same substitution that we used before except now instead of L we are using $\hbar$ this leads to the question is $L \propto \hbar$? They do have the same units so it seems like it could be the case that we can say $\hbar$ are the natural units of frequency. So now let us substitute our expression for E

$$-\frac{1}{2}\left(\frac{d^2\psi(u,v)}{du^2} + \frac{d^2\psi(u,v)}{dv^2}\right) + \frac{1}{2}(u^2 + v^2)\psi(u,v) = \alpha\psi(u,v) \tag{6}$$

Where we will now require $\psi(u, v)$ to be normalized rather then $\phi(x, y)$ this is because we will be working in terms of $\psi(u, v)$ for the duration of the problem however the normalization of $\phi(x, y)$ can be used by doing a change of variables. So we require

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\psi^*(u, v)\psi(u, v)\,dudv = 1 \tag{7}$$

Let us quickly show the normalization of $\phi(x, y)$ from equation (6) we will use the relation $\psi(u, v) = \phi(x = bu, y = bv)$

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\phi^*(x = bu, y = bv)\phi(x = bu, y = bv)\,dudv = 1 \tag{8}$$

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\phi^*(x, y)\phi(x, y) = b^2 \tag{9}$$

So then $\phi(x, y)$ just picks up a factor of $\frac{1}{b}$ from the substitution. Now to solve the problem without the need of assuming we may separate x and y we will use the algebra of operators. In the one dimensional harmonic oscillator we found that we could let $a_u = \frac{1}{\sqrt{2}}\left[\frac{\partial}{\partial u} + u\right]$ and simplify the problem so we will use this same operator, however since we are now working in two dimensions we need another operator a_v which operates on the v component. The expression for a_v follows directly from a_u since a_u only pertains to the u variable and since u and v are orthogonal and don't vary with time we can separate the the operates into a_u and a_v. So we have

$$a_u = \frac{1}{\sqrt{2}}\left[\frac{\partial}{\partial u} + u\right] \tag{10}$$

$$a_v = \frac{1}{\sqrt{2}}\left[\frac{\partial}{\partial v} + v\right] \tag{11}$$

Now we will need to find $a^\dagger$ to do so we will need to show that $\langle\chi|a\psi\rangle = \langle a^\dagger\chi|\psi\rangle$. This is equivalent to saying

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\chi^*(u, v)a\psi(u, v)\,dudv \tag{12}$$

$$= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}(a^\dagger\chi(u, v))^*\psi(u, v)\,dudv \tag{13}$$

So using the constraint that $\psi(u,\nu) \longrightarrow 0$ as $u,\nu \longrightarrow \pm\infty$ we can find that $a_u^\dagger = \frac{1}{\sqrt{2}}\left[-\frac{\partial}{\partial \nu} + \nu\right]$ same for a_ν. For now I will work with only u since ν follows directly from u due to the fact that u and ν are orthogonal and $\hat{u}, \hat{\nu}$ do not vary. Now we define $N_u = a_u^\dagger a_u$.

$$N_u = -\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}u^2} + \frac{1}{2}u^2 - \frac{1}{2} \tag{14}$$

This can be found by acting N_u on $\psi(u,\nu)$ this was done in quantum mechanics I.

Now then we can write N_ν similarly as such

$$N_\nu = -\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}\nu^2} + \frac{1}{2}\nu^2 - \frac{1}{2} \tag{15}$$

So then substituting N_u, N_ν into equation (6) we have

$$[N_u + N_\nu + 1]\,\psi(u,\nu) = \alpha\psi(u,\nu) \tag{16}$$

or

$$[N_u + N_\nu]\,\psi(u,\nu) = (\alpha - 1)\psi(u,\nu) \tag{17}$$

And since N_u, N_ν are semi-positive definite, meaning

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \psi^*(u,\nu)N_u + N_\nu\psi(u,\nu)\,dud\nu \tag{18}$$

$$= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \psi^*(u,\nu)\left(a_u^\dagger a + a_\nu^\dagger a\right)\psi(u,\nu)\,dud\nu \tag{19}$$

$$= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} f^*(u,\nu)f(u,\nu)\,dud\nu \geq 0 \tag{20}$$

$$= \alpha - 1\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \psi^*(u,\nu)\psi(u,\nu)\,dud\nu \geq 0 \tag{21}$$

So we can conclude that $\alpha - 1 \geq 0$. So the lowest energy is proportional to $\alpha = 1$ like in the classical case. Now an interesting implication of this result is that the lowest energy level of a harmonic oscillator in $\mathbb{R}^n$ is proportional to $\alpha = \frac{1}{2}^n$ for $n \in \mathbb{Z}^+$.

Now then since N_u, N_v are semi positive definite and $\alpha = 1$ corresponds to the lowest energy state let us find the solution to $\psi_{\alpha=0}(u, v)$. From equation (17) it follows then that

$$[N_u + N_v]\,\psi(u, v) = 0 \tag{22}$$

Now using the fact that N_u and N_v are both semi-positive definite we can say

$$a_u\psi_0(u, v) = 0 \tag{23}$$

same for a_v

$$a_v\psi_0(u, v) = 0 \tag{24}$$

So we get

$$\left(\frac{\partial}{\partial u} + u\right)\psi_0 = 0 \tag{25}$$

$$\left(\frac{\partial}{\partial v} + v\right)\psi_0 = 0 \tag{26}$$

We can rewrite equation (25) as such

$$\psi_0\frac{\partial}{\partial u}\left(\ln\psi_0 + \frac{1}{2}u^2\right) = 0 \tag{27}$$

So then for the non-trivial solution of ψ_0

$$\ln\psi_0 + \frac{1}{2}u^2 = f(v) \tag{28}$$

Now similarly for equation (26) we get

$$\psi_0\frac{\partial}{\partial v}\left(\ln\psi_0 + \frac{1}{2}v^2\right) = 0 \tag{29}$$

However now we can substitute $\ln \psi_0$

$$\psi_0 \frac{\partial}{\partial \nu} \left(f(\nu) - \frac{1}{2}u^2 + \frac{1}{2}\nu^2 \right) = 0 \tag{30}$$

Again since we want the non-trivial solution of ψ_0 and $\frac{\partial u}{\partial \nu} = 0$ we get

$$f(\nu) + \frac{1}{2}\nu^2 = C \tag{31}$$

Where C is some constant.

$$\ln \psi_0 + \frac{1}{2}(u^2 + \nu^2) = 0 \tag{32}$$

or

$$\psi_0(u, \nu) = C' e^{-\frac{1}{2}(u^2+\nu^2)} \tag{33}$$

Where $C' = e^C$ We can find C' via the requirement that ψ must be normalized to 1 over all space. Meaning

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \psi_0^*(u, \nu)\psi_0(u, \nu)\ dud\nu = 1 \tag{34}$$

$$= C'^2 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-(u^2+\nu^2)}\ dud\nu = 1 \tag{35}$$

$$= C'^2 \int_{0}^{2\pi} \int_{0}^{\infty} e^{-\rho^2}\ \rho d\rho d\phi = 1 \tag{36}$$

$$= C'^2 \pi \left(-e^{-\rho^2} |_0^\infty) \right) = C'^2 \pi = 1 \tag{37}$$

So then $C' = \frac{1}{\sqrt{\pi}}$, giving us

$$\psi_0(u, \nu) = \frac{1}{\sqrt{\pi}} e^{-\frac{1}{2}(u^2+\nu^2)} \tag{38}$$

Now to get to move through energy states we will apply the $a^\dagger$ and a operators. This is because $[N_i, a_j] = -a_i \delta_{ij}$ where $i, j = 1, 2$ here I am using the notation that $u = 1, \nu = 2$ for simplicity. We also know $[N_i, a_j^\dagger] = a_i^\dagger \delta_{ij}$

these commutators were shown in quantum mechanics I, the addition of i, j is due to the fact that now we are in two dimensions and δ_{ij} comes from the fact that u, v are orthogonal, in other words the operator passes through since $\frac{\partial}{\partial u}\frac{\partial}{\partial v} = \frac{\partial}{\partial v}\frac{\partial}{\partial u}$ because we are assuming that $\psi(u, v)$ is smooth. In addition we also have the commutator $[a_i, a_j] = \delta_{ij}$. To list them we have

$$[a_i, a_j] = \delta_{ij} \tag{39}$$

$$[N_i, a_j^\dagger] = a_i^\dagger \delta_{ij} \tag{40}$$

$$[N_i, a_j] = -a_i \delta_{ij} \tag{41}$$

These were all explicitly shown in quantum mechanics I. Now let us denote $\psi(u, v)$ by $\psi(u, v)_{n_1,n_2}$ where n_1, n_2 denote the number of times we acted on ψ with $a_u^\dagger$ and $a_v^\dagger$ respectively. Now let us consider $a_u^\dagger$ operating on equation (17)

$$a_u^\dagger \left[N_u + N_v\right] \psi(u, v) = a_u^\dagger(\alpha - 1)\psi(u, v) \tag{42}$$

$$= \left[N_u + N_v\right] a_u^\dagger \psi(u, v) = (\alpha - 1 + 1) a_u^\dagger \psi(u, v) \tag{43}$$

Therefore $a_u^\dagger$ effectively raises the energy level by 1, where $\alpha + 1$ is the eigenvalue for our Hamiltonian and $a_u^\dagger \psi$ is its corresponding eigenvector. Also since the Hamiltonian is hermitian we know that eigenvectors with different eigenvalues are orthogonal, this was also shown in quantum mechanics I. Same applies for $a_v^\dagger$ and to go to lower energy states we can use a_i where $i = 1$ corresponds to u and $i = 2$ corresponds to v.

Now let us go about figuring out $\psi(u, v)_{n_1,n_2}$. To do so let $a_u^\dagger \psi_{n_1,n_2} = C_{n_1+1,n_2}\psi_{n_1+1,n_2}$ and $a_v^\dagger \psi_{n_1,n_2} = C_{n_1,n_2+1}\psi_{n_1,n_2+1}$, here we are just trying to figure out the normalization that comes about when applying the operators. To figure out that normalization we apply the normalization constraint

$$\int_{-\infty}^{\infty} C_{n_1+1,n_2}^2 \psi_{n_1+1,n_2}^2 \, du dv = \int_{-\infty}^{\infty} a_u^\dagger \psi_{n_1,n_2}^* a_u^\dagger \psi_{n_1,n_2} \tag{44}$$

$$= C_{n_1+1,n_2}^2 = \int_{-\infty}^{\infty} \psi_{n_1,n_2}^* a_u a_u^\dagger \psi_{n_1,n_2} \tag{45}$$

Here the integral on the L.H.S. vanishes since we are requiring ψ_{n_1+1,n_2} to be normalized

$$= \int_{-\infty}^{\infty} \psi^*_{n_1,n_2} \left(1 + a_u^\dagger a_u\right) \psi_{n_1,n_2} \tag{46}$$

This follows from the commutator in equation (39)

$$= 1 + n_1 \tag{47}$$

Here we are saying $N_u \psi(u,v)_{n_1,n_2} = n_1 \psi(u,v)_{n_1,n_2}$ where n_1 is an eigenvalue of N_u.

So we find that $C_{n_1+1,n_2} = \sqrt{1+n_1}$, from this since $[N_u, N_v] = 0$ which follows from the fact that u and v are independent and the operators pass through, we can say that $C_{n_1,n_2+1} = \sqrt{1+n_2}$. Now since these operators are linear we can assume $\psi_{n_1,n_2} = \frac{1}{\sqrt{\pi}} H_{n_1,n_2}(u,v) e^{-\frac{1}{2}(u^2+v^2)}$, so then

$$a_u^\dagger \frac{1}{\sqrt{1+n_1}} \psi_{n_1,n_2} = \psi_{n_1+1,n_2} \tag{48}$$

$$= \frac{1}{\sqrt{2}} \left[-\frac{\partial}{\partial u} + u\right] \frac{1}{\sqrt{1+n_1}} \left(H_{n_1,n_2}(u,v) e^{-\frac{1}{2}(u^2+v^2)}\right) = \psi_{n_1+1,n_2} \tag{49}$$

Now to calculate this we will need to know what $\frac{\partial \psi_{n_1,n_2}(u,v)}{\partial u}$ is. We can find it as such

$$\frac{\partial H_{n_1,n_2} e^{-\frac{1}{2}(u^2+v^2)}}{\partial u} = \left(\frac{\partial H_{n_1,n_2}}{\partial u} - u\right) e^{-\frac{1}{2}(u^2+v^2)} \tag{50}$$

So we get equation (49) to be

$$\left[-\left(\frac{\partial H_{n_1,n_2}}{\partial u}\right) e^{-\frac{1}{2}(u^2+v^2)} + 2u \left(H_{n_1,n_2}(u,v) e^{-\frac{1}{2}(u^2+v^2)}\right)\right] \frac{1}{\sqrt{2(1+n_1)}} = \psi_{n_1+1,n_2} \tag{51}$$

$$\left[-\left(\frac{\partial H_{n_1,n_2}}{\partial u}\right) + 2u \left(H_{n_1,n_2}(u,v)\right)\right] \frac{1}{\sqrt{2(1+n_1)}} = H_{n_1+1,n_2}(u,v) \tag{52}$$

Giving us

$$-\left(\frac{\partial H_{n_1,n_2}}{\partial u}\right)+2u\left(H_{n_1,n_2}(u,v)\right)=\sqrt{2(1+n_1)}H_{n_1+1,n_2}(u,v) \tag{53}$$

Where we found $H_{0,0}=1$ and since v is orthogonal and $\hat{v}$ does not change with time we get,

$$-\left(\frac{\partial H_{n_1,n_2}}{\partial v}\right)+2v\left(H_{n_1,n_2}(u,v)\right)=\sqrt{2(1+n_2)}H_{n_1,n_2+1}(u,v) \tag{54}$$

This can be easily checked.

So we get that $\psi_{n_1,n_2}=\frac{1}{\sqrt{\pi}}H_{n_1,n_2}(u,v)e^{-\frac{1}{2}(u^2+v^2)}$

Notice also that $H_{n_1,n_2}(u,v) = H_{n_2,n_1}(v,u))$ so then $\psi_{n_1,n_2}(u,v) = \psi_{n_2,n_1}(v,u)$. By deriving H_{n_2,n_1} we were able to show a very cool symmetry.

Here are a few H_{n_1,n_2}

$$H_{0,0}=1 \tag{55}$$

$$H_{1,0}=\sqrt{2}u \tag{56}$$

$$H_{1,1}=2uv \tag{57}$$

$$H_{2,0}=\frac{\sqrt{2}}{2}\left(-1+2u^2\right) \tag{58}$$

Where using $H_{n_1,n_2}(u,v)=H_{n_2,n_1}(v,u))$ we can find the corresponding $H_{0,i}$ terms, because of the power of this relation I will also list it

$$H_{n_1,n_2}(u,v)=H_{n_2,n_1}(v,u)) \tag{59}$$

Also like in the one dimensional harmonic oscillator where we had instead H_n our H_{n_1,n_2} is even or odd depending on the values of n_1, n_2 by even or odd I mean in the corresponding direction. so a reflection about the u or v direction causes H_{n_1,n_2} to change directions depending on whether H_{n_1,n_2}

is even or odd with respect to that axis.

Notice also how the $\psi_{0,0}$ solution is a two-dimensional Gaussian centered at $u, v = 0$. Also notice that $\alpha = n_1 + n_2$ and that starting at $\alpha = 1$ we have degeneracy. So looking at the simplest case of degeneracy $\alpha = 1$, we have the two states $\psi_{1,0}$ and $\psi_{0,1}$, are these two states orthogonal?

To answer this question first remember that a hermitian operator requires the eigenvectors of different eigenvalues to be orthogonal but does not require the same for eigenvectors of the same eigenvalue, but they can be made orthogonal. Now to consider whether these two states are orthogonal it is just a matter of considering $H_{1,0}$ and $H_{0,1}$. Notice that in this simple case $H_{1,0}H_{0,1} = H_{1,1}$ so we can see from this that $\psi 1, 0$ and $\psi 0, 1$ are not orthogonal. To form an orthogonal subspace for a given eigenvalue we could simply make a new $\psi'_1(u, v) = C_1\psi_{1,0}(u, v) + C_2\psi_{0,1}(u, v)$ and $\psi'_2(u, v) = B_1\psi_{1,0}(u, v) + B_2\psi_{0,1}(u, v)$ which are orthogonal for a given α so in general we can form orthogonal eigenvectors for a given eigenvalue or energy.

Now like in the classical case we will look at the problem using polar coordinates, the benefit of this will be seeing the effect of angular momentum on the problem.

2 Polar Coordinates

To consider the problem in polar coordinates we will need to make the change of basis $u, v \longrightarrow r, \theta$. This can be done by parameterizing u, v as such

$$u = r\cos\theta \tag{60}$$

$$v = r\sin\theta \tag{61}$$

from this is follows that

$$du = dr\cos\theta - rd\theta\sin\theta \tag{62}$$

$$dv = dr\sin\theta + rd\theta\cos\theta \tag{63}$$

Now let us define $\psi(u, v) = \psi(r\cos\theta, r\sin\theta) = \chi(r, \theta)$ so that

$$\int_0^{2\pi}\int_0^{\infty} \chi^*(r, \theta)\chi(r, \theta)r\ drd\theta = 1 \tag{64}$$

This is actually a natural equivalence since to find the infinitesimal area element we do $dxdy = |dx \times dy| = rdrd\theta = |dr \times d\theta|$.
Now we will also need $dr, d\theta$ so we can find these using equations (62) and (63)

$$dr = du\cos\theta + dv\sin\theta \tag{65}$$

$$d\theta = \frac{1}{r}\left(dv\cos\theta - du\sin\theta\right) \tag{66}$$

so with these we can now find $\frac{\partial\chi(r,\theta)}{\partial u}$ and $\frac{\partial\chi(r,\theta)}{\partial v}$, this is done as such,

$$\frac{\partial\chi}{\partial u} = \left(\frac{\partial\theta}{\partial u}\frac{\partial}{\partial\theta} + \frac{\partial r}{\partial u}\frac{\partial}{\partial r}\right)\chi \tag{67}$$

$$= \frac{\partial\chi}{\partial u} = \left(-\frac{\sin\theta}{r}\frac{\partial}{\partial\theta} + \cos\theta\frac{\partial}{\partial r}\right)\chi \tag{68}$$

Now for $\frac{\partial\chi(r,\theta)}{\partial v}$

$$\frac{\partial\chi}{\partial v} = \left(\frac{\partial\theta}{\partial v}\frac{\partial}{\partial\theta} + \frac{\partial r}{\partial v}\frac{\partial}{\partial r}\right)\chi \tag{69}$$

$$= \frac{\partial\chi}{\partial v} = \left(\frac{\cos\theta}{r}\frac{\partial}{\partial\theta} + \sin\theta\frac{\partial}{\partial r}\right)\chi \tag{70}$$

Now we want $\frac{\partial^2\chi(r,\theta)}{\partial u^2}$ and $\frac{\partial^2\chi(r,\theta)}{\partial v^2}$ so we need to consider

$$\frac{\partial^2\chi}{\partial u^2} = \left(-\frac{\sin\theta}{r}\frac{\partial}{\partial\theta} + \cos\theta\frac{\partial}{\partial r}\right)\left(-\frac{\sin\theta}{r}\frac{\partial}{\partial\theta} + \cos\theta\frac{\partial}{\partial r}\right)\chi \tag{71}$$

and

$$\frac{\partial^2\chi}{\partial v^2} = \left(\frac{\cos\theta}{r}\frac{\partial}{\partial\theta} + \sin\theta\frac{\partial}{\partial r}\right)\left(\frac{\cos\theta}{r}\frac{\partial}{\partial\theta} + \sin\theta\frac{\partial}{\partial r}\right)\chi \tag{72}$$

So starting with equation (71) consider the first term in the left parentheses

$$\frac{-\sin\theta}{r}\frac{\partial}{\partial\theta}\left(-\frac{\sin\theta}{r}\frac{\partial}{\partial\theta} + \cos\theta\frac{\partial}{\partial r}\right) \tag{73}$$

$$= \frac{-\sin\theta}{r}\left(-\frac{\cos\theta}{r}\frac{\partial}{\partial\theta} + \frac{-\sin\theta}{r}\frac{\partial^2}{\partial\theta^2} - \sin\theta\frac{\partial}{\partial r} + \cos\theta\frac{\partial}{\partial\theta}\frac{\partial}{\partial r}\right) \tag{74}$$

The right term in the left parentheses in equation (71) gives us

$$\cos\theta\frac{\partial}{\partial r}\left(-\frac{\sin\theta}{r}\frac{\partial}{\partial\theta} + \cos\theta\frac{\partial}{\partial r}\right) \tag{75}$$

$$= \cos\theta\left(\frac{\sin\theta}{r^2}\frac{\partial}{\partial\theta} - \frac{\sin\theta}{r}\frac{\partial}{\partial r}\frac{\partial}{\partial\theta} + \cos\theta\frac{\partial^2}{\partial r^2}\right) \tag{76}$$

Now to do the same thing for equation (72) notice the only difference in these equation from (71) is that $-\sin\theta \longrightarrow \cos\theta$ and $\cos\theta \longrightarrow \sin\theta$ so taking this into consideration we get

$$\frac{\cos\theta}{r}\left(-\frac{\sin\theta}{r}\frac{\partial}{\partial\theta} + \frac{\cos\theta}{r}\frac{\partial^2}{\partial\theta^2} + \cos\theta\frac{\partial}{\partial r} + \sin\theta\frac{\partial}{\partial\theta}\frac{\partial}{\partial r}\right) \tag{77}$$

From the effect of the left operator in the left parenthesis of equation (72) as for the right operator in the left parenthesis in equation (72) we can see use the same relation where $-\sin\theta \longrightarrow \cos\theta$ and $\cos\theta \longrightarrow \sin\theta$ so we get

$$= \sin\theta \left(-\frac{\cos\theta}{r^2}\frac{\partial}{\partial\theta} + \frac{\cos\theta}{r}\frac{\partial}{\partial r}\frac{\partial}{\partial\theta} + \sin\theta\frac{\partial^2}{\partial r^2} \right) \tag{78}$$

So then equation (71) = equation (74) + (76) and equation (72) = equation (77) + (78). So that equation (71) + (72) gives us

$$\frac{\partial^2}{\partial u^2} + \frac{\partial^2}{\partial v^2} = \frac{1}{r^2}\frac{\partial^2}{\partial\theta^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{\partial^2}{\partial r^2} \tag{79}$$

So let us now rewrite our wave equation in polar coordinates for a two-dimensional harmonic oscillator which are already in natural units since we went from u, v to r, θ

$$\left[-\frac{1}{2}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial\theta^2} \right) + \frac{1}{2}r^2 = \alpha \right] \chi(r,\theta) \tag{80}$$

From this we want to relate it to the classical case where we had an angular momentum term which was tied to the θ coordinate, as such let us define the L_z operator as

$$L_z = \frac{\partial}{\partial\theta} \tag{81}$$

So then we have

$$\left[-\frac{1}{2}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}L_z^2 \right) + \frac{1}{2}r^2 = \alpha \right] \chi(r,\theta) \tag{82}$$

or

$$\left[-\frac{1}{2}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}L_z^2 - r^2 \right) = \alpha \right] \chi(r,\theta) \tag{83}$$

Now from this it is clear that $[H, L_z] = 0$ where H is defined as

$$H = -\frac{1}{2}\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial\theta^2} \right) + \frac{1}{2}r^2 \tag{84}$$

This is because $\frac{\partial}{\partial\theta}$ passes through each term in our Hamiltonian. Intuitively this has to do with the rotational symmetry of the problem, like in the classical case. Now since $[H, L_z] = 0$ we can diagonalize both operators at the same time, meaning

$$L_z H\chi = \alpha L_z \chi \tag{85}$$

$$= HL_z\chi = \alpha L_z \chi \tag{86}$$

So that each eigenvalue α also has an eigenvector $L_z\chi$ this already proves that we must have degeneracy for certain α. Now let us diagonalize L_z

$$L_z\chi_\alpha = \ell\chi_\alpha \tag{87}$$

$$= \frac{\partial}{\partial\theta}\chi_\alpha(r,\theta) = \ell\chi_\alpha(r,\theta) \tag{88}$$

This is only true for periodic functions meaning $\chi(r,\theta) = \chi(r,\theta + 2\pi)$ so then χ must have solutions of the form

$$\chi_\alpha(r,\theta) = R(r)e^{im\theta} \tag{89}$$

Where m must be an integer since we require the function to be periodic meaning

$$e^{im(\theta+2\pi)} = e^{im\theta} \tag{90}$$

so that $m \in \mathbb{Z}$. Also notice how equation (89) showed that χ must split into two functions of each variable, this was a result without the need to assume that our solution must be seperable. Instead it came out of the operators. So now we have

$$L_z\chi(r,\theta) = im\chi(r,\theta) \tag{91}$$

$$H\chi(r,\theta) = \alpha\chi(r,\theta) \tag{92}$$

Now let us plug in our form for χ into our Hamiltonian, in doing so we can expect the $e^{im\theta}$ term to vanish since it is present in both sides. So we have

$$-\frac{1}{2}\left[\frac{\mathrm{d}^2}{\mathrm{d}r^2}+\frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}r}-\frac{m^2}{r^2}-r^2+2\alpha\right]R(r)=0 \tag{93}$$

Where we moved over α to the other side to show that for the non-trivial solution of $R(r)$ the inside term must vanish and we no longer have partial derivatives since R is a function of r alone.

Now we will do a clear change of variables and say

$$R(r)=P(r)e^{-\frac{r^2}{2}} \tag{94}$$

We know this from the Cartesian coordinate case however, if we didn't this wouldn't be a far assumption to make since we expect the particle to behave like the one-dimensional oscillator for the lowest energy $\alpha = 1$. So now substituting this in our Hamiltonian we get

$$\frac{\mathrm{d}^2P}{\mathrm{d}r^2}+(\frac{1}{r}-2P)\frac{\mathrm{d}P}{\mathrm{d}r}+(2\alpha-2-\frac{m^2}{r^2})P=0 \tag{95}$$

Here similarly the $e^{-\frac{r^2}{2}}$ term vanishes since it is everywhere. Now we turn to the normalization of χ for more information. Remember that for χ to be normalized the r term must go to 0 at infinity. The θ term is unaffected since we are only working with r now. So we need to think about the term

$$\int_0^\infty rP^2(r)e^{-r^2}\ dr \tag{96}$$

It must be finite so then

$$\lim_{r\longrightarrow\infty} rP^2(r)e^{-r^2}=0 \tag{97}$$

Therefore P(r) must be a polynomial in r and it must be a finite polynomial. Now let us consider what happens as $r \longrightarrow 0$ since we are approach 0 we are only concerned with the smallest power of r in P(r) as all other terms will approach 0 much faster. So then let $P(r) \propto r^\beta$ then plugging this term in our Hamiltonian expression of equation (96) gives us

$$\left[\beta(\beta-1)+\beta-m^2\right] r^{\beta-2}+Cr^{\beta-1}+\ldots \tag{98}$$

However again we are only concerned with the lowest power of r. So that would be the $r^{\beta-2}$ term. We require that the lowest term in r does not blow up as $r \longrightarrow 0$ so this means that we require the lowest term in r to go to 0 as $r \longrightarrow 0$. Meaning

$$\beta(\beta-1)+\beta-m^2=0 \tag{99}$$

or

$$\beta^2-m^2=0 \tag{100}$$

So we have the constraint that $\beta = \pm m$ but $\beta \geq 0$ for $r^{\beta} \nrightarrow \infty$ as $r \longrightarrow 0$ so then $\beta = |m|$. This can also be seen when looking at the normalization in equation (96) near 0

$$\int_0^{\epsilon} rP^2(r)\ dr \tag{101}$$

Since near 0, $e^{-r^2} \rightarrow 1$ so now inputing the lowest term in P(r) we get

$$\int_0^{\epsilon} r^{1+2\beta}\ dr = \frac{r^{2(1+\beta)}}{2(1+\beta)} \nrightarrow \infty \tag{102}$$

Which for this to be true $\beta > -1$ and since m can only be integers, we get that $\beta = |m| \geq 0$. So now knowing this let us implement this into P(r), we will do this as such

$$P(r) = r^{|m|}u(r) \tag{103}$$

Where u(r) is a polynomial in r which we can write as

$$\sum_{n=0}^{n=N} u_n r^n \tag{104}$$

Now plugging this into our Hamiltonian in the form of equation (95) we get

$$\frac{\mathrm{d}^2 u}{\mathrm{d}r^2} + \left(\frac{2|m|+1}{r} - 2r\right)\frac{\mathrm{d}u}{\mathrm{d}r} + 2\left(\alpha - 1 - |m|\right)u = 0 \tag{105}$$

Now plugging in our form for u(r) in equation (104) we get

$$0 = \frac{2|m|+1}{r}u_1 + \sum_{n=0}^{N}\left[u_{n+2}\left[(n+2)(n+1) + (2|m|+1)(n+2)\right] + u_n\left[2(\alpha - 1 - |m|) - 2n\right]\right] r^n \tag{106}$$

Since each power of r cannot cancel out any other power of r we get that

$$u_1 = 0 \tag{107}$$

and

$$u_{n+2} = -\frac{[2(\alpha - 1 - |m|) - 2n]}{[(n+2)(n+1) + (2|m|+1)(n+2)]}u_n \tag{108}$$

$$= u_{n+2} = -2\frac{[(\alpha - 1 - |m|) - n]}{[(n+2)(n+1) + (2|m|+1)(n+2)]}u_n \tag{109}$$

Equation (109) implies that the even terms are proportional to one another and the same for the odd terms. However we know that $u_1 = 0$ so then every odd term disappears since each one is proportional to u_1. Now to figure out the upper bound of our polynomial in terms of powers of r we will require that $U_{N+2} = 0$. Where we chose the N+2 term since it is the most convenient. Now since this term must be 0 it is equivalent to saying the numerator of equation (109) must be 0. So we get

$$u_{N+2} = 0 = \alpha - 1 - |m| - N \tag{110}$$

or

$$N = \alpha - 1 - |m| \tag{111}$$

equivalently we can say

$$\alpha = N + 1 + |m| \tag{112}$$

From this we get then that

$$\chi(r,\theta) = \sum_{n=0}^{N} [u_n r^n]\, r^{|m|} e^{-\frac{r^2}{2}} e^{im\theta} \tag{113}$$

Where u_{n+2} is defined by

$$u_{n+2} = -\frac{[2(\alpha - 1 - |m|) - 2n]}{[(n+2)(n+1) + (2|m|+1)(n+2)]} u_n \tag{114}$$

and

$$u_1 = 0 \tag{115}$$

We may find u_0 by considering the lowest energy state $\alpha = 1$ in this case we have $u_0 e^{\frac{r^2}{2}}$. Which for this to be the case $u_0 = \frac{1}{\sqrt{\pi}}$ since we require χ to be normalized.

Now then let us make a table of our important quantum numbers: N, m, α and see what comes out.

N	m	α
0	0	1
1	0	2
0	±1	2
2	0	3
1	±1	3
0	±2	3
3	0	4
2	±1	4
1	±2	4
0	±3	4

From this figure it is clear that for any α the allowed values of N are $N = 0, ..., \alpha - 1$ where N increases by 1. Similarly the allowed $|m|$ are $|m| = 0, ..., \alpha - 1$ in increments of 1.

So let us write $\chi(r,\theta) = \chi_{N,m}(r,\theta)$ since knowing N, m specifies α from equation (112).

Let us now consider $\chi^*\chi$ since this is tied to the probability distribution.

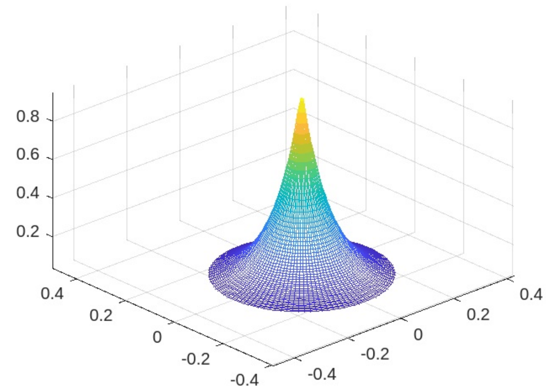
$$\chi^*_{N,m}(r,\theta)\chi_{N,k}(r,\theta) = P_{N,m}P_{N,k}(r)e^{-r^2}e^{i(m-k)} \tag{116}$$

So when $m = k$ we have a rotationally invariant probability distribution, this is due to the rotational symmetry of the problem.

Since u_n for n odd is 0 we may write $u(r) = \sum_{k=0}^{\lfloor N \rfloor}(u_{2k}r^{2k})$. Here we just did $2k = n$ and now the upper limit is the floor function of N because the odd terms in N vanish.

If we look at the $\chi_{0,0}(r,\theta) = \frac{1}{\sqrt{\pi}}e^{-\frac{1}{2}r^2}$ plot in figure 1 we see that is the same as we expect as $\psi_{0,0}(u,v)$.

Fig. 1 Plot of $\chi_{0,0}(r, \theta)$



3 Change of Basis

To change basis let us denote $\psi_{n_1,n_2}(u, v) = |n_1, n_2\rangle$ and $\chi_{N,m}(r, \theta) = |N, m\rangle$. From this we can then write any wave function as

$$\Psi = \sum_{n_1,n_2} b_{n_1,n_2} |n_1, n_2\rangle \tag{117}$$

and also as

$$\Psi = \sum_{N,m} c_{N,m} |N, m\rangle \tag{118}$$

Suppose we want to get b_{j_1,j_2} this can be done by doing the following operation

$$\langle j_1, j_2|\Psi = \sum_{n_1,n_2} b_{n_1,n_2} \langle j_1, j_2|n_1, n_2\rangle = \sum_{n_1,n_2} b_{n_1,n_2} \delta_{j_1+j_2,n_1+n_2} \tag{119}$$

$$= b_{n_1,n_2} \delta_{j_1+j_2,n_1+n_2} \tag{120}$$

In addition

$$\langle j_1, j_2|\Psi = \sum_{N,m} c_{N,m} \langle j_1, j_2|N, m\rangle \tag{121}$$

So that

$$b_{n_1,n_2}\delta_{j_1+j_2,n_1+n_2} = \sum_{N,m} c_{N,m}\langle j_1, j_2|N, m\rangle \tag{122}$$

Now suppose $\Psi = b_{n_1,n_2}|n_1, n_2\rangle$ then we get that

$$b_{n_1,n_2} = \sum_{N,m} c_{N,m}\langle j_1, j_2|N, m\rangle \tag{123}$$

Since $|n_1, n_2\rangle$ is normalized $b_{n_1,n_2} = 1$ so we get

$$1 = \sum_{N,m} c_{N,m}\langle j_1, j_2|N, m\rangle \tag{124}$$

In this case it might be more useful to calculate $\langle N_i, m_j|\Psi$ which is

$$c_{N_i,n_j} = \sum_{n_1,n_2} c_{n_1,n_2}\langle N_i, m_j|n_1, n_2\rangle \tag{125}$$

Now from this we can express $\Psi = |n_1, n_2\rangle$ as

$$|n_1, n_2\rangle = \sum_{N,m} c_{N,m}|N, m\rangle = \sum_{N,m}\sum_{n_1,n_2} c_{n_1,n_2}\langle N, m|n_1, n_2\rangle|N, m\rangle \tag{126}$$

However since n_1, n_2 are fixed in this case we get

$$c_{N_i,n_j} = \langle N_i, m_j|n_1, n_2\rangle \tag{127}$$

and

$$|n_1, n_2\rangle = \sum_{N,m} c_{N,m}|N, m\rangle = \sum_{N,m}\langle N, m|n_1, n_2\rangle|N, m\rangle \tag{128}$$

4 Central Force Problems

The problems we have been working on are all considered central force problems since the force is only depended on the radial component, $\vec{r}$. These problems are of importance in physics because many forces of interest are central forces between particles, so let us now try to solve this group of problems as general as possible in 3 dimensions.

4.1 Angular Momentum

Like in the classical case, central force problems have a rotational symmetry with the angular momentum. Remember that in the classical case we showed $\vec{L} = Const$. This allowed us to simplify the problem and reduce the dimensionality of the problem. Let us find the angular momentum now in quantum mechanics and see if we can use this symmetry for central forces.

Classically, angular momentum is defined as

$$\vec{L} = \vec{r} \times \vec{p} \tag{129}$$

Or written more explicitly,

$$L_x = yp_z - zp_y \tag{130}$$

$$L_y = zp_x - xp_z \tag{131}$$

$$L_z = xp_y - yp_x \tag{132}$$

Now remember from quantum mechanics I that we defined the wave function such that its momentum p is

$$-i\hbar\frac{\partial}{\partial x}\Psi(x) = \hbar k\Psi(x) \tag{133}$$

where $\hbar k$ is our momentum, but remember we are working in 3 dimensions so

$$p_x = -i\hbar\frac{\partial}{\partial x} \tag{134}$$

$$p_y = -i\hbar\frac{\partial}{\partial y} \tag{135}$$

$$p_z = -i\hbar\frac{\partial}{\partial z} \tag{136}$$

Now plugging in these equations into our angular momentum equation gives us the following

$$L_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right) \tag{137}$$

$$L_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right) \tag{138}$$

$$L_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \tag{139}$$

We could have also worked these out in spherical coordinates but Cartesian coordinates are nice for what we are doing now. Now that we have the angular momentum operator, let us see if these commute with each other. This will be of importance because it will tell us the algebra of our group. So let us find $\left[L_x, L_y\right]$ first.

$$\left[L_x, L_y\right] = L_x L_y - L_x, L_y \tag{140}$$

$$\left(L_x L_y\right)\Psi = -\hbar^2\left[\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\right]\Psi \tag{141}$$

$$\left(L_x L_y\right)\Psi = -\hbar^2\left[\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\left(z\frac{\partial\Psi}{\partial x} - x\frac{\partial\Psi}{\partial z}\right)\right] \tag{142}$$

$$\left(L_x L_y\right)\Psi = -\hbar^2\left[y\left(\frac{\partial\Psi}{\partial x} + z\frac{\partial}{\partial z}\frac{\partial\Psi}{\partial x}\right) - xy\frac{\partial^2\Psi}{\partial z^2} - z^2\frac{\partial}{\partial y}\frac{\partial\Psi}{\partial x} + zx\frac{\partial}{\partial y}\frac{\partial\Psi}{\partial z}\right] \tag{143}$$

Were going to assume Ψ is smooth such that $\frac{\partial}{\partial y}\frac{\partial\Psi}{\partial x} = \frac{\partial}{\partial x}\frac{\partial\Psi}{\partial y}$

$$\left(L_y L_x\right)\Psi = -\hbar^2\left[\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\right]\Psi \tag{144}$$

$$\left(L_yL_x\right)\Psi = -\hbar^2\left[zy\frac{\partial}{\partial x}\frac{\partial\Psi}{\partial y} - xy\frac{\partial^2\Psi}{\partial z^2} - z^2\frac{\partial}{\partial x}\frac{\partial\Psi}{\partial y} + x(\frac{\partial\Psi}{\partial y} + z\frac{\partial}{\partial z}\frac{\partial\Psi}{\partial y})\right] \tag{145}$$

Now let us work out $\left(L_xL_y - L_yL_x\right)\Psi$

$$\left(L_xL_y - L_yL_x\right)\Psi = -\hbar^2\left[x\frac{\partial\Psi}{\partial y} - y\frac{\partial\Psi}{\partial x}\right] \tag{146}$$

or we can rewrite this so that it looks more familiar as

$$i\hbar\left(-i\hbar\right)\left[x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right]\Psi \tag{147}$$

Notice this is just $i\hbar L_z$ so that

$$\left[L_x, L_y\right] = i\hbar L_z \tag{148}$$

Let us shortly discuss what this means, since these two operators don't commute we cannot simultaneously diagonalize them. Meaning we cannot pick a frame in which we know both the angular momentum in the x and y directions to infinite precision, there will be some error and this error is proportional to the angular momentum in the z direction.

Let us now work out $[Ly, Lz]$, one may guess that it will look like a permutation of eq. 148 but let us check this to make sure the pattern holds.

$$L_yL_z = -\hbar^2\left[\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\right] \tag{149}$$

$$L_zL_y = -\hbar^2\left[\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)\right] \tag{150}$$

Now notice that in equation eq. 149 and eq. 150 all the operators will "pass through" meaning that when we do the commutator $[Ly, Lz]$ they will cancel, apart from $z\frac{\partial}{\partial y}$ from eq. 149 and $y\frac{\partial}{\partial z}$ from eq. 150. So then we have

$$[Ly, Lz] = -\hbar^2\left[z\frac{\partial}{\partial y} - y\frac{\partial}{\partial z}\right] = i\hbar L_x \tag{151}$$

So this pattern does seem to hold and it makes sense since L_x, L_y, L_z can all be obtained from one another as permutations in the x, y, z coordinates. This can be seen in the set of equations 137. So then finally let us calculate the commutator $[Lz, Lx]$

$$L_zL_x = -\hbar^2\left[\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\right] \tag{152}$$

$$L_xL_z = -\hbar^2\left[\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)\right] \tag{153}$$

Now using the same logic as before the only operators that don't pass through will be $x\frac{\partial}{\partial z}$ from eq. 152 and $z\frac{\partial}{\partial x}$ from eq. 153 giving us

$$[L_z, L_x] = -\hbar^2\left[x\frac{\partial}{\partial z} - z\frac{\partial}{\partial x}\right] = i\hbar L_y \tag{154}$$

Now let us write our results in a more compact form

$$\left[L_i, L_j\right] = i\hbar\epsilon_{ijk}L_k \tag{155}$$

Since the commutator of these operators is another operator in our group, we say that these operators are closed under commutation, this is called the algebra of commutators.

Let us now work out the commutators

$$\left[L_x, L_x^2\right] \tag{156}$$

$$\left[L_x, L_y^2\right] \tag{157}$$

$$\left[L_x, L_z^2\right] \tag{158}$$

The reason being that we are trying to find an invariant operator in our algebra, an operator which commutes with the rest of our angular momentum operator and since we only have L_x, L_y, L_z in our algebra we can only consider these operators. Then let us first work out eq. 156, this one is trivial since L_x commutes with itself so we get

$$\left[L_x, L_x^2\right] = L_x L_x^2 - L_x^2 L_x = L_x^3 - L_x^3 = 0 \tag{159}$$

Then to work out the other commutators it will be useful to remember the property of commutators, consider $[A, BC]$

$$[A, BC] = ABC - BCA \tag{160}$$

but we can add and remove an operator so that the expression still remains unchanged as such

$$[A, BC] = ABC - BCA + BAC - BAC = [A, B]\, C + B\, [A, C] \tag{161}$$

so that we have the property

$$[A, BC] = [A, B]\, C + B\, [A, C] \tag{162}$$

Using this now let us consider eq. 157

$$\left[L_x, L_y^2\right] = \left[L_x, L_y\right] L_y + L_y \left[L_x, L_y\right] \tag{163}$$

Then using eq. 155 we can rewrite this as

$$\left[L_x, L_y^2\right] = i\hbar L_z L_y + i\hbar L_y L_z = i\hbar \left[L_z L_y + L_y L_z\right] \tag{164}$$

Now let us work out eq. 158 similarly,

$$\left[L_x, L_z^2\right] = \left[L_x, L_z\right] L_z + L_z \left[L_x, L_z\right] \tag{165}$$

Where we use again eq. 155 to get the expression

$$\left[L_x, L_z^2\right] = -i\hbar \left[L_y L_z + L_z L_y\right] \tag{166}$$

Now notice that if we add $L_z^2 + L_y^2$ it commutes with L_x since the terms in eq. 164 and eq. 166 cancel out, we can also include L_x^2 since we know it commutes with L_x as well to form an operator which will look similarly to something we have seen before, $L^2 = L_x^2 + L_y^2 + L_z^2$, where we have shown then that

$$\left[L_x, L^2\right] = \left[L_x, L_x^2 + L_y^2 + L_z^2\right] \tag{167}$$

$$\left[L_x, L_x^2 + L_y^2 + L_z^2\right] = \left[L_x, L_x^2\right] + \left[L_x, L_y^2\right] + \left[L_x, L_z^2\right] \tag{168}$$

This follows from the linearly of the commutator,

$$[A, B + C] = A(B+C) - (B+C)A = AB + AC - BA - CA = [A, B] + [A, C] \tag{169}$$

Now using what we have just shown we have

$$\left[L_x, L_x^2 + L_y^2 + L_z^2\right] = 0 + i\hbar\left[L_z L_y + L_y L_z\right] - i\hbar\left[L_y L_z + L_z L_y\right] = 0 \tag{170}$$

So then

$$[L_x, L^2] = 0 \tag{171}$$

Now notice that our choice of L_x was not special meaning we could have picked L_y or L_z and it would have worked out similarly because L^2 is invariant under permutations, if we take $x \rightarrow y$, $y \rightarrow z$, $z \rightarrow x$ then L^2 remains unchanged.

Let us show this by checking $\left[L_y, L^2\right]$, this is equivalent to taking $x \rightarrow y$, $y \rightarrow z$, and $z \rightarrow x$ in $\left[L_x, L^2\right]$, since L^2 remains unchanged. Let us show this result explicitly,

$$\left[L_y, L^2\right] = \left[L_y, L_y^2 + L_z^2 + L_x^2\right] \tag{172}$$

$$\left[L_y, L_y^2 + L_z^2 + L_x^2\right] = \left[L_y, L_y^2\right] + \left[L_y, L_z^2\right] + \left[L_y, L_x^2\right] \tag{173}$$

$$\left[L_y, L_y^2 + L_z^2 + L_x^2\right] = \left[L_y, L_y^2\right] + \left[L_y, L_z^2\right] + \left[L_y, L_x^2\right] \tag{174}$$

$$\left[L_y, L_y^2 + L_z^2 + L_x^2\right] = 0 + \left[L_y, L_z\right] L_z + L_z \left[L_y, L_z\right] + \left[L_y, L_x\right] L_x + L_x \left[L_y, L_x\right] \tag{175}$$

Since L_y commutes with itself and using eq. 155 we get,

$$\left[L_y, L^2\right] = 0 + i\hbar \{L_z, L_x\} - i\hbar \{L_z, L_x\} = 0 \tag{176}$$

Where here I have used the notation

$$\{A, B\} = AB + BA \tag{177}$$

and notice that

$$\{A, B\} = AB + BA = \{B, A\} \tag{178}$$

where this was not the case for the commutator, this notation corresponds to the anti-commutator. Now the same follows for $[L_z, L^2] = 0$ since it is just a permutation where we take $y \to z$, $z \to x$, and $x \to y$. This should make sense because in the classical case L^2 is invariant under rotations since it is the length squared of the angular momentum which is invariant regardless of our choice of coordinates, this also seems to work out analogously in quantum mechanics. Now to summarize we have the two following results,

$$[L_a, L_b] = i\hbar\epsilon_{abc} L_c \tag{179}$$

Here we have introduced a,b,c instead of i,j,k to avoid confusion from $i = \sqrt{-1}$, so a,b,c all go from 1 to 3.

$$\left[L_a, L^2\right] = 0,\ \text{a} = 1,2,3 \tag{180}$$

Now since L_a and L^2 commute we can choose a basis in which both L_a and L^2 are both diagonal. This is because for two commuting operators A, B suppose we diagonalize A so that we have the $A|a\rangle = a|a\rangle$ the fact that the two commute results in the following

$$\langle a|\,[A,B]\,|a'\rangle = \langle a|AB - BA|a'\rangle \tag{181}$$

$$\langle a|AB - BA|a'\rangle = \langle a|AB|a'\rangle - \langle a|BA|a'\rangle \tag{182}$$

$$\langle a|AB|a'\rangle - \langle a|BA|a'\rangle = a\langle a|B|a'\rangle - a'\langle a|B|a'\rangle \tag{183}$$

So that

$$\langle a|\,[A,B]\,|a'\rangle = (a - a')\,\langle a|B|a'\rangle = 0 \tag{184}$$

So either a = a' or $\langle a|B|a'\rangle = 0$ meaning B is also diagonalized.

So let us say $|l,m\rangle$ is our basis in which L_a and L^2 are diagonalized. So then

$$L_a|l,m\rangle = \hbar m|l,m\rangle \tag{185}$$

and

$$L^2|l,m\rangle = \hbar^2 l^2|l,m\rangle \tag{186}$$

Here the $\hbar$ have been added for proper units of angular momentum. It follows from the definition of angular momentum. Since $[L] = [rp] = m\frac{\hbar}{m} = \hbar$

Now let us pick L_a to be L_z, but remember that this choice is not required. Then eq. 185 becomes

$$L_z|l,m\rangle = \hbar m|l,m\rangle \tag{187}$$

Let us also quickly show that L_z is hermitian, remember from the set of equations 137,

$$L_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \tag{188}$$

So let us check what the adjoint of $x\frac{\partial}{\partial y}$ is and the adjoint of $y\frac{\partial}{\partial x}$ follows similarly since the coordinates are independent.

$$\int_{-\infty}^{\infty} \psi^* x \frac{\partial}{\partial y} \phi dxdydz = \int_{-\infty}^{\infty} x \frac{\partial}{\partial y} \left[\psi^* \phi\right] dxdydz - x\phi \frac{\partial}{\partial y} \psi^* dxdydz \quad (189)$$

Then using the condition that our functions $\psi, \phi \to 0$ as $x, y, z \to \infty$ in each direction we have

$$\int_{-\infty}^{\infty} \psi^* x \frac{\partial}{\partial y} \phi dxdydz = \int_{-\infty}^{\infty} \left[\psi^* \phi\right] |_{-\infty}^{\infty} xdxdz - \int_{-\infty}^{\infty} \phi \frac{\partial}{\partial y} \psi^* xdxdydz \quad (190)$$

$$\int_{-\infty}^{\infty} \psi^* x \frac{\partial}{\partial y} \phi dxdydz = -\int_{-\infty}^{\infty} \phi x \frac{\partial}{\partial y} \psi^* dxdydz \quad (191)$$

So we found that the adjoint of $x\frac{\partial}{\partial y}$ is $-x\frac{\partial}{\partial y}$, the result will be the same for $y\frac{\partial}{\partial x}$ since the coordinates are indepedent so we get that

$$L_z^\dagger = i\hbar \left(-x\frac{\partial}{\partial y} - \left(-y\frac{\partial}{\partial x}\right)\right) = -i\hbar \left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) \quad (192)$$

So then

$$L_z^\dagger = L_z \quad (193)$$

This is also true for L_x and L_y since the coordinates are independent and can also be obtained by permutations of x, y, z in L_z. So then

$$\langle l, m|L_a^2|l, m\rangle \geq 0 \quad (194)$$

Since we can write this as

$$\int_{-\infty}^{\infty} \psi_{l,m}^* L_a^\dagger L_a \psi_{l,m} dxdydz = \int_{-\infty}^{\infty} \left[L_a \psi_{l,m}\right]^* L_a \psi_{l,m} dxdydz \geq 0 \quad (195)$$

because $L_a^\dagger = L_a$.

Then it also follows that

$$\langle l, m|L_1^2 + L_2^2|l, m\rangle \geq 0 \tag{196}$$

Where $1, 2, 3$ correspond to x, y, z we can also write as this as

$$\langle l, m|L^2|l, m\rangle - \langle l, m|L_3^2|l, m\rangle \geq 0 \tag{197}$$

So then since L^2 and L_3 are diagonalized in our basis we have

$$\hbar^2 l^2 - \hbar^2 m^2 \geq 0 \tag{198}$$

or

$$l^2 \geq m^2 \tag{199}$$

so

$$|m| \leq |l| \tag{200}$$

This should make sense since the total angular momentum squared is going to be greater then or equal to the square of the projection of it onto the z axis in the classical sense. Now to move between these levels of m it will be convenient to define

$$L_+ = L_1 + iL_2 \tag{201}$$

$$L_- = L_1 - iL_2 \tag{202}$$

Notice $L_+^\dagger = L_-$ since $L_a\dagger = L_a$ and $L_-^\dagger = L_+$. Now let us work out the commutator of these new operators with our existing operators.

$$[L_3, L_+] = [L_3, L_1] + i\,[L_3, L_2] = i\hbar L_2 - i(i\hbar L_1) = \hbar L_+ \tag{203}$$

$$[L_3, L_-] = -\,[L_3, L_+]^\dagger = -\,(L_3 L_+ - L_+ L_3)^\dagger = -L_+^\dagger L_3^\dagger + L_3^\dagger L_+^\dagger = [L_3, L_-] \tag{204}$$

Since $L_3^\dagger = L_3$ and $L_+^\dagger = L_-$

$$[L_3, L_-] = -[L_3, L_+]^\dagger = -\hbar L_+^\dagger = -\hbar L_- \tag{205}$$

Then

$$[L_+, L_-] = [L_1 + iL_2, L_1 - iL_2] = [L_1, L_1] - i[L_1, L_2] + i[L_2, L_1] \tag{206}$$

$$[L_+, L_-] = -i[L_1, L_2] + i[L_2, L_1] = -2i[L_1, L_2] = -2i(i\hbar L_3) = 2\hbar L_3 \tag{207}$$

Since $[A, B] = -[B, A]$ this can be quickly shown $[A, B] = AB - BA = -(BA - AB) = -[B, A]$ and using eq. 179. Continuing with the other commutators we have

$$\left[L^2, L_+\right] = \left[L^2, L_1 + iL_2\right] = \left[L^2, L_1\right] + i\left[L^2, L_2\right] = 0 \tag{208}$$

$$\left[L^2, L_-\right] = -\left[L^2, L_+\right]^\dagger = 0 \tag{209}$$

Since $[A, B]^\dagger = (AB - BA)^\dagger = B^\dagger A^\dagger - A^\dagger B^\dagger = -[A^\dagger, B^\dagger]$ and $L_+^\dagger = L_-$ and $\left(L^2\right)^\dagger = L^2$

L^2 is trivially hermitian since L_1, L_2, L_3 are hermitian and $L^2 = L_1^2 + L_2^2 + L_3^2$.

Now let us work out how these operators L_+, L_- operate on our function $|l, m\rangle$, to do so consider

$$L^2 (L_+|l, m\rangle) = L_+L^2|l, m\rangle \tag{210}$$

Since L^2 and L_+ commute then it follows that

$$L_+\hbar^2 l^2|l, m\rangle = \hbar^2 l^2 (L_+|l, m\rangle) \tag{211}$$

So $L_+|l,m\rangle$ is also an eigenvector of L^2 with eigenvalue $\hbar l^2$ so l has remained unchanged by L_+ let us now check

$$L_3\left(L_+|l,m\rangle\right) = \left(L_+L_3 + \hbar L_+\right)|l,m\rangle \tag{212}$$

From the commutator in eq. 203, this gives us

$$L_+\hbar m|l,m\rangle + L_+\hbar|l,m\rangle = \hbar(m+1)\left(L_+|l,m\rangle\right) \tag{213}$$

So L_+ is an eigenvector of L_3 as well but with eigenvalue $\hbar(m+1)$ so we know it must be proportional to $|l,m+1\rangle$ but we do not know its normalization. Using the same process we find L_- is an eigenvector of L^2 with eigenvalue $\hbar^2 l^2$ so l remains unchanged this is trivial since L^2 doesn't care about $L_, L+$ because its commutator is the same. However as for L_3 we can work it out to see that

$$L_3\left(L_-|l,m\rangle\right) = \left(L_-L_3 - \hbar L_+\right)|l,m\rangle \tag{214}$$

$$L_-\hbar m|l,m\rangle - L_-\hbar|l,m\rangle = \hbar(m-1)\left(L_+|l,m\rangle\right) \tag{215}$$

So L_- is an eigenvector of L_3 with eigenvalue $\hbar(m-1)$ so it must be proportional to $|l,m-1\rangle$. The reason these are proportional and not equal to these states is because the constant depends on the normalization of these states.

So we have shown that L_+, L_- are indeed the raising and lowering operators for our basis. So we can now raise and lower m while keeping l fixed but remember the constraint shown in eq. 200. This says that there is a ceiling so L_+ cannot go on forever and since it is the magnitude of $|m| \leq |l|$ there is also a floor so L_- cannot go on forever as well. So then our space is finite as long as l is finite. This implies that there is a state

$$|l, m_{max}\rangle \tag{216}$$

and

$$|l, m_{min}\rangle \tag{217}$$

Which must terminate the L_+, L_- corresponding to each one. So that

$$L_+|l, m_{max}\rangle = 0 \tag{218}$$

and

$$L_-|l, m_{min}\rangle = 0 \tag{219}$$

Let us abuse this result a bit and consider the following expression

$$L_-L_+|l, m_{max}\rangle = 0 \tag{220}$$

but also

$$L_-L_+|l, m_{max}\rangle = (L_1 - iL_2)(L_1 + iL_2)|l, m_{max}\rangle \tag{221}$$

$$(L_1 - iL_2)(L_1 + iL_2)|l, m_{max}\rangle = \left(L_1^2 + L_2^2\right) + i(L_1L_2 - L_2L_1)|l, m_{max}\rangle = 0 \tag{222}$$

Then using 179 we can write this as

$$L_-L_+|l, m_{max}\rangle = \left(L_1^2 + L_2^2\right) + i(i\hbar L_3)|l, m_{max}\rangle = 0 \tag{223}$$

$$L_-L_+|l, m_{max}\rangle = \left(L^2 - L_3^2\right) - (\hbar L_3)|l, m_{max}\rangle = 0 \tag{224}$$

$$L_-L_+|l, m_{max}\rangle = \left(\hbar^2 l^2 - \left(m_{max}^2\hbar^2 + m_{max}\hbar^2\right)\right)|l, m_{max}\rangle = 0 \tag{225}$$

So then we get the result

$$l^2 = m_{max}^2 + m_{max} \tag{226}$$

Let us now consider the other end

$$L_+L_-|l, m_{min}\rangle = 0 \tag{227}$$

$$L_+L_-|l, m_{min}\rangle = \left(L_1^2 + L_2^2\right) - i(i\hbar L_3)|l, m_{min}\rangle = 0 \tag{228}$$

$$L_{-}L_{+}|l, m_{min}\rangle = \left(L^2 - L_3^2\right) + (\hbar L_3)\,|l, m_{min}\rangle = 0 \tag{229}$$

$$L_{-}L_{+}|l, m_{min}\rangle = \left(\hbar^2 l^2 - \left(m_{min}^2\hbar^2 - m_{min}\hbar^2\right)\right)|l, m_{min}\rangle = 0 \tag{230}$$

So then we get the result

$$l^2 = m_{min}^2 - m_{min} \tag{231}$$

Using these two results we can equate eq.226 and eq.231 to get the expression

$$m_{max}^2 + m_{max} = m_{min}^2 - m_{min} \tag{232}$$

Which gives us the solutions

$$m_{max} = m_{min} - 1, -m_{min} \tag{233}$$

but by choice $m_{max} \geq m_{min}$ so $m_{min} - 1$ cannot be our solution, this leaves us with

$$m_{max} = -m_{min} \tag{234}$$

So then

$$m_{max} - m_{max} \in \{\mathbb{Z} \geq 0\} \tag{235}$$

or using 234

$$2m_{max} \in \{\mathbb{Z} \geq 0\} \tag{236}$$

Let $2j \in \{\mathbb{Z} \geq 0\}$ then we have

$$2m_{max} \equiv 2j \tag{237}$$

or

$$m_{max} \equiv j;\ j = \frac{n}{2}, n \in \{\mathbb{Z} \geq 0\} \tag{238}$$

So we have then

$$l^2 = j(j+1) \tag{239}$$

Since $l^2 = m_{max}(m_{max}+1)$, then using this result it would be more useful to label our basis with j instead of l so that we now have,

$$|j, m\rangle \tag{240}$$

$$L_3|j, m\rangle = \hbar m|j, m\rangle \tag{241}$$

$$L^2|j, m\rangle = \hbar^2 j(j+1)|j, m\rangle \tag{242}$$

Where L_3 and L^2 are hermitian operators which we showed in quantum mechanics I have real eigenvalues and orthogonal eigenvectors meaning

$$\langle j_1, m_1|j_2, m_2\rangle = \delta_{j_1 j_2}\delta_{m_1 m_2} \tag{243}$$

Where here we have set the normalization such that $\langle j_1, m_1|j_1, m_1\rangle = 1$.

4.2 Experiment

Let us now discuss what the experimentalists would measure. Remember that in the classical case for central force problems we had $\frac{d\vec{L}}{dt} = 0$ so we could pick $\vec{L} = L\hat{z}, L \geq 0$. Let us now compare this to our results in wave mechanics, in wave mechanics we say we can measure L^2 with eigenvalue $\hbar^2 j(j+1)$ and L_z with eigenvalue $\hbar m$ and remember that L_z was a choice and we could have picked any other direction L_x, L_y, L_z. We just showed earlier that $m_{max} \equiv j$ so from this we can only pick L_z to be $\hbar j$ as a maximum so we cannot pick it so that $\vec{L}$ is in the direction L_z since this would require L_z^2 to have the corresponding eigenvalue $\hbar^2 j(j+1)$ but we can only maximize L_z such that L_z^2 has eigenvalue $\hbar^2 j^2$ which implies $L_z^2 \neq L^2$ for any choice of m. This is already a deviation from our expectations from classical mechanics, it serves as a cautious tale as to taking analogies as truth, it is always necessary to confirm the intuition with the math. Now the question "why can we not pick L to be completely along L_z?" naturally arises. To answer this consider the trivial problem from vector calculus $\vec{L} \times \vec{L}$ but now consider $\vec{L} = L_i \hat{i}$, i = 1,2,3 where we are using Einstein notation to sum over the i and L_i are the operators in wave mechanics. Then

$$\vec{L} \times \vec{L} = (L_2 L_3 - L_3 L_2)\,\hat{1} + (L_3 L_1 - L_1 L_3)\,\hat{2} + (L_2 L_3 - L_3 L_2)\,\hat{3} \quad (244)$$

Classically these are not operators so we get the trivial result $\vec{L} \times \vec{L} = 0$ but in wave mechanics we get the result

$$\vec{L} \times \vec{L} = i\hbar \vec{L} \quad (245)$$

Here we using again 179. To further illustrate this effect, consider a hydrogen gas, at low temperatures lets say an experimentalist can measure the angular momentum in certain state, what they measure is

$$\int_{-\infty}^{\infty} dx dy dz \psi^* O \psi = \text{Measurement of O} \quad (246)$$

Where O is an operator. So suppose they measure the angular momentum and of a state $|s\rangle$ which we write as,

$$\langle s|\vec{L}|s\rangle = \langle s|L_x|s\rangle \hat{x} + \langle s|L_y|s\rangle \hat{y} + \langle s|L_z|s\rangle \hat{z} \quad (247)$$

Let us call this measurement $\langle s|\vec{L}|s\rangle = \vec{l}$. Notice now that $\vec{l} \times \vec{l} = 0$ because $\langle s|L_i|s\rangle$ are numbers now. Now suppose we want to take the magnitude of this measurement squared,

$$\vec{l} \cdot \vec{l} = (\langle s|L_x|s\rangle)^2 + \left(\langle s|L_y|s\rangle\right)^2 + (\langle s|L_z|s\rangle)^2 \quad (248)$$

We could have also have done

$$\langle s|L_1 L_1\rangle + \langle s|L_2 L_2\rangle + \langle s|L_3 L_3\rangle \quad (249)$$

Are these two expressions the same? The answer is no, this is because of the difference in the expressions, consider

$$(\langle s|L_1|s\rangle)^2 \tag{250}$$

and

$$\langle s|L_1 L_1\rangle \tag{251}$$

The first is the measurement of L_x which is then being squared, whereas the second is the measurement of L_x^2 these need not be the same in wave mechanics. For example in quantum mechanics I we have the wave function

$$\psi(x) = \frac{1}{\sqrt{2\pi}} e^{-\frac{x^2}{2}} \tag{252}$$

It is easily shown that the measurement of x,

$$\int_{-\infty}^{\infty} \psi^*(x) x \psi(x) = 0 \tag{253}$$

since this is an odd function, whereas the measurement of x^2

$$\int_{-\infty}^{\infty} \psi^*(x) x^2 \psi(x) \neq 0 \tag{254}$$

This difference $\langle s|L_1^2|s\rangle - (\langle s|L_x|s\rangle)^2$ is called the variance of our measurement and it is of large importance in wave mechanics, this here shows that any measurement will have some variance, a profound result. This is because our wave functions are probability distributions and as such have moments which are an important quantity in statistics, useful for calculating the mean, variance, and other properties of our distribution. Now let us again consider

$$\langle jm|L^2|jm\rangle = \hbar^2 j(j+1) \tag{255}$$

and

$$\vec{l} = \langle jm|\vec{L}|jm\rangle = \hbar m \hat{z} \tag{256}$$

Since we have picked our basis to be with respect to L^2, L_z, now the variance of this quantity comes out to be

$$V = \langle jm|L^2|jm\rangle - \left(\langle jm|\vec{L}|jm\rangle\right)^2 = \hbar^2\left[j(j+1) - m^2\right] \tag{257}$$

So our variance is at a minimum when $m = m_{max} = j$ or $m = m_{min} = -j$.

$$V \geq \hbar^2\left[j(j+1) - j^2\right] = \hbar^2 j \tag{258}$$

4.3 Normalization's

Recall that we said L_+ and L_- raised and lowered our eigenvalue m respectively while keeping j fixed, eq. 213 and eq. 215. Where we showed they were eigenvectors of L^2, L_3 proportional to the $|jm+1\rangle$ and $jm-1\rangle$ states respectively. Let us now find that proportionality constant

$$L_+|jm\rangle = N_{+jm}|jm+1\rangle \tag{259}$$

$$L_-|jm\rangle = N_{-jm}|jm-1\rangle \tag{260}$$

Where N_{+jm}, N_{-jm} are our normalization constants. Also notice that we can pick $|jm\rangle \rightarrow e^{i\theta_{jm}}|jm\rangle$ since it doesn't change the orthogonality of the eigenfunctions. So we may pick N_{+jm}, N_{-jm} to be real and positive. Now consider again

$$L_+|jm\rangle = N_{+jm}|jm+1\rangle \tag{261}$$

We can transpose this equation to get

$$\langle jm|L_- = N_{+jm}\langle jm+1| \tag{262}$$

Since $L_+^\dagger = L_-$ Now let us combine eq. 261 and eq 262 to get

$$\langle jm|L_-L_+|jm\rangle = N_{+jm}\langle jm+1|N_{+jm}|jm+1\rangle \tag{263}$$

The R.H.S. is just N_{+jm}^2 since $\langle jm+1|jm+1\rangle = \delta_{j,j}\delta_{m+1,m+1} = 1$. So expanding the L.H.S. we get

$$\langle jm|L_-L_+|jm\rangle = \langle jm|\left(L_1 - iL_2\right)\left(L_1 + iL_2\right)|jm\rangle \tag{264}$$

$$\langle jm| (L_1 - iL_2)(L_1 + iL_2)|jm\rangle = \langle jm| \left(L_1^2 + L_2^2 - \hbar L_3\right)|jm\rangle \tag{265}$$

here we have used eq. 179 again to represent $[L_1, L_2]$ in terms of L_3. This can also be written as

$$\langle jm| \left(L^2 - L_3^2 - \hbar L_3\right)|jm\rangle = \hbar j(j+1) - \hbar^2 m^2 - \hbar^2 m\langle jm|jm\rangle \tag{266}$$

but $\langle jm|jm\rangle = 1$ so we have the normalization

$$N_{+jm}^2 = \hbar^2 \left[j(j+1) - m(m+1)\right] \tag{267}$$

or

$$N_{+jm} = \hbar\sqrt{j(j+1) - m(m+1)} \tag{268}$$

For N_{-jm} we can find it the same way and from earlier we showed $\langle jm|L_+L_-|jm\rangle$, starting on eq.227. So we have

$$N_{-jm} = \hbar\sqrt{j(j+1) - m(m-1)} \tag{269}$$

It is a good check also to verify our earlier result that

$$L_+|jj\rangle = 0 \tag{270}$$

and

$$L_-|jj\rangle = 0 \tag{271}$$

Let is verify the first equation

$$L_+|jj\rangle = \hbar\sqrt{j(j+1) - j(j+1)}|jj\rangle = 0 \tag{272}$$

This is trivially true so it justifies our earlier statements. Now to check the second equation

$$L_-|j-j\rangle = \hbar\sqrt{j(j+1) + j(-j-1)}|j-j\rangle = \hbar\sqrt{j^2 + j - j^2 - j}|j-j\rangle = 0 \tag{273}$$

Again justifying our earlier statements so the algebra checks out.

4.4 State Operations

We know how L^2, L_3, L_+, L_- operate on our state $|jm\rangle$ but what about L_1 and L_2. These can be found from our other operators. We can write L_1 as such

$$L_1 = \frac{L_+ + L_-}{2} = \frac{L_1 + iL_2 + L_1 - iL_2}{2} \tag{274}$$

and

$$L_2 = \frac{L_+ - L_-}{2i} = \frac{L_1 + iL_2 - L_1 + iL_2}{2i} \tag{275}$$

Now then let us apply L_1, L_2 on our state gives us

$$L_1|j,m\rangle = \frac{1}{2}\left[L_+|jm\rangle + L_-|jm\rangle\right] \tag{276}$$

$$L_1|j,m\rangle = \hbar\frac{1}{2}\left[\sqrt{j(j+1) - m(m+1)}|jm+1\rangle + \sqrt{j(j+1) - m(m-1)}|jm-1\rangle\right] \tag{277}$$

and

$$L_2|j,m\rangle = \frac{1}{2i}\left[L_+|jm\rangle - L_-|jm\rangle\right] \tag{278}$$

$$L_2|j,m\rangle = -i\hbar\frac{1}{2}\left[\sqrt{j(j+1) - m(m+1)}|jm+1\rangle - \sqrt{j(j+1) - m(m-1)}|jm-1\rangle\right] \tag{279}$$

Now let us determine the "shape" of our operators, since j, m are finite for finite j we can represent these operators as a matrix, where we can determine the elements of the matrix by applying the operators on these states, first let is consider L_3

$$\langle j_1 m_1|L_3|j_2 m_2\rangle = \hbar m_2 \delta_{j_1 j_2}\delta_{m_1 m_2} \tag{280}$$

Now what about L^2

$$\langle j_1 m_1 | L^2 | j_2 m_2 \rangle = \hbar^2 j(j+1)\delta_{j_1 j_2}\delta_{m_1 m_2} = \hbar^2 j(j+1) I \tag{281}$$

This is because we picked our basis $|j, m\rangle$ such that L_3, L^2 are diagonal. Which we see here from the delta functions to clearly be the case. Now what about L_1, L_2. Let us first consider L_1

$$\langle j_1 m_1 | L_1 | j_2 m_2 \rangle = \frac{\hbar}{2}\sqrt{j_2(j_2+1) - m_2(m_2+1)}\langle j_1 m_1 | j_2 m_2 + 1\rangle \tag{282}$$

$$+\frac{\hbar}{2}\sqrt{j_2(j_2+1) - m_2(m_2-1)}\langle j_1 m_1 | j_2 m_2 - 1\rangle \tag{283}$$

Where

$$\langle j_1 m_1 | j_2 m_2 + 1\rangle = \delta_{j_1 j_2}\delta_{m_2 m_2+1} \tag{284}$$

$$\langle j_1 m_1 | j_2 m_2 - 1\rangle = \delta_{j_1 j_2}\delta_{m_2 m_2-1} \tag{285}$$

So we will have a matrix which is off-diagonal and the elements are one row above and below the diagonal. L_2 will be similar since we have

$$\langle j_1 m_1 | L_2 | j_2 m_2 \rangle = -\frac{i\hbar}{2}\sqrt{j_2(j_2+1) - m_2(m_2+1)}\langle j_1 m_1 | j_2 m_2 + 1\rangle \tag{286}$$

$$+\frac{i\hbar}{2}\sqrt{j_2(j_2+1) - m_2(m_2-1)}\langle j_1 m_1 | j_2 m_2 - 1\rangle \tag{287}$$

Where again

$$\langle j_1 m_1 | j_2 m_2 + 1\rangle = \delta_{j_1 j_2}\delta_{m_2 m_2+1} \tag{288}$$

$$\langle j_1 m_1 | j_2 m_2 - 1\rangle = \delta_{j_1 j_2}\delta_{m_2 m_2-1} \tag{289}$$

so L_1, L_2 will have the same structure however, L_2 will have different constants. To illustrate this let us pick $j = 1$ and see what comes out from L_1, L_2, L_3, L^2

Table 1 L_1

m1/m2	-1	0	1
-1	0	$\frac{\sqrt{2}}{2}\hbar$	0
0	$\frac{\sqrt{2}}{2}\hbar$	0	$\frac{\sqrt{2}}{2}\hbar$
1	0	$\frac{\sqrt{2}}{2}\hbar$	0

Table 2 L_2

m1/m2	-1	0	1
-1	0	$i\frac{\sqrt{2}}{2}\hbar$	0
0	$-i\frac{\sqrt{2}}{2}\hbar$	0	$i\frac{\sqrt{2}}{2}\hbar$
1	0	$\frac{-i\sqrt{2}}{2}\hbar$	0

Table 3 L_3

m1/m2	-1	0	1
-1	$-\hbar$	0	0
0	0	0	0
1	0	0	$\hbar$

Table 4 L_+

m1/m2	$-\hbar$	0	0
-1	0	0	0
0	$\sqrt{2}\hbar$	0	0
1	0	$\sqrt{2}\hbar$	0

Table 5 L_-

m1/m2	-1	0	1
-1	0	$\sqrt{2}\hbar$	0
0	0	0	$\sqrt{2}\hbar$
1	0	0	0

Table 6 L^2

m1/m2	-1	0	1
-1	$2\hbar^2$	0	0
0	0	$2\hbar^2$	0
1	0	0	$2\hbar^2$

Table 7 L_1^2

m1/m2	-1	0	1
-1	$\frac{1}{2}\hbar$	0	$\frac{1}{2}\hbar$
0	0	$\hbar$	0
1	$\frac{1}{2}\hbar$	0	$\frac{1}{2}\hbar$

Table 8 L_2^2

m1/m2	-1	0	1
-1	$\frac{1}{2}\hbar$	0	$-\frac{1}{2}\hbar$
0	0	$\hbar$	0
1	$-\frac{1}{2}\hbar$	0	$\frac{1}{2}\hbar$

Table 9 L_3^2

m1/m2	-1	0	1
-1	$\hbar^2$	0	0
0	0	0	0
1	0	0	$\hbar^2$

Table 10 $L_1 L_2$

m1/m2	-1	0	1
-1	$-\hbar^2 \frac{i}{2}$	0	$\hbar^2 \frac{i}{2}$
0	0	0	0
1	$-\hbar^2 \frac{i}{2}$	0	$\hbar^2 \frac{i}{2}$

L^2 can also be calculated explicitly using the other matrices, L_1^2, L_2^2, L_3^2 and it will result in the same quantity. This is clearly seen from adding tables 7 + 8+ 9 = 6. Notice L_3^2 is diagonal but L_1^2, L_2^2 are not, this is about although $\left[L_a^2, L_a\right] = 0$ so that $\left[L^2, L_a^2\right] = 0$, $[L_3, L_a] \neq 0$ for $a \neq 3$ so that L_1^2, L_2^2 are not diagonal since we picked L_3, L^2 to be diagonal.

Let us now also check eq. 179, using the matrices $L_1 L_2, L_2 L_1$ we get 12 which is $i\hbar L_3$ as seen in table 13. L_+, L_- can also be calculated almost trivially using their equations, eq. 274 and eq. 275, the result of which is

Table 11 $L_2 L_1$

m1/m2	-1	0	1
-1	$\hbar^2 \frac{i}{2}$	0	$\hbar^2 \frac{i}{2}$
0	0	0	0
1	$-\hbar^2 \frac{i}{2}$	0	$-\hbar^2 \frac{i}{2}$

Table 12 $i\hbar L_3$

m1/m2	-1	0	1
-1	$-i\hbar^2$	0	0
0	0	0	0
1	0	0	$i\hbar^2$

shown in table 14, 15 respectively. So our commutator checks out as well. $[L_1, L_3]$ and $[L_2, L_3]$ follow since they are just permutations.

This model is called the ”Rotor Model” since expirements of this model are sensitive only to j and not m. This makes sense since j corresponds to the invariant property whereas m depends on our choice of basis. Suppose we have an eigenvector $|E\rangle$ which depends on time like $e^{-i\frac{E}{\hbar}t}$ so that at time t = 0 we have the state $C_1|E\rangle + C_2|E\rangle$ but over time our states devolve into $C_1 e^{-i\frac{E}{\hbar}t}|E\rangle + C_2 e^{-i\frac{E}{\hbar}t}|E\rangle$. This energy E depends only on j not on m so that we for our choice of basis we have $C_1|j_1 m_1\rangle + C_2|j_2 m_2\rangle$ at t= 0 and $C_1 e^{-i\frac{E(j_1)}{\hbar}t}|j_1 m_1\rangle + C_2 e^{-i\frac{E(j_2)}{\hbar}t}|j_2 m_2\rangle$ at time t. where this state is not the same as our original state unless $j_1 = j_2$.

Also the eigenvalues of L_1 can be found explicitly by considering $|\lambda I - L_1| = 0$ which gives us the expression $\lambda\left[\lambda^2 - \frac{\hbar^2}{2} - \frac{\hbar^2}{2}\right]$ so that $\lambda = -\hbar, 0, \hbar$. The same eigenvalues as L_3 this is because we could have chosen a basis in which L_1 was diagonal instead and the other two become what is called block diagonal.

4.5 Change of basis

Suppose we want to change our basis $|jm\rangle$ to another basis which still obeys the same commutator algebra of eq. 179 and eq. 180. To change basis we must introduce an operator U which only rotates the basis, this is because any dilation will disrupt the algebra. So let U be defined such that $U^\dagger U = I$ these transformations are called unitary transformations. So we want to take $L_a \rightarrow L'_a$ which we can do as such

$$L_a \rightarrow L'_a = U^\dagger L_a U \tag{290}$$

Let us now see if our commutator from eq.179 still functions the same,

$$\left[L'_a, L'_b\right] = L'_a L'_b - L'_b L'_a = U^\dagger L_a U U^\dagger L_b U - U^\dagger L_b U U^\dagger L_a U = U^\dagger\left[L_a, L_b\right] U \tag{291}$$

Here we used the properties of unitary transformations where $UU^\dagger = I$

$$U\left[L_a, L_b\right] U^\dagger = i\hbar\epsilon_{abc} U L_c U^\dagger = i\hbar\epsilon_{abc} L_c \tag{292}$$

so then

$$\left[L'_a, L'_b\right] = i\hbar\epsilon_{abc}L_c \tag{293}$$

and our commutator remains unchanged. Also by definition we said $L'_a = U^\dagger L_a U$ so we can rewrite this to get $UL'_a = UL_a$ which can is a useful property of unitary transformations. So we can pick a unitary transformation U and our algebra doesn't change. This will be helpful for understanding $\left[L^2, L_a\right] = 0$, where we made the choice of $L_a = L_z$.

Let us pick a basis in which L_1 is diagonalized to do so we need to consider the expression $L_1C = \lambda X$ Where $X = (a, b, c)^T$. However for simplicity let us omit for now the constant $\frac{\hbar}{\sqrt{2}}$. This gives us the following equations

$$b = a\lambda \tag{294}$$

$$a + c = b = b\lambda \tag{295}$$

$$b = c\lambda \tag{296}$$

Then by multiplying the second equation by λ and substituting the first and third equation we get

$$b + b = b\lambda^2 \tag{297}$$

assuming $\lambda \neq 0$ so we will need to check if this is a solution as well. Notice then from this that $\lambda = -\sqrt{2}, 0, \sqrt{2}$. Now for the $\lambda = 0$ case we simply have

$$X_0 = \frac{1}{\sqrt{2}}(1, 0, -1)^T \tag{298}$$

Where the constant in front was introduced to normalize the solution X_0. Also we have picked $b = 1$. For $\lambda = \sqrt{2}$ we have

$$X_{\sqrt{2}} = \frac{1}{\sqrt{2}}(\frac{1}{\sqrt{2}}, 1, \frac{1}{\sqrt{2}})^T \tag{299}$$

and for $\lambda = -\sqrt{2}$ we have

$$X_{-\sqrt{2}} = \frac{1}{\sqrt{2}}(-\frac{1}{\sqrt{2}}, 1, -\frac{1}{\sqrt{2}})^T \tag{300}$$

Where we also picked $b = 1$. Now our unitary transformation U is our solutions $(X_{-\sqrt{2}}, X_0, X_{\sqrt{2}})$. This is clear since $LU = UL'$ from what we found earlier. So we have now diagonalized L_1 to be $L_1' = L_3$ once we put back in the constant $\frac{\hbar}{\sqrt{2}}$. This might give the hint that the transformation permuted the different angular momenta L_1, L_2, L_3 but a quick calculation shows otherwise. Consider $U \dagger L_2 U = L_2'$.

$$L_2' = U \dagger L_2 U = \frac{\hbar}{\sqrt{2}} \begin{bmatrix} -\frac{1}{2} & \frac{1}{\sqrt{2}} & -\frac{1}{2} \\ \frac{1}{\sqrt{2}} & 0 & -\frac{1}{\sqrt{2}} \\ \frac{1}{2} & \frac{1}{\sqrt{2}} & \frac{1}{2} \end{bmatrix} \begin{bmatrix} 0 & i & 0 \\ -i & 0 & i \\ 0 & -i & 0 \end{bmatrix} \begin{bmatrix} -\frac{1}{2} & \frac{1}{\sqrt{2}} & \frac{1}{2} \\ \frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\ -\frac{1}{2} & -\frac{1}{\sqrt{2}} & \frac{1}{2} \end{bmatrix} \tag{301}$$

$$L_2' = \frac{\hbar}{\sqrt{2}} \begin{bmatrix} 0 & -i & 0 \\ i & 0 & i \\ 0 & -i & 0 \end{bmatrix} \tag{302}$$

Here it is clear that L_2' is not like any of the previous matrices L_1, L_2, L_3. however it does look similar to L_2 as seen in table 17. So instead let us consider a different transformation so that $L_2 \rightarrow L_1$ and $L_3 \rightarrow L_2$. To do so let us go back to set of eqs. 294 however, instead of picking $b = 1$ let us say $b = e^{i\theta_1}$ So that we are only introducing a phase. This tells us that U is

$$U = \begin{bmatrix} -\frac{e^{i\theta_1}}{2} & \frac{e^{i\theta_1}}{\sqrt{2}} & \frac{e^{i\theta_1}}{2} \\ \frac{e^{i\theta_1}}{\sqrt{2}} & 0 & \frac{e^{i\theta_1}}{\sqrt{2}} \\ -\frac{e^{i\theta_1}}{2} & -\frac{e^{i\theta_1}}{\sqrt{2}} & \frac{e^{i\theta_1}}{2} \end{bmatrix} \tag{303}$$

4.6 Back to Central Force Problems

To tackle the central force problem in 3-dimensions it will be useful to work out the problem in spherical coordinates when we want to so let us first define the spherical coordinates. First Let us form a plane with the $\hat{z}, \hat{r}$ unit vectors. Where $\hat{r}$ is the unit vector pointing towards our point in space. Let θ be the angle between these two unit vectors such that $0 \leq \theta \leq \pi$. Then the projection of $\vec{r}$ onto the plane perpendicular to $\hat{z}$ has magnitude $rsin\theta$ and we say that this vector lies on a plane perpendicular to the z axis which we will say is the x, y plane. Where ϕ is the angle from $\hat{x}$ to $rsin\theta$ the projection of the vector $\vec{r}$ onto the x, y plane. Then we have the components $x = rsin\theta cos\phi$, $y = rsin\theta sin\phi$, and $z = rcos\theta$. Where in our new frame we have the unit vectors $\hat{r}, \hat{\theta}, \hat{\phi}$, which form a right-handed coordinate system in $\mathbb{R}^3$

Now let us define $\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}$ in terms of these new coordinates r, θ, ϕ. To do so first notice that this same formulation can be realized as two rotations in space around the z-axis and the $\hat{\rho}$ where we say $\vec{\rho} = \vec{r}$ in x,y plane. Then we can write the relation between the two systems as such

$$\begin{bmatrix} \hat{r} \\ \hat{\theta} \\ \hat{\phi} \end{bmatrix} = \begin{bmatrix} sin\theta cos\phi & sin\theta sin\phi & cos\theta \\ cos\theta sin\phi & cos\theta sin\phi & -sin\phi \\ -sin\theta & cos\phi & 0 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} \tag{304}$$

Which we can then use to find

$$\begin{bmatrix} dx \\ dy \\ dz \end{bmatrix} = \begin{bmatrix} sin\theta cos\phi & rcos\theta cos\phi & -rsin\theta sin\phi \\ sin\theta sin\phi & rcos\theta sin\phi & rsin\theta cos\phi \\ cos\theta & -rsin\theta & 0 \end{bmatrix} \begin{bmatrix} dr \\ d\theta \\ d\phi \end{bmatrix} \tag{305}$$

But we want $dr, d\theta, d\phi$ in terms of x, y, z so let us invert the transformation matrix and to do so we must also find the determinant of the matrix however, this is simple since it is equivalent to the volume of the column vectors which forms a parallelepiped of infinitesimal volume which is $r^2 \sin\theta$. So then we have

$$\begin{bmatrix} dr \\ d\theta \\ d\phi \end{bmatrix} = \frac{1}{r^2 sin\theta} \begin{bmatrix} sin\theta cos\phi & sin\theta sin\phi & cos\theta \\ rcos\theta cos\phi & rcos\theta sin\phi & -rsin\theta \\ -rsin\theta sin\phi & rsin\theta cos\phi & 0 \end{bmatrix} \begin{bmatrix} dx \\ dy \\ dz \end{bmatrix} \tag{306}$$

Now we can do,

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial x} + \frac{\partial \theta}{\partial x}\frac{\partial}{\partial x} + \frac{\partial}{\partial x}\frac{\partial \phi}{\partial x} \tag{307}$$

$$\frac{\partial}{\partial y} = \frac{\partial r}{\partial y}\frac{\partial}{\partial y} + \frac{\partial \theta}{\partial y}\frac{\partial}{\partial y} + \frac{\partial}{\partial y}\frac{\partial \phi}{\partial y} \tag{308}$$

$$\frac{\partial}{\partial z} = \frac{\partial r}{\partial z}\frac{\partial}{\partial z} + \frac{\partial \theta}{\partial z}\frac{\partial}{\partial z} + \frac{\partial}{\partial z}\frac{\partial \phi}{\partial z} \tag{309}$$

Which we will use to get L_1, L_2, L_3 as such

$$L_1 = -i\hbar \left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y} \right) \tag{310}$$

$$L_1 = -i\hbar \left(rsin\theta sin\phi \left(cos\theta\frac{\partial}{\partial r} - \frac{1}{r}sin\theta\frac{\partial}{\partial \theta} \right) - rcos\theta \left(sin\theta sin\phi\frac{\partial}{\partial r} + \frac{1}{r}cos\theta sin\theta\frac{\partial}{\partial \theta} + \frac{cos\theta}{rsin\theta}\frac{\partial}{\partial \theta} \right) \right) \tag{311}$$

Which after simplification gives us

$$L_1 = -i\hbar \left(-sin\theta\frac{\partial}{\partial \theta} - cos\phi cot\theta\frac{\partial}{\partial \phi} \right) \tag{312}$$

or

$$L_1 = i\hbar \left(sin\theta\frac{\partial}{\partial \theta} + cos\phi cot\theta\frac{\partial}{\partial \phi} \right) \tag{313}$$

Notice how L_1 does not depend on r. L_2 can be found similarly, however since L_2 must be orthogonal to L_1 we can simply obtain L_2 by rotating our solution for L_1 by $\frac{pi}{2}$ in the ϕ direction which corresponds to our coordinates moving in $\frac{pi}{2}$ in the ϕ direction, which we found L_3 to be

$$L_2 = i\hbar \left(-cos\phi \frac{\partial}{\partial \theta} + sin\phi cot\theta \frac{\partial}{\partial \psi} \right) \tag{314}$$

L_3 can be found explicitly and from noticing that it must be orthogonal to L_1, L_2 so it must all be in the ϕ direction which makes sense since it corresponds to a rotation about z.

$$L_3 = -i\hbar \frac{\partial}{\partial \phi} \tag{315}$$

Now let us emphasis the fact that L_1, L_2, L_3 do not depend on r by stating $[f(r)\frac{\partial}{\partial r}, L_a] = 0$. Now what about L_+, L_-, let us first focus on L_+

$$L_+ = L_1 + iL_2 = i\hbar \left[(sin\phi - icos\phi) \frac{\partial}{\partial \theta} + (sin\phi + icos\phi)\, cot\theta \frac{\partial}{\partial \phi} \right] \tag{316}$$

Or

$$L_+ = \hbar \left[e^{i\phi} \frac{\partial}{\partial \theta} + ie^{i\phi} cot\theta \frac{\partial}{\partial \phi} \right] \tag{317}$$

Now we use the fact that $L_- = L_+^\dagger$ to find L_-

$$L_- = \hbar \left[e^{i\phi} \frac{\partial}{\partial \theta} - ie^{i\phi} cot\theta \frac{\partial}{\partial \phi} \right] \tag{318}$$

Now since L_a only depends on θ, ϕ we can say $|jm\rangle = Y_{jm}(\theta, \phi)$ where $R(r)$ is an integration constant since it passes through L_a, so we are able to separate r from θ, ϕ. Now let us apply L_3 on our wave function $Y_{jm}(\theta, \phi)$

$$-i\hbar \frac{\partial}{\partial \phi} Y_{jm}(\theta, \phi) = \hbar m Y_{jm}(\theta, \phi) \tag{319}$$

Solutions to this are of the form of $sin, cos, e^{i\phi}$, so we have the solution

$$Y_{jm}(\theta, \phi) = P_j^m(\theta) e^{im\phi} \tag{320}$$

Where $P_j^m(\theta)$ is an integration constant from our solution. So the variables θ, ϕ separated as well. Now notice $Y_{jm}(\theta,\phi) = Y_{jm}(\theta,\phi+2\pi)$ from our formulation of spherical coordinates. So then we require that

$$Y_{jm}(\theta,\phi) = P_j^m(\theta)e^{im\phi} = P_j^m(\theta)e^{im(\phi+2\pi)} \tag{321}$$

Meaning m must be an integer, however if m is an integer then by definition of j, half integers are not allowed so that our solutions are only those which satisfy $j \in \mathbb{Z}$. Let us now apply L_+, L_- to our solution $Y_{jm}(\theta,\phi)$, using the equations we found, eq. 317 and eq. 318.

$$L_+Y_{jm}(\theta,\phi) = \hbar\sqrt{j(j+1)-m(m+1)}P_j^m(\theta)e^{i(m+1)\phi} \tag{322}$$

$$L_+Y_{jm}(\theta,\phi) = \hbar\left[e^{i\phi}\frac{\partial}{\partial\theta} + ie^{i\phi}cot\theta\frac{\partial}{\partial\phi}\right]Y_{jm}(\theta,\phi) \tag{323}$$

Where the ϕ terms cancel out giving us the recursion relation

$$\sqrt{j(j+1)-m(m+1)}P_j^{m+1}(\theta) = \left[\frac{\partial}{\partial\theta}P_j^m(\theta) - mcot\theta P_j^m(\theta)\right] \tag{324}$$

Similarly for L_- we get

$$\sqrt{j(j+1)-m(m-1)}P_j^{m-1}(\theta) = \left[\frac{\partial}{\partial\theta}P_j^m(\theta) + mcot\theta P_j^m(\theta)\right] \tag{325}$$

Let us now solve again $L_+|jj\rangle = 0$ to find an expression for P_j^j

$$\frac{d}{d\theta}P_j^j(\theta) - jcot\theta P_j^j(\theta) = 0 \tag{326}$$

This gives us the solution $P_j^j = N_j\,[sin\theta]^j$
Now let us also solve $L_-|j-j\rangle = 0$

$$\frac{d}{d\theta}P_j^{-j}(\theta) - jcot\theta P_j^{-j}(\theta) = 0 \tag{327}$$

Notice we get the same differential equation so we have the same solution

$$P_j^{-j}(\theta) = N_j\,[sin\theta]^j = P_j^j(\theta) \tag{328}$$

Where N_j is our normalization constant which we can find using

$$\int_{\pi}^{0}\int_{2\pi}^{0} sin\theta d\phi d\theta Y_{jm}Y_{jm}^* = \int_{\pi}^{0}\int_{2\pi}^{0} sin\theta d\phi d\theta \left[N_j^2\,[sin\theta]^{2j}\right] = 1 \tag{329}$$

To solve this us rewrite this as follows

$$\int_{0}^{\pi} 2\pi sin\theta d\theta \left[N_j^2\left[-\cos^2\theta + 1\right]^j\right] = 1 \tag{330}$$

Now let $u = \cos\theta$ so $du = -\sin\theta$ giving us

$$-\int_{1}^{-1} 2\pi du \left[N_j^2\left[u^2 + 1\right]^j\right] = 1 \tag{331}$$

Now we can expand $(u^2+1)^2$ as such

$$-N_j^2\int_{1}^{-1} 2\pi du \sum_{k=0}^{j} C_k^j (-u^2)^k = 1 \tag{332}$$

Where $C_k^j = \frac{n!}{k!(n-k)!}$. Then after integrating we have

$$N_j^2 2\pi\left[2\sum_{k=0}^{j} C_k^j \frac{(-1)^k}{2k+1}\right] = 1 \tag{333}$$

Giving us the normalization

$$N_j = \left[\frac{1}{4\pi}\frac{1}{\sum_{k=0}^{j} C_k^j \frac{(-1)^k}{2k+1}}\right]^{1/2} \tag{334}$$

Now to go between states, since the operators L_+, L_- are linear we can say

$$P_j^m = H_{j,m}(\theta) N_j\,[[\sin\theta]]^j \tag{335}$$

Where $H_{j,m}(\theta)$ is some linear function in θ, for simplicity let $H_{j,m} \equiv H_{j,m}(\theta)$. Now using this solution in eq. 324 we have

$$H'_{j,m} + H_{j,m} \cot\theta [j - m] = H_{j,m+1}\sqrt{j(j+1) - m(m+1)} \tag{336}$$

Or using the lowering operator one can show

$$H'_{j,m} + H_{j,m} \cot\theta [j + m] = H_{j,m-1}\sqrt{j(j+1) - m(m-1)} \tag{337}$$

Where $H_{j,j} = H_{j,-j} = 1$.

Now let us consider the total energy operator H in spherical coordinates

$$\frac{L^2}{2mr^2} - \frac{\hbar^2}{2mr^2}\left[\left(r\frac{\partial}{\partial r}\right)^2 + r\frac{\partial}{\partial r}\right] + V(r) \tag{338}$$

Since L_a, L^2 only depend on θ, ϕ they will pass through the commutator with H meaning $[L_a, H] = 0$ and $[L^2, H] = 0$. So we have 3 commuting operators L_a, L^2, H. This is because V(r) is only a function of r. Let us then define a new basis $|E, j, m\rangle$ where

$$H|E, j, m\rangle = E|E, j, m\rangle \tag{339}$$

$$L_3|E, j, m\rangle = \hbar m|E, j, m\rangle \tag{340}$$

$$L^2|E, j, m\rangle = \hbar^2 j(j+1)|E, j, m\rangle \tag{341}$$

We can write $|E, j, m\rangle = R_{E,j}(r)Y_{j,m}(\theta, \phi)$ since we mentioned earlier $R(r)$ comes out as integration constant since L_a, L^2 only depend on ϕ, θ. Now plugging in $|E, j, m\rangle = R_{E,j}(r)Y_{j,m}(\theta, \phi)$ into $H|E, j, m\rangle = E|E, j, m\rangle$ gives us the following expression

$$\left[-\frac{\hbar^2}{2mr^2}\left[\left(r\frac{d}{dr}\right)^2 + r\frac{d}{dr} - j(j+1)\right] + V(r) - E\right] = 0 \tag{342}$$

Where we have moved E over to the left side and canceled out the ϕ, θ components. Now to solve this let us introduce $R_{Ej}(r) = \frac{U_{Ej}(r)}{r}$ this will help reduce the problem. Now plugging in $R_{Ej}(r) = \frac{U_{Ej}(r)}{r}$ into the equation above gives us the following expression

$$0 = \frac{d^2U}{dr^2} + \frac{2m}{\hbar^2}\left[E - V(r) - \frac{\hbar^2}{2m}\frac{j(j+1)}{r^2}\right]U \tag{343}$$

So in total we have the solution

$$|E, j, m\rangle = \frac{U_{Ej}(r)}{r}P_j^m(\theta)e^{im\theta} \tag{344}$$

Now let us turn to our normalization

$$\int_0^\infty \int_0^{2\pi} \int_0^\pi d\phi d\theta sin\theta r^2 \frac{U^2}{r^2}P^2 \tag{345}$$

The factor we need to worry about is the $\frac{U^2}{r^2}$ term, to make sure it does not blow up at $r \longrightarrow 0, \infty$. So let $U \approx r^p$ for small r so that

$$\int_0^\epsilon r^{2p}dr = \frac{2^{2p+1}}{2p+1}|_0^\epsilon \tag{346}$$

is finite, meaning $2p + 1 > 0$ or $p > -\frac{1}{2}$ $p = -\frac{1}{2}$ also blows up because it goes like lnr which blows up at 0. Let us now turn back to eq. 342 and plug in r^p

$$p(p-1)r^{p-2} + \frac{2m}{\hbar^2}(E - V(r))r^p - j(j+1)r^{p-2} = 0 \tag{347}$$

This means that $V(r)r^p < r^{p-2}$ so $V(r) < \frac{1}{r^2}$ because we are saying $r^p \longrightarrow 0$. Now we must also require that

$$r^{p-2}\left(p(p-1) - j(j+1)\right) = 0 \tag{348}$$

So either $p = -j$ or $p = j + 1$ but we said earlier $p > -\frac{1}{2}$ so then we have $p = j + 1$, $p = -j$ being the solution only when $j = 0$. Now if $j = 0$ then $m = 0$ and $P_0^0 = 0$ so our wave function

$$|E, 0, 0\rangle = \frac{U_{Ej}}{r} = \frac{1}{r} \tag{349}$$

So that our kinetic energy

$$-\frac{\hbar^2}{2m}\left[\nabla \cdot \nabla\right]\frac{1}{r} \tag{350}$$

becomes

$$-\frac{\hbar^2}{2m}\left[\nabla \cdot \nabla\left(\frac{1}{r}\right)\right] \tag{351}$$

This looks like the potential in electromagnetism, which we found the Laplacian of $\frac{1}{r}$ to be $\nabla \cdot \nabla\left(\frac{1}{r}\right) = 4\pi\delta^3(r - r_0)$. So to remove this case let us assume the potential has no delta function term.

So now we can further restrict $R(r)$ using the fact that $U(r) \to r^p = r^{j+1}$ giving us

$$R(r) = r^j W_{E,j}(r) \tag{352}$$

Where $U_{E,j}(r) = r^{j+1} W_{E,j}(r)$. Now let us plug in this solution to eq. 343, notice this will give us a differential equation in terms of $W_{E,j}$ removing the r^{j+1} term in $U(r)$. For simplicity let $W \equiv W_{E,j}(r)$

$$W'' + \frac{2m}{\hbar^2}\left[E - V(r)\right]W + \frac{2(j+1)}{r}W' = 0 \tag{353}$$

To further solve the problem we will need to introduce a potential so we will leave the mathematical foundation here and work on physics problems next.

4.7 The Hydrogen Atom

Let us now consider the problem of an electron orbiting a nucleus of charge $+ze$, with a potential of the form

$$V(r) = -\frac{1}{4\pi\epsilon_0}\frac{ze^2}{r} \tag{354}$$

We know that the mass of the electron is much smaller then the mass of the nucleus so we can say that the mass of the system $m \approx m_e$. Where m_e is the mass of the electron. Now let us model this problem using quantum mechanics and the mathematics we have worked out. Since $V \equiv V(r)$ we know we can diagonalize the Hamiltonian of this system simultaneously with L^2 and L_i^2, where we pick $L_i = L_3$ for convenience since we have already worked out the mathematics for this case and we can achieve the others from a unitary transformation. So we will denote the wave functions as $|E, j, m\rangle$. There is nothing left for us to work out in terms of the angular components since we have worked this out already so let us consider the radial component which we had shown in the last section is reduced to the differential equation shown in eq. 353. Where $R_{E,j} = r^j W_{E,j}(r)$. Now then let us introduce our potential and also look for natural units of the problem, to do so we will say $r = ub$. Also now let us introduce a new function $\chi(u)$ such that $\chi \equiv \chi_{E,j}(u) \equiv W_{E,j}(r = ub)$. We are allowed to do this since all this will change is a factor in the normalization of the functions proportional to b. This gives us the differential equation

$$\frac{1}{b^2}\chi'' + \frac{2(j+1)}{b^2 u}\chi' + \frac{2m_e}{\hbar^2}(E + \frac{ze^2}{4\pi\epsilon_0}\frac{1}{bu})\chi = 0 \tag{355}$$

This equation suggests that $\frac{1}{b} = \frac{ze^2}{4\pi\epsilon_0}\frac{2m_e}{\hbar^2}$ or

$$b = \frac{4\pi\epsilon_0}{ze^2}\frac{\hbar^2}{2m_e} \tag{356}$$

Let us now check the units of b, since we said $r = bu$ we should expect b to have units of length $[m]$.

$$[b] = [\frac{4\pi\epsilon_0}{ze^2}\frac{\hbar^2}{2m_e}] = \frac{[\epsilon_0]}{C^2}\frac{J^2 s^2}{kg} \tag{357}$$

To find the units of ϵ_0 recall the potential equation from eq. 353 and that $[V] = J$ From this we can work out

$$[V] = J = \frac{C^2}{m[\epsilon_0]} \tag{358}$$

From this we can solve for $[\epsilon_0]$ and we get

$$[\epsilon_0] = \frac{C^2}{Jm} \tag{359}$$

Plugging this back into eq.357 we get

$$[b] = \frac{Js^2}{mkg} = m \tag{360}$$

Since $[J] = \frac{kgm^2}{s^2}$. So we get units of length as expected. Now let us try to put our energy E in terms of these units as well. To do so we will multiply eq. 355 by b^2. This gives us

$$\chi'' + \frac{2(j+1)}{u}\chi' + \frac{2m_e}{\hbar^2}(b^2E + \frac{ze^2}{4\pi\epsilon_0}\frac{b}{u})\chi = 0 \tag{361}$$

So it looks natural to choose the natural units of energy as

$$E = \frac{\hbar^2}{2mb^2}(-\alpha) \tag{362}$$

Where the negative sign is to make the problem look nicer in future steps. Let us make sure again that the we have the correct units of energy.

$$[E] = \frac{J^2s^2}{kgm^2} = J \tag{363}$$

So the units are correct. Now substituting these values in eq. 361 we have

$$\chi'' + \frac{2(j+1)}{u}\chi' + (-\alpha + \frac{1}{u})\chi = 0 \tag{364}$$

Now let us look at the limiting case where $u \to \infty$. This gives us the equations

$$\chi'' - \alpha\chi = 0 \tag{365}$$

For u near infinity. Solutions to this equation are of the form

$$\chi = e^{\pm\sqrt{\alpha}u} \tag{366}$$

However recall that we require $\chi \to 0$ as $u \to 0$. So we do not have the positive solution meaning

$$\chi = e^{-\sqrt{\alpha}u} \tag{367}$$

Also from this we get the condition that $\alpha \geq 0$. Now to clean up the results let

$$E = \frac{\hbar^2}{2mb^2}(-\alpha^2) \tag{368}$$

This will give us

$$\chi(u \to \infty) = e^{-\alpha u} \tag{369}$$

This will also effect eq. 364 giving us

$$\chi'' + \frac{2(j+1)}{u}\chi' + (-\alpha^2 + \frac{1}{u})\chi = 0 \tag{370}$$

So Let $\chi_{E,j}(u) = R_{E,j}(u)e^{-\alpha u}$. Now eq.369 implies that $R(u)$ for large n must be smaller then $e^{\alpha u}$ since we require this term to dominate at large u. Meaning

$$\lim_{u \to \infty} R(u)e^{-\alpha u} = e^{-\alpha u} \tag{371}$$

We will suppose that $R(u)$ is infinitely differentiable so that we may express it as a power series of the form

$$R(u) = \sum_{k=0}^{P} C_k u^k \tag{372}$$

Where P is the upper limit since eq. 372 requires $R(u)$ to be finite. This can be shown by Taylor expanding $e^{-\alpha u} = 1 - \alpha x + \ldots = \sum_{k=0}^{\infty} \frac{(-\alpha u)^k}{k!}$. So $R(u)$ is a finite polynomial of order P. Let us now introduce the solution $\chi_{E,j}(u) = R_{E,j}(u)e^{-\alpha u}$ into eq. 364. Again we will let $R \equiv R_{E,j}(u)$.

$$uR'' + 2((j+1) - \alpha u)R' + \frac{1}{u}\left[1 - 2\alpha(j+1)\right] R = 0 \tag{373}$$

And let us introduce eq. 372 for R. To do this it will be useful to write the derivatives of R

$$R'(u) = \sum_{k=1}^{P} kC_k u^{k-1} = \sum_{k=0}^{P} (k+1)C_{k+1}u^k \tag{374}$$

$$R''(u) = \sum_{k=2}^{P} k(k-1)C_k u^{k-2} = \sum_{k=0}^{P} (k+1)kC_{k+1}u^{k-1} \tag{375}$$

Here we have rewritten these for convenience but all forms are equivalent. Now substituting these into eq. 375 we get

$$\sum_{k=0}^{P} C_{k+1}\left(k(k+1) + 2(j+1)(k+1)\right) C_k \left(1 - 2\alpha(k+j+1)\right) u^k = 0 \tag{376}$$

Here I have shifted the index of the final term so that all terms are of kth order. Now since this equation must be true for all u we require

$$C_{k+1} = \frac{2\alpha(k+j+1) - 1}{(k+1)\left(k + 2(j+1)\right))} \tag{377}$$

with $C_0 = 1$. Now recall that we require $R_{E,j}(u)$ to be finite meaning it must terminate at some integer P. This means

$$C_{P+1} = 0 = \frac{2\alpha(P+j+1) - 1}{(k+1)\left(k + 2(j+1)\right))} \tag{378}$$

Or

$$2\alpha(P+j+1) - 1 = 0 \tag{379}$$

Giving us the condition

$$\alpha = \frac{1}{2(P+j+1)} \tag{380}$$

So we have 3 degrees of freedom. Traditionally we let $n = (P + j + 1)$ so that

$$\alpha = \frac{1}{2n} \tag{381}$$

Giving us the quantum numbers n, j, m corresponding to our 3 degrees of freedom. As such we will stick with this notation. So we have solved the problem for the hydrogen atom where our solution was

$$|n, j, m\rangle = \psi_{n,j,m}(r, \theta, \phi) = R_{n,j}(r)Y_{j,m}(\theta, \phi) \tag{382}$$

Also using the commutators $[H, L_z] = 0$, $[H, L^2] = 0$, $[L^2, L_z] = 0$ we can show that as follows

$$\langle n_1, j_1, m_1|[H, L_z]|n_2, j_2, m_2\rangle = \langle n_1, j_1, m_1|(E_{n_1} - E_{n_2})L_z|n_2, j_2, m_2\rangle \tag{383}$$

So we have

$$\langle n_1, j_1, m_1|(E_{n_1} - E_{n_2})L_z|n_2, j_2, m_2\rangle \propto \delta_{n_1,n_2} \tag{384}$$

and

$$\langle n_1, j_1, m_1|[H, L_z]|n_2, j_2, m_2\rangle = \langle n_1, j_1, m_1|\hbar(m_1 - m_2)H|n_2, j_2, m_2\rangle \tag{385}$$

so

$$\langle n_1, j_1, m_1|\hbar(m_1 - m_2)H|n_2, j_2, m_2\rangle \propto \delta_{n_1,n_2}\delta_{m_1,m_2} \tag{386}$$

Similarly

$$\langle n_1, j_1, m_1|[H, L^2]|n_2, j_2, m_2\rangle = \langle n_1, j_1, m_1|\hbar^2(j_1(j_1{+}1){-}j_2(j_2{+}1))H|n_2, j_2, m_2\rangle \tag{387}$$

so

$$\langle n_1, j_1, m_1|\hbar^2(j_1(j_1 + 1) - j_2(j_2 + 1))H|n_2, j_2, m_2\rangle \propto \delta_{j_1,j_2} \tag{388}$$

Giving us

$$\langle n_1, j_1, m_1|n_2, j_2, m_2\rangle = \delta_{n_1,n_2}\delta_{j_1,j_2}\delta_{m_1,m_2} \tag{389}$$

Now for our solutions since we want to work in natural units let $R_{n,j} = r^j W_{E,j}(r) \equiv \Omega_{n,j}(u)$ so that

$$\Omega_{n,j}(u) = u^j \chi(u) = u^j e^{-\alpha u} \sum_{k=0}^{P} C_k u^k \tag{390}$$

Using this let $\psi_{n,j,m}(r,\theta,\phi) \equiv \tilde{\psi}_{n,j,m}(u,\theta,\phi)$ this is fine since it will just change the normalization by a factor of b. So we now have

$$\tilde{\psi}_{n,j,m}(u,\theta,\phi) = \Omega_{n,j}(u) Y_{j,m}(\theta,\phi) \tag{391}$$

Let us quickly find this factor so we may quickly transform between ψ and $\tilde{\psi}$, i will drop the quantum numbers for brevity. Suppose $\tilde{\psi}$ is normalized meaning

$$\int_{-\infty}^{\infty} \tilde{\psi}^* \tilde{\psi} u^2 \sin\theta du d\theta d\phi = 1 \tag{392}$$

Then using the relation $r = bu$ we have $dr = bdu$ Using this we can transform the integral from u to r.

$$\frac{1}{b^3} \int_{-\infty}^{\infty} \tilde{\psi}^* \tilde{\psi} r^2 \sin\theta dr d\theta d\phi = 1 \tag{393}$$

and since $\psi_{n,j,m}(r,\theta,\phi) \equiv \tilde{\psi}_{n,j,m}(u,\theta,\phi)$ we have

$$\frac{1}{b^3} \int_{-\infty}^{\infty} \psi^* \psi r^2 \sin\theta dr d\theta d\phi = 1 \tag{394}$$

Meaning that if we want to normalize with respect to r instead we just need to include a factor N_t which I denote the normalization of the transition from u to r

$$N_t = \frac{1}{b^{3/2}} \tag{395}$$

So we will work with $\tilde{\psi}$ which is normalized with respect to u, I will denote this to be in u-space and to go to r-space where ψ is normalized with respect to r instead we just use the relation

$$\psi = \frac{1}{b^{3/2}}\tilde{\psi} \tag{396}$$

Now let us work out the normalization of Ω, since we were able to separate r, θ, ϕ we had the choice to normalize them how we wanted, we have normalized θ, ϕ already and found N_j for those in eq.**??** so we only need to worry about the u component now,

$$1 = N^2(u)_{n,j}\int_0^\infty u^2 du\Omega^2 = \int_0^\infty duu^2u^{2j}e^{-\frac{u}{n}}\left(\sum_{k=0}^{P} C_k u^k\right)^2 \tag{397}$$

Here I have used $\alpha = \frac{1}{2n}$ which we found earlier and I denoted the normalization as $N^2(u)_{n,j}$ just to emphasis that it is the normalization with respect to u. So now we have

$$1 = N^2(u)_{n,j}\int_0^\infty duu^{2(j+1)}e^{-\frac{u}{n}}\left(\sum_{k=0}^{P} C_k u^k\right)^2 \tag{398}$$

Now it will be useful to use the gamma function which is defined as such

$$\Gamma(s) = \int_0^\infty t^{s-1}e^{-s}ds \tag{399}$$

From this we can see that by doing a change of variables $t = \frac{u}{n}$ $dt = \frac{du}{n}$ we have from eq.398

$$1 = N^2(u)_{n,j}n^{2(j+1)+1}\int_0^\infty t^{2(j+1)}e^{-t}\left(\sum_{k=0}^{P} C_k (nt)^k\right)^2 \tag{400}$$

Now we can find the normalization to be

$$N(u)_{n,j} = \left(\sum_{l=0}^{P}\sum_{k=0}^{P} C_l C_k n^{l+k}\Gamma\left(2(j+1)+1+k+l\right)\right)^{-1/2}\frac{1}{\sqrt{n^{2(j+1)+1}}} \tag{401}$$

So we have the wave equation

$$\tilde{\psi}_{n,j,m}(u,\theta,\phi) = N_{n,j}(u)N_j(\theta,\phi)u^j e^{\frac{u}{2n}} \sum_{k=0}^{P} \left(C_k u^k\right) H_{j,m}(\theta) [\sin\theta]^j e^{im\phi} \tag{402}$$

Where

$$C_{k+1} = \frac{\frac{1}{n}(k+j+1)-1}{(k+1)\left(k+2(j+1)\right)} C_k \tag{403}$$

$$N(u)_{n,j} = \left(\sum_{l=0}^{P}\sum_{k=0}^{P} C_l C_k n^{l+k} \Gamma\left(2(j+1)+1+k+l\right)\right)^{-1/2} \frac{1}{\sqrt{n^{2(j+1)+1}}} \tag{404}$$

$$N_j(\theta,\phi) = \left[\frac{1}{4\pi}\frac{1}{\sum_{k=0}^{j} C_k^j \frac{(-1)^k}{2k+1}}\right]^{1/2} \tag{405}$$

Where I let $N_j \equiv N_j(\theta,\phi)$ to denote that this is the normalization of the θ, ϕ part of our wave equation.

Let us also now rewrite our energy in terms of our quantum number n. Recall that we had

$$E = \frac{\hbar^2}{2mb^2}(-\alpha^2) \tag{406}$$

but knowing b and $\alpha = \frac{1}{2n}$ and letting $z = 1$ for the case of the hydrogen atom we can now write this as

$$E_n = -\frac{z^2 e^4 m_e}{(4\pi\epsilon_0\hbar)^2}\frac{1}{2n^2} \tag{407}$$

We can also write this as

$$E_n \approx -\frac{13.6067e}{n^2} \tag{408}$$

Where we found b to be

$$b = 2.6459 \cdot 10^{-11} \tag{409}$$

Let us look at what u gives us maximal probability in the ground state $|1, 0, 0\rangle$. To do so we just need to consider the probability of the radial component of our wave function, meaning we have integrated over θ, ϕ giving us

$$P(u) = \frac{1}{2}u^2 e^{-u} \tag{410}$$

Where the $\frac{1}{2}$ comes from $N_{n,j}^2(u) = \frac{1}{2}$. This corresponds to the probability of finding the electron in a shell centered at the nucleus of thickness dr. Now to find where it is most probable to find the electron we must find u such that $\frac{\mathrm{d}P(u)}{\mathrm{d}u} = 0$

$$\frac{\mathrm{d}P(u)}{\mathrm{d}u} = ue^{-u} - \frac{1}{2}u^2 e^{-u} = 0 \tag{411}$$

or

$$\left(1 - \frac{1}{2}u\right) ue^{-u} = 0 \tag{412}$$

So we have the point $u = 2, 0$ but $u = 0$ cannot be the solution since we know the function increases from $u = 0$ so $u = 2$ or $r = bu$ must be where the electron is most likely to be found. This is usually whats called the Bohr radius and is denoted by $a_0 = 2b = 5.2918 \cdot 10^{-11}m$ where $r = a_0$.

Let us now consider the average or expected position of the electron for the ground state, $< u >$. Since this only on u we can integrate over the θ and ϕ parts and are left only to consider

$$< u >= \int_0^\infty \frac{1}{2}u^3 e^{-u} du = 3 \tag{413}$$

So we find that the average position of the electron in the ground state is $r = 3b$ or $u = 3$ in natural units. Notice that this is not the same as the most likely position to find the electron which we found to be $r = 2b$.

5 Dirac Equation

Dirac was interested in taking the square root of the Klein-Gordan wave equation, something which at the time seemed meaningless, however we will work through the mathematics which Dirac considered and show that it indeed an interesting problem. To begin considered the relativistic energy of a particle

$$E^2 = p^2c^2 + m^2c^4 \tag{414}$$

Where

$$E = c\sqrt{p^2 + m^2c^2} \tag{415}$$

Since we require $0 \leq E$. For small momentum this is the classical energy equation

$$E = mc^2 + \frac{p^2}{2m} + \ldots \tag{416}$$

Now we start with the one dimensional Klein-Gordan Wave equation which satisfies eq. 414

$$\left[-\hbar^2\frac{\partial^2}{\partial t^2} = -\hbar^2c^2\frac{\partial^2}{\partial x^2} + m^2c^4\right]\psi(x,t) \tag{417}$$

Dirac said consider the square root of this equation

$$i\hbar\frac{\partial}{\partial t}\psi(x,t) = \left(\sqrt{-\hbar^2c^2\frac{\partial^2}{\partial x^2} + m^2c^4}\right)\psi(x,t) \tag{418}$$

To consider what type of operators satisfy this we must consider

$$\left(\alpha\frac{\partial}{\partial x}+\beta\right)^2=-\hbar^2c^2\frac{\partial^2}{\partial x^2}+m^2c^4 \tag{419}$$

Where once we expand the L.H.S. we get

$$\alpha^2\frac{\partial^2}{\partial x^2}+\beta^2+\alpha\beta\frac{\partial}{\partial x}+\beta\alpha\frac{\partial}{\partial x}+\alpha\frac{\partial\alpha}{\partial x}\frac{\partial}{\partial x}+\alpha\frac{\partial\beta}{\partial x} \tag{420}$$

Now to understand the solution which Dirac proposed for this let us go back to the central force problem solutions that we found. Recall that we had shown that j had to be an integer from the periodicity of $e^{im\phi}$, suppose we ignored this for now and worked out the operators L^2, L_3, L_+, L_- for this case. Let us denote the angular solutions by $|j,m\rangle$ as before where $j=\frac{1}{2}$ so we have $m=-\frac{1}{2},\frac{1}{2}$. Then we have

$$L^2|\frac{1}{2},\pm\frac{1}{2}\rangle=\frac{3\hbar^2}{4}|\frac{1}{2},\pm\frac{1}{2}\rangle \tag{421}$$

$$L_3|\frac{1}{2},\pm\frac{1}{2}\rangle=\pm\frac{\hbar}{2}|\frac{1}{2},\pm\frac{1}{2}\rangle \tag{422}$$

$$L_+|\frac{1}{2},\frac{1}{2}\rangle=\hbar|\frac{1}{2},\frac{1}{2}\rangle \tag{423}$$

$$L_-|\frac{1}{2},-\frac{1}{2}\rangle=\hbar|\frac{1}{2},-\frac{1}{2}\rangle \tag{424}$$

These follow from the algebra of the group which we showed earlier from eq. 148. Now let us look at the matrix representation of these states.

Table 13 L_3

m1/m2	-1/2	1/2
-1/2	$-\frac{\hbar}{2}$	0
1/2	0	$\frac{\hbar}{2}$

Table 14 L_+

m1/m2	-1/2	1/2
-1/2	0	0
1/2	$\hbar$	0

Where $L_1 = \frac{L_+ + L_-}{2}$ and $L_2 = \frac{L_+ - L_-}{2i}$ from the definition of L_+, L_-.

Table 15 L_-

m1/m2	-1/2	1/2
-1/2	0	$\hbar$
1/2	0	0

Table 16 L_1

m1/m2	-1/2	1/2
-1/2	0	$\frac{\hbar}{2}$
1/2	$\frac{\hbar}{2}$	0

Table 17 L_2

m1/m2	-1/2	1/2
-1/2	0	$i\frac{\hbar}{2}$
1/2	$-i\frac{\hbar}{2}$	0

Now from these we can define a new matrix σ_a where $L_a = \frac{\hbar}{2}\sigma_a$ and since from eq. 148 we have the commutator of L_a, L_b we can find the commutator of σ_a, σ_b

$$\frac{\hbar^2}{4}\left[\sigma_a, sigma_b\right] = i\frac{\hbar^2}{2}\epsilon_{abc}\sigma_c \tag{425}$$

or

$$[\sigma_a, sigma_b] = 2i\epsilon_{abc}\sigma_c \tag{426}$$

Notice how $\sigma_a^2 = 1_{2x2}$ from the tables above. We can also see from these two that

$$\sigma_a\sigma_b = i\epsilon_{abc} + \delta_{ab}1_{2x2} \tag{427}$$

Meaning

$$\{\sigma_a, \sigma_b\} = 2\delta_{ab} \tag{428}$$

Where $\{A, B\} = AB + BA$ denotes the anti-commutator of A, B. There is a further generalization of this called Clifford Algebra, where Clifford asked the question, what about matrices which satisfy

$$\gamma_a, \gamma_b = 2\delta_{ab} \tag{429}$$

This generalizes these properties for any arbitrary space-time dimensions. However we we will only work with the algebra of σ_a which corresponds to $j = 1/2$. Again the problem we are interested in are operators which satisfy

$$(\not{D})^2 = -\hbar^2 \frac{\partial^2}{\partial t^2} + \hbar^2 c^2 \frac{\partial^2}{\partial x^2} \tag{430}$$

Recall that this came from $E^2 = p^2c^2 + m^2c^4$. Now let

$$(\not{D} = i\hbar\gamma_0 \frac{\partial}{\partial t} - i\hbar c\gamma_1 \frac{\partial}{\partial x} \tag{431}$$

From this we have $(\not{D})^2$

$$(\not{D})^2 = -\hbar^2\gamma_0^2 \frac{\partial^2}{\partial t^2} - \hbar^2 c^2 \gamma_1^2 \frac{\partial^2}{\partial x^2} + \hbar^2 c\gamma_1\gamma_0 \frac{\partial}{\partial x}\frac{\partial}{\partial t} + \hbar^2 c\gamma_0\gamma_1 \frac{\partial}{\partial t}\frac{\partial}{\partial x} \tag{432}$$

Meaning that

$$\gamma_0 = 1_{2x2} \tag{433}$$

$$\gamma_i^2 = -1_{2x2}, i \neq 0 \tag{434}$$

and

$$\{\gamma_0, \gamma_1\} = 0 \tag{435}$$

From what we worked out before this looks just like σ_a. So let $\gamma_0 = \sigma_1$ and $\gamma_1 = i\sigma_2$. Now we have $\not{D}$ which we need to understand however before we do let us now consider the problem in 2 space 1 time dimensions. This is just

$$\not{D}_{2,1}^2 = \not{D}_{1,1}^2 + \hbar^2 c^2 \frac{\partial^2}{\partial y^2} \tag{436}$$

In this case we now require

$$\gamma_0 = 1_{2x2} \tag{437}$$

$$\gamma_i^2 = -1_{2x2}, i \neq 0 \tag{438}$$

$$\{\gamma_i, \gamma_j\} = 0, i \neq j \tag{439}$$

So we must now introduce σ_3, giving us $\gamma_2 = i\sigma_3$. Now let us consider the case of 3 space and 1 time dimensions

$$\not{D}_{3,1}^2 = \not{D}_{2,1}^2 + \hbar^2 c^2 \frac{\partial^2}{\partial z^2} \tag{440}$$

Which gives us the requirements

$$\gamma_0 = 1_{2x2} \tag{441}$$

$$\gamma_i^2 = -1_{2x2}, i \neq 0 \tag{442}$$

$$\{\gamma_i, \gamma_j\} = 0, i \neq j \tag{443}$$

However we do not have any more σ left to choose from. The solution to this is to increase the size of the matrix so that

$$\gamma_0 = \begin{bmatrix} 1_{2x2} & 0 \\ 0 & -1_{2x2} \end{bmatrix} \tag{444}$$

$$\gamma_i = \begin{bmatrix} 0 & -\sigma_i \\ \sigma_i & 0 \end{bmatrix} \tag{445}$$

This satisfies the algebra required because σ satisfies the algebra, this is just an extension to 3 space 1 time. Now we have

$$E^2 - p^2c^2 = m^2c^4 \tag{446}$$

or

$$\not{D}^2 = m^2c^4 \tag{447}$$

Meaning we have two solutions

$$\not{D} = \pm mc^2 \tag{448}$$

For now let us pick the positive solution. We will be working with what is called the Dirac wave equation however once it was fully understood it was called Dirac field theory. Let us now solve this wave equation $\not{D} - mc^2 = 0$

$$(\not{D} - mc^2)\Psi_{4x1} = \begin{bmatrix} i\hbar\frac{\partial}{\partial t} - mc^2 & i\hbar c\sum_{i=1}^{3}\left(\sigma_i\frac{\partial}{\partial x_i}\right) \\ -i\hbar c\sum_{i=1}^{3}\left(\sigma_i\frac{\partial}{\partial x_i}\right) & -i\hbar\frac{\partial}{\partial t} - mc^2 \end{bmatrix}\Psi_{4x1} = 0 \tag{449}$$

Where now Ψ has 4 components and seems like a vector as opposed to a scalar which is what we had before. Notice how for this to not be a trivial solution we require the determinant of our matrix to be 0 but this is just

$$m^2c^4 - \hbar^2c^2\nabla^2 + \hbar^2\frac{\partial^2}{\partial t^2} = 0 \tag{450}$$

but this is just

$$\not{D}^2 = m^2c^4 \tag{451}$$

Which is the condition that $E^2 = p^2c^2 + m^2c^4$, so these solutions satisfy conservation of energy. Now then will have to require $\not{D}$ to be hermitian so that it has real solutions. As such we have to consider of $\not{D}^\dagger = \not{D}$. Since time acts as space-time component we know

$$\frac{\partial}{\partial x_\mu}^\dagger = -\frac{\partial}{\partial x_\mu}, \mu = 0, 1, 2, 3 \tag{452}$$

Where $\mu = 0$ corresponds to the time component. We also know that $\sigma_i^\dagger = \sigma_i$, $\gamma_0^\dagger = \gamma_0$ and $\gamma_i^\dagger = -\gamma_i$ so then writing $\not{D}$ in terms of these we have

$$\not{D} = i\hbar\gamma_0\frac{\partial}{\partial t} - i\hbar c(\gamma_j\frac{\partial}{\partial x_j}) \tag{453}$$

Where summation over j is implied. The adjoint of this then becomes

$$\not{D}^{\dagger} = i\hbar\gamma_0\frac{\partial}{\partial t} + i\hbar c(\gamma_j\frac{\partial}{\partial x_j}) \tag{454}$$

This is clearly not hermitian so to make our solution hermitian we will need to consider

$$\not{D}^{\dagger} = \gamma_\mu \not{D} \gamma_\mu \tag{455}$$

Where we will pick $\mu = 0$. This is because $\gamma_0^3 = \gamma_0$ and $\gamma_0\gamma_i\gamma_0 = -\gamma_i$ from the algebra of the group. Now then we have

$$\not{D}\gamma_0 = \gamma_0\not{D}^{\dagger} \tag{456}$$

or

$$\gamma_0\not{D} = \not{D}^{\dagger}\gamma_0 \tag{457}$$

So then we can have $\gamma_0\not{D}$ or $\not{D}\gamma_0$ being our hermitian operator.

Let us now go back and solve eq. 449 with γ_0 now. We will pick $\gamma_0\not{D}$ as our hermitian operator. This gives us

$$(\gamma_0\not{D} - mc^2)\Psi_{4x1} = \begin{bmatrix} I & 0 \\ 0 & -I \end{bmatrix} \begin{bmatrix} i\hbar\frac{\partial}{\partial t} - mc^2 & i\hbar c\sum_{i=1}^{3}\left(\sigma_i\frac{\partial}{\partial x_i}\right) \\ -i\hbar c\sum_{i=1}^{3}\left(\sigma_i\frac{\partial}{\partial x_i}\right) & -i\hbar\frac{\partial}{\partial t} - mc^2 \end{bmatrix}\Psi_{4x1} = 0 \tag{458}$$

and we will assume solutions of the form

$$\Psi = \begin{bmatrix} \psi_L \\ \psi_R \end{bmatrix} \tag{459}$$

This gives us the two equations

$$I(i\hbar\frac{\partial}{\partial t} - mc^2)\psi_L + i\hbar c(\sigma_i\frac{\partial}{\partial x_i})\psi_R = 0 \tag{460}$$

$$i\hbar c(\sigma_i \frac{\partial}{\partial x_i})\psi_L + I(i\hbar\frac{\partial}{\partial t} - mc^2)\psi_R = 0 \tag{461}$$

4 coupled equations in total. We know from wave mechanics that we should expect solutions of the form

$$\psi_{L,R} = \chi_{L,R} e^{\frac{i}{\hbar}(p_i x_i - Et)} \tag{462}$$

Plugging in these solutions into our two equations give us the relations

$$(E - mc^2)\chi_L = c(\sigma_i p_i)\chi_R \tag{463}$$

$$(E + mc^2)\chi_R = c(\sigma_i p_i)\chi_L \tag{464}$$

Which we can solve to get the equation

$$(E^2 - m^2c^4)\chi_R = p^2c^2\chi_R \tag{465}$$

Then from this equation in matrix form we have

$$I_{2x2}(E^2 - m^2c^4 - p^2c^2)\begin{bmatrix}\chi_{R_1}\\ \chi_{R_2}\end{bmatrix} = 0 \tag{466}$$

So from this we can also see that these solutions require $E^2 = c^2p^2 + m^2c^4$. Now χ_{R_1}, χ_{R_1} can be anything since we have two degrees of freedom. So we ca pick the solutions

$$\chi_R = \begin{bmatrix}1\\0\end{bmatrix}, \begin{bmatrix}0\\1\end{bmatrix} \tag{467}$$

Also remember that these must have a connection to $j = 1/2$ since we started with its corresponding group. Using eq. 463 we can get the components of χ_L as well. So we only have two independent solutions for positive and negative energy. Let us call

$$E = \sqrt{m^2c^4 + c^2p^2} \tag{468}$$

the "physical" solution since this is what we would expect and

$$E = -\sqrt{m^2c^4 + c^2p^2} \tag{469}$$

the ”nonphysical” solution. It is also worth considering when $E = 0$ but this corresponds to massless particles at rest since $p = 0$ and $m = 0$ so this is truly a nonphysical case. Let us consider the case where $E > 0$ first for this case we have the solutions

$$\chi_L = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \tag{470}$$

$$\chi_R = \frac{1}{E + mc^2} \begin{bmatrix} -cp_3 \\ cp_1 - icp_2 \end{bmatrix} \tag{471}$$

and

$$\chi_L = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \tag{472}$$

$$\chi_R = \frac{1}{E + mc^2} \begin{bmatrix} cp_1 + icp_2 \\ cp_3 \end{bmatrix} \tag{473}$$

For negative energy $E < 0$ we have the solutions

$$\chi_R = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \tag{474}$$

$$\chi_L = \frac{1}{E - mc^2} \begin{bmatrix} -cp_3 \\ cp_1 - icp_2 \end{bmatrix} \tag{475}$$

and

$$\chi_R = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \tag{476}$$

$$\chi_L = \frac{1}{E - mc^2} \begin{bmatrix} cp_1 + icp_2 \\ cp_3 \end{bmatrix} \tag{477}$$

Notice that solution 1 and 2 for both cases are orthogonal with one another. Now let us normalize these but it is also worth thinking about how

γ_0 changes this since we require $\gamma_0 \not{D}$ to be our hermitian operator. The normalization we get is $\sqrt{\frac{|E|+mc^2}{2|E|}}$ when we don't consider the effect of γ_0 and $|E|$ is the magnitude of the energy. Let us now write our solutions with this normalization and also put the solutions in terms of $|E|$. This gives us the solutions for positive energy $E > 0$

$$\chi_L = \sqrt{\frac{|E|+mc^2}{2|E|}} \begin{bmatrix} 1 \\ 0 \end{bmatrix} \tag{478}$$

$$\chi_R = \sqrt{\frac{|E|+mc^2}{2|E|}} \frac{1}{|E|+mc^2} \begin{bmatrix} -cp_3 \\ cp_1 - icp_2 \end{bmatrix} \tag{479}$$

and

$$\chi_L = \sqrt{\frac{|E|+mc^2}{2|E|}} \begin{bmatrix} 0 \\ 1 \end{bmatrix} \tag{480}$$

$$\chi_R = \sqrt{\frac{|E|+mc^2}{2|E|}} \frac{1}{|E|+mc^2} \begin{bmatrix} cp_1 + icp_2 \\ cp_3 \end{bmatrix} \tag{481}$$

For negative energy $E < 0$ we have the solutions

$$\chi_R = \sqrt{\frac{|E|+mc^2}{2|E|}} \begin{bmatrix} 1 \\ 0 \end{bmatrix} \tag{482}$$

$$\chi_L = \sqrt{\frac{|E|+mc^2}{2|E|}} \frac{1}{|E|+mc^2} \begin{bmatrix} cp_3 \\ -(cp_1 - icp_2) \end{bmatrix} \tag{483}$$

and

$$\chi_R = \sqrt{\frac{|E|+mc^2}{2|E|}} \begin{bmatrix} 0 \\ 1 \end{bmatrix} \tag{484}$$

$$\chi_L = \sqrt{\frac{|E|+mc^2}{2|E|}} \frac{1}{|E|+mc^2} \begin{bmatrix} -(cp_1 + icp_2) \\ -cp_3 \end{bmatrix} \tag{485}$$

If we considered $\gamma_0 \not{D}$ as our hermitian operator and we normalize now with respect to γ_0, so that we now consider the quantity $\psi^\dagger \gamma_0 \psi$ when normalizing our wave solutions. From this we get the normalization

$$\psi^\dagger \gamma_0 \psi = N^2 \left(\chi_L^\dagger \chi_L - \chi_R^\dagger \chi_R \right) \tag{486}$$

$$N^2 : \left(\chi_L^\dagger \chi_L - \chi_R^\dagger \chi_R \right) = 1 - \frac{c^2 p^2}{(|E| + mc^2)^2} = \frac{2mc^2}{|E| + mc^2} \tag{487}$$

Where here we used $c^2 p^2 = |E|^2 - m^2 c^4$. From which we can now get N which we find to be

$$N_{\gamma_0} = \sqrt{\frac{|E| + mc^2}{2mc^2}} \tag{488}$$

Where I denote it as N_{γ_0} to differentiate this normalization since we took into account γ_0.

Let us now try the case where $p = 0$ but $m > 0$, in this case we have the solutions

$$\Psi_1^+ = \begin{bmatrix} 1 \\ 0 \\ 0 \\ 0 \end{bmatrix} \tag{489}$$

$$\Psi_2^+ = \begin{bmatrix} 0 \\ 1 \\ 0 \\ 0 \end{bmatrix} \tag{490}$$

and

$$\Psi_1^- = \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \end{bmatrix} \tag{491}$$

$$\Psi_2^- = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \end{bmatrix} \tag{492}$$

Where $\Psi^{\pm}$ denotes the energy of the solution. These solutions seem to correspond to $m_z = \pm\frac{1}{2}$ where $\chi_L = \begin{bmatrix} 0 \\ 1 \end{bmatrix}, \begin{bmatrix} 1 \\ 0 \end{bmatrix}$ since recall that $\sigma_3 \begin{bmatrix} 1 \\ 0 \end{bmatrix} = -1 \begin{bmatrix} 1 \\ 0 \end{bmatrix}$ and $\sigma_3 \begin{bmatrix} 0 \\ 1 \end{bmatrix} = +1 \begin{bmatrix} 0 \\ 1 \end{bmatrix}$

We call this intrinsic spin and it seems to be there even in the non relativist case where $p = 0$ showing that this is not just a relativist effect but a fundamental property of the particle. Julian Schwinger later showed that Dirac's wave equation was experimentally correct and that electrons do have intrinsic spin.

6 Wave Equation with a Magnetic Field

Let us consider how we would take into account the effects of a magnetic field on Schrodinger's wave equation. To do so first consider the classical problem of a particle with velocity $\vec{v_0}$ in a magnetic field $\vec{B} = B\hat{z}$ where we pick B to be in the $\hat{z}$ direction since we have the freedom of choice of coordinates. To simplify the problem let us also put the constraint that $\vec{v_0} \cdot \vec{B} = 0$. So the initial motion lines on a plane perpendicular to the magnetic field. Recall that $\vec{F} = e\vec{v} \times \vec{B}$ for an electron in a magnetic field so we have

$$m\dot{\vec{v}} = eB\vec{v} \times \hat{z} \tag{493}$$

Where e is the charge of the electron. We want to show that the speed is constant so consider

$$\frac{\mathrm{d}\vec{v} \cdot \vec{v}}{\mathrm{d}t} = 2\vec{v} \cdot \frac{\mathrm{d}v}{\mathrm{d}t} = 2\frac{eB}{m_e}\vec{v} \cdot (\vec{v} \times \hat{z}) = 0 \tag{494}$$

So we have shown that only the direction will change not the speed of the electron. Now let us solve the equations of motion for the electron. Using eq. 493 we get the equations

$$\frac{dv_x}{dt} = \frac{eB}{m} v_y \tag{495}$$

$$\frac{dv_y}{dt} = -\frac{eB}{m} v_x \tag{496}$$

and

$$\frac{dv_z}{dt} = 0 \tag{497}$$

since we said the initial velocity lies on the x, y plane. From this we expect solutions to v_x, v_y to be of the form

$$v_x = v_0 sin(\frac{eB}{m} t) \tag{498}$$

$$v_x = v_0 cos(\frac{eB}{m} t) \tag{499}$$

Where

$$v_x^2 + v_y^2 + v_0^2 \tag{500}$$

$\omega = \frac{eB}{m}$ is the called the cyclotron frequency. So we have the equations of motion

$$\vec{v} = v_0 \left[sin(\omega t)\hat{x} + cos(\omega t)\hat{y} \right] \tag{501}$$

$$\vec{r} = \frac{v_0}{\omega} \left[-cos(\omega t)\hat{x} + sin(\omega t)\hat{y} \right] \tag{502}$$

Now let us consider the angular momentum of the electron since it will orbit the magnetic field, recall the formula for angular momentum

$$\vec{L} = m\vec{r} \times \vec{v} \tag{503}$$

So plugging in our solutions we have

$$\vec{L} = \frac{m^2}{eB} v_0^2 \hat{z} = e\frac{m^2}{e^2 B^2} v_0^2 \vec{B} \tag{504}$$

Where we have just rewritten $\vec{L}$ in terms of $\vec{B}$ so that now we have quantity

$$\vec{L} \cdot \vec{B} = \frac{m^2 v_0^2}{e} \tag{505}$$

Which looks like kinetic energy due to the magnetic field so we can write

$$\frac{1}{2} m v_0^2 = \frac{1}{2}\frac{e}{m}\vec{L} \cdot \vec{B} \tag{506}$$

Giving us the total energy

$$\frac{p^2}{2m} + V(r) + \frac{1}{2}\frac{e}{m}\vec{L} \cdot \vec{B} \tag{507}$$

Now if we try to convert this wave mechanics all we have added is an extra term $\frac{e}{2m}\vec{L} \cdot \vec{B}$ so we have the wave equation

$$\left[\frac{-\hbar^2}{2m}\nabla^2 + V(r) + \mu\vec{L} \cdot \vec{B}\right]\psi = H_B\psi = i\hbar\frac{\partial}{\partial t}\psi \tag{508}$$

Where $\mu = \frac{e}{2m}$ and $H_B = H + \mu\vec{L} \cdot \vec{B}$ is our new Hamiltonian with the addition of the magnetic field. Now recall that we have showed that H, L_a, L^2 all commute. If $\vec{B} = B\hat{z}$ then we can pick $L_a = L_3$ since we have already worked it out for this case. Suppose this is the case then we have

$$H_B = H + \mu L_z B_z \tag{509}$$

Now consider the potential of the hydrogen atom where we found solutions which we denoted by $|n, j, m\rangle$ such that

$$L_z|n, j, m\rangle = \hbar m|n, j, m\rangle \tag{510}$$

$$L^2|n, j, m\rangle = \hbar^2 j(j+1)|n, j, m\rangle \tag{511}$$

$$H|n, j, m\rangle = -\frac{1}{2}\left[\frac{ze^2}{4\pi\epsilon_0}\right]^2 \frac{m_e}{\hbar^2 n^2}|n, j, m\rangle = E_n|n, j, m\rangle \tag{512}$$

Then applying this solution to our new Hamiltonian gives us

$$H_B|n, j, m\rangle = H|n, j, m\rangle + \frac{eB}{2m_e}L_z|n, j, m\rangle \tag{513}$$

$$H_B|n, j, m\rangle = E_n|n, j, m\rangle + \frac{eB}{2m_e}\hbar m|n, j, m\rangle \tag{514}$$

$$H_B|n, j, m\rangle = E_n + \frac{eB}{2m_e}\hbar m|n, j, m\rangle = E_{n,j,m}|n, j, m\rangle \tag{515}$$

So we now get our energy shifted and notice that now the energy depends on n,j,m. However notice how the rest of our solution stayed the same. This is because we introduced a term proportional to L_a where L_a already commuted with H, L^2 leaving are solution unchanged for the most part. However this shifting of energy causes the energy levels to split at each state apart from the ground state where $n = 1$. It is also important to note that in laboratory's the strongest magnetic fields we can produce are $B_{lab} \leq\approx 100T$.

Now in the case where we cannot pick the direction of $\vec{B}$ we would have to consider $\vec{B} \cdot L$ along the direction of B. So we would have L_B denoting the component of $\vec{L}$ in the B direction. However we showed before that we can rotate L_z to L_B through a unitary matrix U such that $U^\dagger U = 1$ where we require U to satisfy $U^\dagger L_z U = L_B$. Then we can use our previous solutions.

7 Perturbation Theory

Some problems in quantum mechanics are not solvable exactly, and there are different techniques which try to approximate these solutions. We will be going over one of these methods known as perturbation theory. Perturbation theory is the study of more complicated systems from systems which we can solve exactly.

Let H_0 be exactly solvable and hermitian with eigenfunctions $|n\rangle$ such that

$$H_0|n\rangle = E_n|n\rangle \tag{516}$$

Now suppose we have H such that

$$H = H_0 + \lambda V_1 \tag{517}$$

Where H cannot be solved exactly and λ is a constant. Let us assume solutions for this Hamiltonian of the form

$$H|\phi\rangle = E_\phi|\phi\rangle \tag{518}$$

so that we now have

$$H|\phi\rangle = H_0|\phi\rangle + \lambda V_1|\phi\rangle = E_\phi|\phi\rangle \tag{519}$$

Now let us assume we can write $E_\phi, |\phi\rangle$ as infinite series, meaning

$$E_\phi = \sum_{k=0}^{\infty} \lambda^k \mu_k \tag{520}$$

and

$$|\phi\rangle = \sum_{k=0}^{\infty} \lambda^k |\phi_k\rangle \tag{521}$$

where μ_k are numbers and $|\phi_k\rangle$ are different vectors which need not be normalized. We will now try to solve for all μ_k and $|\phi_k\rangle$. To do so, let us plug solutions of these forms into eq. 519

$$(H_0 + \lambda V_1) \sum_{j=0}^{\infty} \lambda^j |\phi_j\rangle = \left(\sum_{k=0}^{\infty} \lambda^k \mu_k \right) \sum_{j=0}^{\infty} \lambda^j |\phi_j\rangle \tag{522}$$

Now for this to work we must have the series converge for a range of λ. Therefore this equation must be true term by term in λ. Let us list a few of these terms

$$\lambda^0 : H_0|\phi_0\rangle = \mu_0|\phi_0\rangle \tag{523}$$

$$\lambda^1 : (H_0 - \mu_0)\,|\phi_1\rangle = (\mu_1 - V_1)|\phi_0\rangle \tag{524}$$

$$\lambda^2 : (H_0 - \mu_0)\,|\phi_2\rangle = (\mu_2)|\phi_0\rangle + (\mu_1 - V_1)|\phi_1\rangle \tag{525}$$

and so on. We can write these in general for λ^p as

$$\lambda^p : (H_0 - \mu_0)\,|\phi_p\rangle = (\mu_{p-1} - V_1)|\phi_{p-1}\rangle + \sum_{k=2}^{p} \mu_k|\phi_{p-k}\rangle \tag{526}$$

for $p > 2$.

Now from eq. 523 we can see that $|\phi_0\rangle = |n\rangle$ with eigenvalues $\mu_0 = E_n$ is the natural choice since H_0 acting on it is an eigenvalue problem. So that we have

$$\lambda^0 : H_0|n\rangle = E_n|n\rangle \tag{527}$$

Now it is important to not that we will assume solutions for the exactly solvable Hamiltonian H_0 to be orthonormal, meaning

$$\langle n|m\rangle = \delta_{n,m} \tag{528}$$

From this we can take the inner product of eq. 524 with $\langle m|$ giving us

$$\langle m|H_0 - E_n|\phi_1\rangle = \mu_1\langle m|n\rangle - \langle m|V_1|n\rangle \tag{529}$$

Where we can use $\langle m|H_0 = \langle m|E_m$ since H_0 hermitian. Giving us

$$\langle m|E_m - E_n|\phi_1\rangle = \mu_1\delta_{m,n} - \langle m|V_1|n\rangle \tag{530}$$

Now if we let $m = n$ we get

$$\mu_1 = \langle n|V_1|n\rangle \tag{531}$$

Now without loss of generality we may write $|\phi_1\rangle$ in terms of our $|n\rangle$ basis since they form an orthonormal set of basis eigenfunctions over our space. As such we have

$$|\phi_1\rangle = \sum_{m=0}^{\infty} C_{1,m}|m\rangle \tag{532}$$

Let us now plug in solutions of this form into eq. 524

$$\lambda^1 : \sum_{m=0}^{\infty} (E_m - E_n)\, C_{1,m}|m\rangle = (\mu_1 - V_1)|n\rangle \tag{533}$$

Here I have brought in the operator H_0 since it must act on each of our eigenfunctions $|m\rangle$ and now let us again take the inner product with $\langle k|$ giving us

$$\lambda^1 : \sum_{m=0}^{\infty} (E_m - E_n)\, C_{1,m}\langle k|m\rangle = \langle k|(\mu_1 - V_1)|n\rangle \tag{534}$$

Which then using the orthogonality of our solutions $|n\rangle$ we get

$$\lambda^1 : (E_k - E_n)\, C_{1,k} = \mu_1\delta_{k,n} - \langle k|V_1|n\rangle \tag{535}$$

From which we can then get $C_{1,k}$ to be

$$C_{1,k} = \frac{\mu_1\delta_{k,n} - \langle k|V_1|n\rangle}{(E_k - E_n)} \tag{536}$$

However this can only be valid for $k \neq n$ since $k = n$ causes the coefficient to blow up. So we have

$$C_{1,k} = -\frac{\langle k|V_1|n\rangle}{(E_k - E_n)} \tag{537}$$

So that we now have $|\phi_1\rangle$

$$|\phi_1\rangle = C_{1,n}|n\rangle + \sum_{m\neq n} \frac{\langle m|V_1|n\rangle}{E_n - E_m}|m\rangle \tag{538}$$

To find $C_{1,n}$ we must use the normalization condition. From this we then have the first and order approximations of E_ϕ, $|\phi\rangle$ which we can write of the form

$$E_\phi = E_n + \lambda\langle n|V_1|n\rangle + ... \tag{539}$$

$$|\phi\rangle = (1 + \lambda C_{1,n}) + \lambda \sum_{m\neq n} \frac{\langle m|V_1|n\rangle}{E_n - E_m}|m\rangle + ... \tag{540}$$

However recall that for this method to work our solutions must converge for a radius of λ.

Repeating the process for eq. 525 we can find $|\phi_2\rangle$ which we will write in terms of our orthonormal basis $|n\rangle$ as such

$$|\phi_2\rangle = \sum_k C_{2,k}|k\rangle \tag{541}$$

Which if we now write 525 with solutions of this form and take the inner product with $\langle m|$ we have

$$\sum C_{2,k}(E_k - E_n)\langle m|k\rangle = \sum_l C_{1,l}\left(\mu_1\delta_{m,l} - \langle m|V_1|l\rangle\right) + \mu_2\delta_{m,n} \tag{542}$$

Now if we take $m = n$ we have

$$0 = \mu_1 C_{1,n} - \sum_l \langle n|V_1|l\rangle C_{1,l} + \mu_2 \tag{543}$$

However the nth term in our sum is exactly $\mu_1 C_{1,n}$ so that we now have

$$0 = -\sum_{l\neq n} \langle n|V_1|l\rangle C_{1,l} + \mu_2 \tag{544}$$

or substituting our solutions for $C_{1,l}$ we have

$$\mu_2 = \sum_{l \neq n} \frac{(\langle n|V_1|l\rangle)^2}{E_n - E_l} \tag{545}$$

Where I have used the property that $\langle l|V_1|n\rangle = \langle n|V_1|l\rangle$ where V_1 we take to be hermitian since in quantum mechanics we require our operators to correspond to observable quantities that we can measure, meaning we require operators which are hermitian so that our eigenvalues are real.

Now similarly we can show

$$C_{2,m} = \frac{\mu_1 C_{1,m} - \sum_l C_{1,l}\langle m|V_1|l\rangle}{E_m - E_n} \tag{546}$$

by taking eq. 542 with $m \neq n$ where again $C_{2,n}$ can be found by normalization.

7.1 Degeneracies

So far we have assumed that each energy level has exactly 1 unique solution $|n\rangle$ but we will now loosen this assumption to see how we can incorporate these degeneracies into our perturbation. For now let us assume two degenerate states where

$$E_n = E_{n+1} \tag{547}$$

with eigenfunctions

$$|n\rangle, |n+1\rangle \tag{548}$$

Once this simple case is shown we can include an arbitrary amount of degeneracies. Now notice that

$$C_n|n+1\rangle + C_{n+1}|n+1\rangle \tag{549}$$

also has the same energy. So let us assume this sort of solution where we have a linear combination of $|n\rangle, |n+1\rangle$ since this is the most general case. So that we now have

$$|\phi_0\rangle = C_n|n+1\rangle + C_{n+1}|n+1\rangle \tag{550}$$

with

$$\mu_0 = E_n = E_{n+1} \tag{551}$$

Now we found earlier that we can write

$$|\phi_1\rangle = \sum_k C_{1,k}|k\rangle \tag{552}$$

which if we plug into eq. 524 gives us

$$H_0 - E_n \sum_k C_{1,k}|k\rangle = (\mu_1 - V_1)(C_n|n\rangle + C_{n+1}|n+1\rangle) \tag{553}$$

Now let us take the inner product of this equation with $\rangle n|$ so that we get

$$0 = \mu_1 C_n - C_n\langle n|V_1|n\rangle - C_{n+1}\langle n|V_1|n+1\rangle \tag{554}$$

and let us also take the inner product of eq. 553 with $\langle n+1|$ giving us

$$0 = \mu_1 C_{n+1} - C_n\langle n+1|V_1|n\rangle - C_{n+1}\langle n+1|V_1|n+1\rangle \tag{555}$$

Now we can solve these equations, to write this in a more compact way let us use matrix notation.

$$\begin{bmatrix} \langle n|V_1|n\rangle & \langle n|V_1|n+1\rangle \\ \langle n+1|V_1|n\rangle & \langle n+1|V_1|n+1\rangle \end{bmatrix} \begin{bmatrix} C_n \\ C_{n+1} \end{bmatrix} = \mu_1 \begin{bmatrix} C_n \\ C_{n+1} \end{bmatrix} \tag{556}$$

and let us denote $\tilde{V} = \begin{bmatrix} \langle n|V_1|n\rangle & \langle n|V_1|n+1\rangle \\ \langle n+1|V_1|n\rangle & \langle n+1|V_1|n+1\rangle \end{bmatrix}$ as well as $\tilde{C} = \begin{bmatrix} C_n \\ C_{n+1} \end{bmatrix}$

So that we now have

$$\tilde{V}\tilde{C} = \mu_1 \tilde{C} \tag{557}$$

From this we can clearly see that this equation is just an eigenvector equation. So that if we diagonalize $\tilde{V}$ we can find the corresponding μ_1 and $\tilde{C}$ which diagonalizes this matrix. To find higher order approximations we would then apply the same methods for the λ^2 term and so on.

7.2 Properties of $\tilde{V}$

This section will go over some of the properties of $\tilde{V}$. First notice that $\tilde{V} = \tilde{V}^\dagger$. This is because we require V_1 to be hermitian so that $V_1 = V_1^\dagger$, as such $\tilde{V}$ is also hermitian which makes sense since we require μ_1 to be real since it correspond to energy. From this it follows that we need not calculate n^2 elements but rather $\frac{n(n+1)}{2}$ terms.

Now suppose our solution to the solvable Hamiltonian, H_0, is of the form $|\alpha_1, \alpha_2, ..., \alpha_m\rangle$ where each of the α_i for $i = 1, 2, ..., m$ correspond to eigenfunction solutions to some operator A_i such that $[A_i, A_j] = 0$ and $A_i|\alpha_1, \alpha_2, ..., \alpha_m\rangle = \alpha_i|\alpha_1, \alpha_2, ..., \alpha_m\rangle$. For each A_i which commutes with V_1 we will have a corresponding symmetry. Let us show this.

Consider $[A_i, V_1] = 0$ so that V_1 commutes with A_i. If we now take the inner product with another eigenfunction $\langle\alpha_1', \alpha_2', ..., \alpha_m'|$ so that we have

$$\langle\alpha_1', \alpha_2', ..., \alpha_m'|[A_i, V_1]|\alpha_1, \alpha_2, ..., \alpha_m\rangle \tag{558}$$

it follows that

$$\langle\alpha_1', \alpha_2', ..., \alpha_m'|[A_i, V_1]|\alpha_1, \alpha_2, ..., \alpha_m\rangle = 0 \tag{559}$$

However since A_i corresponds to an α_i with which we have diagonalized $|\alpha_1, \alpha_2, ..., \alpha_m\rangle$ we can also write

$$\langle\alpha_1', \alpha_2', ..., \alpha_m'|A_iV_1 - V_1A_i|\alpha_1, \alpha_2, ..., \alpha_m\rangle = 0 \tag{560}$$

which we can then write as

$$\left(\alpha_i' - \alpha_i\right)\langle\alpha_1, \alpha_2, ..., \alpha_m|V_1|\alpha_1, \alpha_2, ..., \alpha_m\rangle = 0 \tag{561}$$

From this we can clearly see that if $\alpha_i' \neq \alpha_i$ we have

$$\langle \alpha_1', \alpha_2', ..., \alpha_i, ..., \alpha_m' | V_1 | \alpha_1, \alpha_2, ..., \alpha_i, ..., \alpha_m \rangle = 0 \tag{562}$$

So that $\tilde{V}$ is diagonal with respect to A_i if $[A_i, V_1] = 0$. qed

Now suppose we have $V_1(x_1, x_2, ..., x_n)$, from this we have two possible cases. First consider the case

$$V_1(-x_1, -x_2, ..., -x_n) = -V_1(x_1, x_2, ..., x_n) \tag{563}$$

We will call these as odd potentials.

The other case being

$$V_1(-x_1, -x_2, ..., -x_n) = V_1(x_1, x_2, ..., x_n) \tag{564}$$

These we will call even potentials.

Now assume we have solutions $|\alpha_1, \alpha_2, ..., \alpha_n\rangle = \psi(x_1, x_2, ..., x_n)$. which may be odd or even in similar fashion as $(x_1, x_2, ..., x_n) \rightarrow (-x_1, -x_2, ..., -x_n)$.

Let us now examine the case where V_1 is odd. First recall that we can write $\tilde{V}_{i,j}$ as

$$\tilde{V}_{i,j} = \langle i | V_1 | j \rangle \tag{565}$$

If we take $(x_1, x_2, ..., x_n) \rightarrow (-x_1, -x_2, ..., -x_n)$ we then have

$$\tilde{V}_{i,j} = -\langle i | V_1 | j \rangle \tag{566}$$

if the eigenfuncions$|i\rangle, |j\rangle$ are either both even or both odd and in general we have

$$\tilde{V}_{i,i} = -\langle i | V_1 | i \rangle \tag{567}$$

Since $\langle i | V_1 | i \rangle$ will always be positive semi-definite.

From this we then have $\tilde{V}(x_1, x_2, ..., x_n) = -\tilde{V}(x_1, x_2, ..., x_n)$ for odd and $\tilde{V}(x_1, x_2, ..., x_n) = \tilde{V}(x_1, x_2, ..., x_n)$ for even potentials.

In the case $V(-x_1, -x_2, ..., -x_n) = -V(x_1, x_2, ..., x_n)$ we then have

$$\tilde{V}_{ij}\tilde{C}_j = \mu_1\tilde{C}_j \tag{568}$$

and

$$-\tilde{V}_{ij}\tilde{C}_j = \mu_1\tilde{C}_j \tag{569}$$

from eq. 557, but then either $\mu_1 = -\mu_1$ so that $\mu_1 = 0$ or $\tilde{V}_{ij} = 0$ when V_1 is odd and $|i\rangle, |j\rangle$ are of same oddness.

Now consider the case $\tilde{V}(x_1, x_2, ..., x_n) = \tilde{V}(-x_1, -x_2, ..., -x_n)$, if $|i\rangle, |j\rangle$ are of opposite oddness we then have again

$$\tilde{V}_{ij}\tilde{C}_j = \mu_1\tilde{C}_j \tag{570}$$

and

$$-\tilde{V}_{ij}\tilde{C}_j = \mu_1\tilde{C}_j \tag{571}$$

from which we can deduce either $\mu_1 = -\mu_1$ so that $\mu_1 = 0$ or $\tilde{V}_{ij} = 0$ when V_1 is even and $|i\rangle, |j\rangle$ are of opposite oddness.

7.3 Problems in Perturbation Theory

First let us consider the problem of a one-dimensional harmonic oscillator with the perturbation $V_1 = x$. Let us calculate the corresponding energy corrections μ_1, μ_2. First for μ_1 recall that we must calculate

$$\mu_1 = \langle n|V_1|n\rangle \tag{572}$$

In this case we have the eigenfunctions $\chi_n(y) = \frac{H_n(y)}{\pi^{1/4}}e^{-\frac{y^2}{2}}$ where $x = by$ and $b^2 = \frac{\hbar}{m\omega}$. So what we want to calculate is

$$\mu_1 = b\langle\tilde{n}|y|\tilde{n}\rangle \tag{573}$$

where $\tilde{n} = \chi_n(y)$. Without further calculation we can tell $\mu_1 = 0$. This is because $\mu_1 \geq 0$ since $\tilde{n}$ is even when n is even and odd when n is odd, this follows from $H_n(y)$ since $e^{-\frac{y^2}{2}}$ is even and the $V_1 \propto y$ is odd giving us an overall odd term when we integrate and since we integrate over all of space this gives us

$$\mu_1 = \int_{-\infty}^{\infty} (f_{odd}) dy = 0 \tag{574}$$

Now to calculate μ_2 we need to first calculate $\langle m|V_1|n\rangle = b\langle m|y|n\rangle$. Calculating $\langle m|y|n\rangle$ we have

$$\langle m|y|n\rangle = \int_{-\infty}^{\infty} H_m(y)H_n(y)e^{-y^2} y dy \tag{575}$$

Now using our recursion relation for $H_n(y)$ we can write

$$yH_n(y) = \frac{1}{2}\left(\sqrt{2(n+1)}H_{n+1}(y) + H_n'(y)\right) \tag{576}$$

so that we have

$$\int_{-\infty}^{\infty} H_m(y)\left(\sqrt{2(n+1)}H_{n+1}(y) + H_n'(y)\right) e^{-y^2} dy \tag{577}$$

I will avoid the constants until the end where we can just plug them back in. Now we can split this into two integrals

$$I_1 : \int_{-\infty}^{\infty} H_m(y) 2(n+1) H_{n+1}(y) e^{-y^2} dy \tag{578}$$

and

$$I_2 : \int_{-\infty}^{\infty} H_m(y)H_n'(y)e^{-y^2} dy \tag{579}$$

Now using integration by parts on I_2 we can write

$$I_2 : -\int_{-\infty}^{\infty} H_n(y)\frac{\mathrm{d}}{\mathrm{dy}}\left(H_m(y)e^{-y^2}\right) dy \tag{580}$$

Where I have used the property that our functions must go to 0 as $x \longrightarrow \pm\infty$. Now if we differentiate $\frac{\mathrm{d}}{\mathrm{d}y}\left(H_m(y)e^{-y^2}\right)$ we can get

$$\frac{\mathrm{d}}{\mathrm{d}y}\left(H_m(y)e^{-y^2}\right) = e^{-y^2}(H'_m - 2yH_m) \tag{581}$$

giving us

$$I_2 : -\frac{1}{2}\int_{-\infty}^{\infty} H_n e^{-y^2} H'_m dy + \int_{-\infty}^{\infty} H_n e^{-y^2} y H_m dy \tag{582}$$

However notice that the second term is just I_{tot} the integral we want to solve so that in total we have

$$I_{tot} = I_1 - \frac{1}{2}\int_{-\infty}^{\infty} H_n e^{-y^2} H'_m dy + I_{tot} \tag{583}$$

giving us the relation

$$I_1 = \frac{1}{2}\int_{-\infty}^{\infty} H_n e^{-y^2} H'_m dy \tag{584}$$

Now let us use this in I_{tot}. First using the recursion relation of $H_m(y)$ again we have

$$I_{tot} = \frac{1}{2}\int_{-\infty}^{\infty}\left(\sqrt{2(m+1)}H_{m+1}(y) + H'_m(y)\right)H_m(y)e^{-y^2} y dy \tag{585}$$

Now using our relation we have

$$I_{tot} = \frac{1}{2}\int_{-\infty}^{\infty} e^{-y^2} H_n H_{m+1}\sqrt{2(m+1)}dy + \frac{1}{2}\int_{-\infty}^{\infty} e^{-y^2} H_m H_{n+1}\sqrt{2(n+1)}dy \tag{586}$$

Now using the even and oddness of $H_n(y)$ we can see that this integral is 0 unless $n = m+1$ or $m = n+1$. Suppose $m = n+1$ we then have

$$I_{tot} = \frac{1}{2}\int_{-\infty}^{\infty} e^{-y^2} H_{n+1} H_{n+1}\sqrt{2(n+1)}dy = \frac{\sqrt{2}}{2}\sqrt{n+1} \tag{587}$$

Since chi_{n+1} is normalized. Giving us

$$I_{tot} = \frac{\sqrt{2}}{2}\sqrt{n+1} \tag{588}$$

The other case $n = m + 1$ gives us

$$I_{tot} = \frac{\sqrt{2}}{2}\sqrt{n+1} \tag{589}$$

Which makes sense this V_1 is hermitian. So that we have

$$\mu_2 = \frac{1/2(n+1)}{-\hbar\omega} + \frac{1/2(n-1+1)}{\hbar\omega} = -\frac{1}{2\hbar\omega} \tag{590}$$

where I used $E_n = (n+1)\hbar\omega$ and the only non-zero terms are $m = n - 1$ and $m = n + 1$. These results make sense since we have a potential $V_1 = x$ which corresponds to a constant force. Classically this would just shift the equilibrium point and leave the physics unchanged so that we have $\mu_1 = 0$. Looking at the μ_2 corrections we see that these are similar to the L_1, L_2 matrices we had when we diagonalized L_3 for central potentials, where the only nonzero terms where the off-diagonals. This could correspond to a change of basis which would better suit this problem. It makes sense that our solution does not diagonalize this new potential since $[H_0, V_1] \neq 0$ clearly. Where H_0 is our Hamiltonian for the one dimensional harmonic oscillator.

Let us now consider adding a potential $V_1 = x^4$ to our one-dimensional harmonic oscillator. In this case we will use the raising and lowering operators $a^\dagger, a$ which we showed in quantum mechanics 1 to be

$$a^\dagger = \frac{1}{\sqrt{2}}(-\frac{d}{dy} + y) \tag{591}$$

$$a = \frac{1}{\sqrt{2}}(\frac{d}{dy} + y) \tag{592}$$

from these we can write $y^4 = \frac{1}{4}((a + a^\dagger)^4$. Now to calculate μ_1 we need only consider

$$\langle n|(a+a^{\dagger})^4|n\rangle \tag{593}$$

As such it will be important to review how $a, a^{\dagger}$ operate on $|n\rangle$. recall

$$a^{\dagger}|n\rangle = \sqrt{n+1}|n+1\rangle \tag{594}$$

$$a|n\rangle = \sqrt{n}|n-1\rangle \tag{595}$$

where $\sqrt{n+1}, \sqrt{n}$ correspond to their normalization. From this we can already see that only the terms which raise and lower twice will remain whereas any other combination will lead to a product $\langle m|n\rangle = 0$ where $m \neq n$. From carrying out the calculations for only the operators which have two raising and lowering operations in any order we get the quanity

$$6n^2 + 6n + 3\langle n|n\rangle = 3(2n^2 + 2n + 1) \tag{596}$$

Now recall $x = by$ so that we have

$$\mu_1 = b^4 \frac{1}{4}\langle n|(a+a^{\dagger})^4|n\rangle \tag{597}$$

after adding back all the constants, giving us the first order correction

$$\mu_1 = \frac{3}{4}(2n^2 + 2n + 1)\frac{\hbar^2}{m^2\omega^2} \tag{598}$$

So that the nth state has energy

$$E_{\psi} \approx (n+1)\hbar\omega + \lambda\frac{3}{4}(2n^2 + 2n + 1)\frac{\hbar^2}{m^2\omega^2} \tag{599}$$

The fractional correction then of μ_1 to the energy E_n is

$$f(n) = \frac{3(2n^2 + 2n + 1)}{4(n+1)}\frac{\hbar}{m^2\omega^3} \tag{600}$$

where $f(n) \cdot (n+1)\hbar\omega = \mu$

From this we can see that this fraction increases as n increases meaning for large n our fractional correction goes towards infinity, so that the only valid choice of λ for all n is $\lambda = 0$.

Let us now consider the two-dimensional harmonic oscillator with potential $V_1 = r$. In this case we have the solutions

$$|n_1, n_2\rangle = \frac{H_{n1,n2}(u,v)}{\sqrt{\pi}} e^{-\frac{1}{2}(u^2+v^2)} \tag{601}$$

Where $H_{n1,n2}(u,v) = H_{n1}(u)H_{n2}(v)$ the same H_n as for our one-dimensional harmonic oscillator. Where we have the corresponding energies $E_n = (n1 + n2 + 1)\hbar\omega$. From this we see that the lowest states correspond to $n1, n2 = 0$ with $E_1 = \hbar\omega$ and $n1 = 1, n2 = 0$ and $n1 = 0, n2 = 1$ with $E_2 = 2\hbar\omega$. Here are solutions are in natural units so that we have to convert between r and u, v. To do so we use the following relation $x = bu$ and $y = bv$ where $b^2 = \frac{\hbar}{m\omega}$. So we may write $r = b\sqrt{u^2 + v^2}$. Let us first calculate μ_1 for $|0,0\rangle = \frac{1}{\sqrt{\pi}} e^{-\frac{1}{2}(u^2+v^2)}$

$$\mu_1 = \langle 0,0|b\sqrt{u^2+v^2}|0,0\rangle \tag{602}$$

where we will need to find

$$\int_{-\infty}^{\infty} \sqrt{u^2+v^2} e^{-(u^2+v^2)} du dv \tag{603}$$

let us now go to polar coordinates so let $u = \rho cos\theta$, $v = \rho sin\theta$ giving us $dA = |du \times dv| = \rho d\rho d\theta$, so that we now have

$$2\pi \int_{0}^{\infty} \rho^2 e^{-\rho^2} d\rho = \frac{\pi\sqrt{\pi}}{2} \tag{604}$$

So that we have

$$\mu_1 = \frac{\sqrt{\pi}}{2}\sqrt{\frac{\hbar}{m\omega}} \tag{605}$$

after including the constants. Now to do μ_1 for the E_2 case we will have to look at the matrix $\tilde{V}$ since we have degeneracy. First notice that in our polar basis $|N, m\rangle$ we were able to diagonalize H, L where L was the angular momentum. Notice that $[L, r] = 0$ since L is only dependent on our angle, meaning our added potential will be diagonal with respect to L, so that off-diagonal terms will be 0. We will check this later.

We will need to check the terms $\langle 1,0|b\sqrt{u^2+v^2}|0,1\rangle$, $\langle 1,0|b\sqrt{u^2+v^2}|1,0\rangle$, $\langle 0,1|b\sqrt{u^2+v^2}|0,1\rangle$, and $\langle 0,1|b\sqrt{u^2+v^2}|1,0\rangle$. Notice that because n_1, n_2 are independent of each other both $n1', n1$ and $n2', n2$ must be the same meaning $n1' = n1$ and $n2' = n2$. Where n' denotes the left term in the inner product. So then we only need to calculate the terms $\langle 1,0|b\sqrt{u^2+v^2}|1,0\rangle$ and $\langle 0,1|b\sqrt{u^2+v^2}|0,1\rangle$ but again $\langle 1,0|b\sqrt{u^2+v^2}|1,0\rangle = \langle 0,1|b\sqrt{u^2+v^2}|0,1\rangle$ since $n1, n2$ are independent. So we only need to calculate $\langle 0,1|b\sqrt{u^2+v^2}|0,1\rangle$

$$\langle 0,1|b\sqrt{u^2+v^2}|0,1\rangle = \int_{-\infty}^{\infty} \sqrt{u^2+v^2}v^2 e^{-(u^2+v^2)} du dv \tag{606}$$

which we can write as

$$\int_0^{\infty} \rho^2 e^{-(u^2+v^2)} d\rho \int_0^{2\pi} cos^2\theta d\theta = \frac{3}{4}\sqrt{\pi} \tag{607}$$

Here I am using the integral I_n which I define as

$$I_n = \int_0^{\infty} r^n e^{-r^2} dr \tag{608}$$

Then using integration by parts we get

$$I_n = \frac{n-1}{2} I_{n-2} \tag{609}$$

Where

$$I_1 = \frac{1}{2} \tag{610}$$

and

$$I_0 = \frac{\sqrt{\pi}}{2} \tag{611}$$

So that we have

$$\tilde{V} = \sqrt{\frac{\hbar}{m\omega}} \begin{bmatrix} \frac{3}{4}\sqrt{\pi} & 0 \\ 0 & \frac{3}{4}\sqrt{\pi} \end{bmatrix} \begin{bmatrix} C_{0,1} \\ C_{1,0} \end{bmatrix} = \mu_1 \begin{bmatrix} C_{0,1} \\ C_{1,0} \end{bmatrix} \tag{612}$$

Giving us

$$\mu_1 = \frac{3\sqrt{\pi}}{4}\sqrt{\frac{\hbar}{m\omega}} \tag{613}$$

for both states. Where our matrix $\tilde{V}$ is diagonal, this must be because this basis is a basis which diagonalizes L, the momentum operator. Notice that the higher energy level was raised by a larger amount $\frac{3}{4}$ rather then $\frac{1}{2}$ compared to the $|0,0\rangle$ state. This must be because of the radial component of our wave function, as n increases where $n = n1 + n2$ we would expect this fraction increase and possibly be bounded as it approaches 1.

Let us now consider the hydrogen atom. Suppose we introduce a constant electric field in the z-direction so that $\vec{E} = E\hat{z}$. Classically this would change the energy by $eE(z - z_0)$, let us suppose we can pick $z_0 = 0$ so that we have eEz. Let us try introducing this term into our hydrogen atom solutions using perturbation theory. So we are introducing $V_1 = eEz$. We will only consider the $n = 1, 2$ states. For these states we had the solutions

$$|1,0,0\rangle = \frac{1}{\sqrt{4\pi}}\frac{1}{\sqrt{2}}e^{-\frac{u}{2}} \tag{614}$$

$$|2,0,0\rangle = \frac{1}{4\sqrt{4\pi}}(1 - \frac{1}{4}u)e^{-\frac{u}{4}} \tag{615}$$

$$|2,1,\pm 1\rangle = \sqrt{\frac{3}{8\pi}}\frac{1}{16\sqrt{3}}ue^{-\frac{u}{4}}sin\theta e^{\pm i\phi} \tag{616}$$

$$|2,1,0\rangle = \frac{3}{4\pi}\frac{1}{16\sqrt{3}}ue^{-\frac{u}{4}}cos\theta \tag{617}$$

Where these states are in terms of the natural units u where we have $r = bu$. $b = \frac{2\pi\epsilon_0\hbar^2}{m_e} \approx 2.6459 \cdot 10^{-11}m$. Now notice that V_1 is odd so that our diagonal terms will be 0 meaning we have

$$\mu_1^{1,0,0} = 0 \tag{618}$$

Now Since E_2 has degeneracies we will need to look at the matrix $\tilde{V}$. Recall that we mentioned the diagonal terms must be zero since V_1 is odd, we showed this in the previous section when discussing properties of $\tilde{V}$. Notice also that $[L_z, V_1 \propto z] = 0$ clearly since z only depends on r, θ so that our matrix $\tilde{V}$ will be diagonal with respect to the eigenvalues m. Meaning that for different m we will have $\tilde{V}_{ij} = 0$. Notice also that $|2, 1, \pm 1\rangle$ is odd so that every non-diagonal term will be zero since we will have an overall odd integral. This only leaves the term $\langle 2, 1, 0|V_1|2, 0, 0\rangle = \langle 2, 0, 0|V_1|2, 1, 0\rangle$ this equality follows from V_1 being hermitian. Let us find $\langle 2, 1, 0|V_1|2, 0, 0\rangle$

$$\langle 2, 1, 0|V_1|2, 0, 0\rangle \propto 2\pi \int_0^\infty e^{-\frac{u}{2}} u^3 (1 - \frac{1}{4}u) du \int_0^\pi cos\theta sin\theta cos^2\theta d\theta \tag{619}$$

which gives us

$$\langle 2, 1, 0|V_1|2, 0, 0\rangle \propto -1152 \tag{620}$$

Now adding back the constants we have

$$\langle 2, 1, 0|V_1|2, 0, 0\rangle = -6eEb \approx -15.8754eE \cdot 10^{-11} \approx -25.435E \cdot 10^{-30} \tag{621}$$

giving us

$$\tilde{V} = \begin{bmatrix} 0 & 0 & -6eEb & 0 \\ 0 & 0 & 0 & 0 \\ 0 & -6eEb & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} C_{2,0,0} \\ C_{2,1,-1} \\ C_{2,1,0} \\ C_{2,1,1} \end{bmatrix} = \mu_1 \begin{bmatrix} C_{2,0,0} \\ C_{2,1,-1} \\ C_{2,1,0} \\ C_{2,1,1} \end{bmatrix} \tag{622}$$

Giving us the solutions $\mu_1 = 0, 0, \pm - 6eEb$ where $\mu_1 = 0, 0$ corresponds to $|2, 0, \pm 1\rangle$ which makes since since we said $[L_z, V_1] = 0$ and we observed V_1 was odd, so we expected this symmetry. This makes physical sense since we expect an electric field in the z-direction not affect the angular momentum in the z-direction since, regardless of whether we have an angular momentum in the $\pm\hat{z}$ direction the electric field would affect both the same since the rotation is perpendicular to the direction of $\hat{E}$.

Now suppose instead of putting the hydrogen atom in a field we model the proton to have some radius, so that we no longer treat it as a point particle. To do this consider a volume of charge with density $\rho = \frac{Q}{V}$ using Gauss's law we can show $E = \frac{Q}{4\pi\epsilon_0 R^3}$ inside the sphere and $E = \frac{Q}{4\pi\epsilon_0 r^2}$ outside the sphere. So outside the sphere our potential will be left unchanged since it behaves like a point charge, so let us focus on inside the sphere. Here we say the sphere is of radius R. Now integrating the electric field with respect to infinity we get

$$V = \frac{Q}{4\pi\epsilon_0}\frac{1}{2R}(3 - \frac{r^2}{R^2}) \tag{623}$$

However we want to add an opposing potential to the potential outside the sphere to counteract the initial potential for which we calculated the eigenfunctions $|n, j, m\rangle$. So we have

$$V_1 = \frac{e^2}{4\pi\epsilon}\left[\frac{1}{bu} - \frac{1}{2R}\left(3 - \left(\frac{ub}{R}\right)^2\right)\right], u < \frac{R}{b} \tag{624}$$

We will focus on the $n = 1, 2$ states. Let us first look at $|1, 0, 0\rangle$

$$\mu_1 = \langle 1, 0, 0|V_1|1, 0, 0\rangle \tag{625}$$

Where we must now integrate inside the sphere since our potential is only changed inside the sphere. It will be useful to define

$$I_n(a) = \int_0^{\frac{R}{b}} e^{-au}u^n du = \frac{1}{a}e^{a\frac{R}{b}}\left(\frac{R}{b}\right)^n + \frac{n}{a}I_{n-1} \tag{626}$$

Where

$$I_0(a) = -\frac{1}{a}e^{-a\frac{R}{b}} + \frac{1}{a} \tag{627}$$

From this we find

$$\mu_1^{1,0,0} = \frac{e^2}{4\pi\epsilon_0}[\frac{1}{2b}\left(-e^{-R/b}(\frac{R}{b}+1)+1\right) - \frac{3}{2R}(-e^{-\frac{R}{b}}(\frac{1}{2}(\frac{R}{b})^2 + \frac{R}{b}+1)+1)+\ldots \tag{628}$$

$$+\frac{b^2}{2R^3}(e^{-\frac{R}{b}}(\frac{1}{2}(\frac{R}{b})^4 + 2(\frac{R}{b})^3) + 6(\frac{R}{b}^2 + 12\frac{R}{b} + 12) + 12)] \tag{629}$$

Similarly we can find

$$\mu_1^{2,0,0} = \frac{e^2}{4\pi\epsilon_0}[\frac{1}{16b}(I_1(1/2) - \frac{1}{2}I_2(1/2) + \frac{1}{16}I_3(1/2)) - \frac{3}{32R}(I_2(1/2) - \frac{1}{2}I_3(1/2) + \frac{1}{16}I_4(1/2)) + \ldots \tag{630}$$

$$+\frac{b^2}{32R^3}(I_4(1/2) - \frac{1}{2}I_5(1/2) + \frac{1}{16}I_6(1/2))] \tag{631}$$

Where if we take $R \longrightarrow 0$ we have

$$\lim_{R\to 0} I_n(a) = -\frac{1}{a}(0) + \lim_{R\to 0}\frac{n}{a}I_{n-1}(a) \tag{632}$$

and

$$\lim_{R\to 0} I_0(a) = -\frac{1}{a} + \frac{1}{a} = 0 \tag{633}$$

So then we have

$$\lim_{R\to 0} I_n(a) = 0 \tag{634}$$

so we see that all these corrections go to 0 as $R \longrightarrow 0$ which is what we would expect.

Continuing with the corrections we have

$$\mu_1^{2,1,0} = \frac{e^2}{4\pi\epsilon_0}\left[\frac{1}{786b}I_3(1/2) - \frac{1}{524R}I_4(1/2) + \frac{b^2}{1572R^3}I_6(1/2)\right] \tag{635}$$

as for the rest we have $\mu_1^{2,1,-1} = \mu_1^{2,1,-1} = \mu_1^{2,1,0}$ since for each the radial part of the wave function is left unaffected.