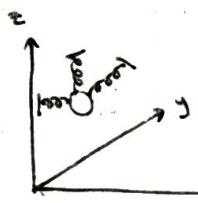


Quantum Mechanics in 3D

Until now we have only really considered problems in 1D but let's see if we can now extend our thinking to 3D. After all, this is how things work in real life. Let's start with the simple harmonic oscillator and expand it to 3D:

3D Simple Harmonic Oscillator



We can think of this as a particle with 3 springs attached. The potential here is given by a 3D vector. Each dimension has the same potential as a 1D SHO, i.e. $V = \frac{1}{2} M \omega^2 x^2$ so:

$$V(\vec{r}) = \frac{1}{2} M \sum_{i=1}^3 \omega_i^2 x_i^2 \quad \text{where } \vec{r} = (x_1, x_2, x_3) = (x, y, z)$$

The hamiltonian operator is:

$$\hat{H} = \frac{\vec{p}^2}{2M} + V(\vec{r})$$

$$\text{where } \vec{p} \text{ is the momentum operator } \vec{p} = \frac{\hbar}{i} \left(\frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z} \right) = \frac{\hbar}{i} \vec{\nabla}$$

so we can write the time independent schrodinger equation:

$$\text{in 1D: } -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi = E\Psi$$

$$\text{in 3D: } -\frac{\hbar^2}{2M} \vec{\nabla}^2 \Psi(\vec{r}) + \frac{1}{2} M (\omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2) \Psi(\vec{r}) = E\Psi = \hat{H}\Psi(\vec{r})$$

let's separate the variables in our ansatz to make things easier:

$$\text{ansatz: } \Psi(\vec{r}) = f_1(x_1) f_2(x_2) f_3(x_3)$$

from $\hat{H}\Psi(\vec{r}) = E\Psi(\vec{r})$ we can say:

$$f_2 f_3 \hat{H}_1 f_1 + f_1 f_3 \hat{H}_2 f_2 + f_1 f_2 \hat{H}_3 f_3 = E f_1 f_2 f_3 \quad \text{so:}$$

$$\frac{1}{f_1(x_1)} \hat{H}_1 f_1(x_1) + \frac{1}{f_2(x_2)} \hat{H}_2 f_2(x_2) + \frac{1}{f_3(x_3)} \hat{H}_3 f_3(x_3) = E$$

$$\frac{1}{f_1(x_1)} \hat{H}_1 f_1(x_1) + \frac{1}{f_2(x_2)} \hat{H}_2 f_2(x_2) + \frac{1}{f_3(x_3)} \hat{H}_3 f_3(x_3) = E$$

This only holds true if the individual terms are constant so:

$$\hat{H}_1 f_1(x_1) = E_1 f_1(x_1)$$

$$\hat{H}_2 f_2(x_2) = E_2 f_2(x_2)$$

$$\hat{H}_3 f_3(x_3) = (E - E_1 - E_2) f_3(x_3)$$

Here we have made sub $E = E_1 + E_2 + E_3$
by conservation of energy just so we only
have to work out 2 unknowns instead of 3

$$\text{We know } \hat{H}_i = \frac{\hat{p}_i^2}{2m} + V(x_i)$$

We can write the 1D solution in 3D form since we can think of
3D SHO as 3 individual harmonic oscillators:

$$\Psi_{N_1, N_2, N_3}(x_i) = \sqrt{\frac{m\omega_i}{\pi}}^{-1} (2^{N_i} \pi^{1/2})^{-1/2} e^{-\frac{m\omega_i}{2} x_i^2} H_{N_i}\left(\sqrt{\frac{m\omega_i}{\hbar}} x_i\right) \quad i=1,2,3$$

The corresponding energies depend on λ_i :

$$E_{N_1, N_2, N_3} = \sum_{i=1}^3 \hbar \omega_i (N_i + \frac{1}{2})$$

It is possible to have degeneracy between energy levels, for example
in the case $\omega_1 = \omega_2 = \omega_3 = \omega$:

$$E_N = \hbar(N + \frac{3}{2})$$

We can compute degeneracy of a given energy level. Say you
choose a value for N , so $N = N_1 + N_2 + N_3$:

$$\sum_{N_i=0}^N (N - N_i + 1) = \frac{1}{2}(N+1)(N+2)$$

It was fairly easy to move the harmonic oscillator to 3D
since it was easily expressed in Cartesian coordinates. If instead
the potential does not separate so easily in 3 dimensions,
we would have to use another system like spherical coordinates.

Schrodinger Equation in Spherical Coordinates

The 3D SE is:

$$i\hbar \frac{\partial \Psi(\vec{r}, t)}{\partial t} = -\frac{\hbar^2}{2m} \vec{\nabla}^2(\vec{r}, t) + V(\vec{r}) \Psi(\vec{r}, t)$$

[we are assuming
V depends only on \vec{r}]

$$\text{where } \int | \Psi |^2 d\vec{r} = \int | \Psi |^2 dx dy dt = 1 \text{ is normalisation}$$

For time-independent potentials, we can say $\Psi_n(\vec{r}, t) = \Psi_n(\vec{r}) e^{-iE_n t/\hbar}$

$$\Psi(\vec{r}, t) = \sum C_n \Psi_n(\vec{r}) e^{-iE_n t/\hbar} \text{ subject to the TISE:}$$

$$-\frac{\hbar^2}{2m} \vec{\nabla}^2 \Psi + V\Psi = E\Psi \text{ which is solved by}$$

$$\Psi(\vec{r}, t) \sum_n C_n \Psi_n(\vec{r}) e^{-iE_n t/\hbar}$$

We will now try and do all of this in spherical coordinates.

First lets write down mapping from cartesian to spherical:

$$x = r \sin\theta \cos\varphi$$

$$y = r \sin\theta \sin\varphi$$

$$z = r \cos\theta$$

$$\text{so } \vec{r} = r \sin\theta \cos\varphi \hat{e}_x + r \sin\theta \sin\varphi \hat{e}_y + r \cos\theta \hat{e}_z \text{ where } \hat{e}_x, \hat{e}_y, \hat{e}_z \text{ are cartesian unit vectors}$$

we can define unit vectors for spherical coordinates as well:

$$\hat{e}_r = N_r \frac{\partial \vec{r}}{\partial r} = N_r \{ \sin\theta \cos\varphi \hat{e}_x + \sin\theta \sin\varphi \hat{e}_y + \cos\theta \hat{e}_z \}$$

$$\hat{e}_\theta = N_\theta \frac{\partial \vec{r}}{\partial \theta} = N_\theta \{ r \cos\theta \cos\varphi \hat{e}_x + r \cos\theta \sin\varphi \hat{e}_y - r \sin\theta \hat{e}_z \}$$

$$\hat{e}_\varphi = N_\varphi \frac{\partial \vec{r}}{\partial \varphi} = N_\varphi \{ -r \sin\theta \cos\varphi \hat{e}_x + r \sin\theta \sin\varphi \hat{e}_y \}$$

In order to find an expression for the $\vec{\nabla}$ operator in spherical coordinates we project \vec{r} in cartesian coordinates onto our new unit vectors \hat{e}_r , \hat{e}_θ and \hat{e}_φ

$$\hat{e}_r \cdot \nabla = N_r \frac{\partial \vec{r}}{\partial r} \cdot \nabla = N_r \left(\frac{\partial x}{\partial r} \frac{\partial}{\partial x} + \frac{\partial y}{\partial r} \frac{\partial}{\partial y} + \frac{\partial z}{\partial r} \frac{\partial}{\partial z} \right) = N_r \frac{\partial}{\partial r} = \underline{\underline{\frac{\partial}{\partial r}}}$$

$$\hat{e}_\theta \cdot \nabla = N_\theta \frac{\partial \vec{r}}{\partial \theta} \cdot \nabla = N_\theta \left(\frac{\partial x}{\partial \theta} \frac{\partial}{\partial x} + \frac{\partial y}{\partial \theta} \frac{\partial}{\partial y} + \frac{\partial z}{\partial \theta} \frac{\partial}{\partial z} \right) = N_\theta \frac{\partial}{\partial \theta} = \underline{\underline{\frac{1}{r} \frac{\partial}{\partial \theta}}}$$

$$\hat{e}_\phi \cdot \nabla = N_\phi \frac{\partial \vec{r}}{\partial \phi} \cdot \nabla = N_\phi \left(\frac{\partial x}{\partial \phi} \frac{\partial}{\partial x} + \frac{\partial y}{\partial \phi} \frac{\partial}{\partial y} + \frac{\partial z}{\partial \phi} \frac{\partial}{\partial z} \right) = N_\phi \frac{\partial}{\partial \phi} = \underline{\underline{\frac{1}{r \sin \theta} \frac{\partial}{\partial \phi}}}$$

$$\therefore \vec{\nabla} = \underline{\underline{\left(\frac{\partial}{\partial r} + \frac{1}{r} \frac{\partial}{\partial \theta} + \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} \right)}}$$

the $\vec{\nabla}^2$ is just stated below and is tedious to prove:

$$\vec{\nabla}^2 = \underline{\underline{\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \left(\frac{\partial^2}{\partial \phi^2} \right)}}$$

Notice that the Laplacian operator ($\vec{\nabla}^2$) has angle-dependent and radial-dependent parts separately so we can make a separation of variables ansatz to simplify the problem:

$$\Psi(\vec{r}) = R(r) Y(\theta, \phi)$$

Subbing this into the TISE: $-\frac{\hbar^2}{2m} \vec{\nabla}^2 \Psi + V\Psi = E\Psi$

$$-\frac{\hbar^2}{2m} \left\{ \frac{Y}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial R}{\partial r} \right) + \frac{R}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{R}{r^2 \sin^2 \theta} \left(\frac{\partial^2 Y}{\partial \phi^2} \right) \right\} + VRY = ERY$$

Subtract ERY, divide by RY and multiply by $-\frac{2Mr^2}{\hbar^2}$

$$\underbrace{\left\{ \frac{1}{R} \frac{d}{dr} \left(r^2 \frac{\partial R}{\partial r} \right) - \frac{2Mr^2}{\hbar^2} (V - E) \right\}}_A + \underbrace{\left\{ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \left(\frac{\partial^2 Y}{\partial \phi^2} \right) \right\}}_B = 0$$

depends only on r
A

depends only on θ, ϕ
B

since A and B depend on different variables, this can only be true if they both equal a constant with opposite signs (since $A = -B$)

$$\text{our choice: } A = l(l+1) \quad B = -l(l+1)$$

radial eqn angular eqn

What is l? We will find out soon!

The angular equation

$$\sin\theta \frac{\partial}{\partial\theta} (\sin\theta \frac{\partial Y}{\partial\theta}) + \frac{\partial^2 Y}{\partial\varphi^2} = -l(l+1)\sin^2\theta Y$$

We can decompose this again into a θ part and a φ part if we write $Y(\theta, \varphi) = \Theta(\theta)\Phi(\varphi)$

$$\underbrace{\left\{ \frac{1}{\Theta} \left[\sin\theta \frac{\partial}{\partial\theta} (\sin\theta \frac{\partial\Theta}{\partial\theta}) + l(l+1)\sin^2\theta \right] \right\}}_{C \text{ polar equation}} + \underbrace{\left\{ \frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial\varphi^2} \right\}}_{D \text{ azimuthal equation}} = 0$$

so we know C and D are equal to the same constant, say m^2 , with different signs so $C = m^2$ and $D = -m^2$

$$D = -m^2 \Rightarrow \frac{1}{\Phi} \frac{\partial^2 \Phi}{\partial\varphi^2} = -m^2 \text{ can be solved immediately to } \underline{\Phi = e^{im\varphi}}$$

Since φ has range $0 \rightarrow 2\pi$ before a full rotation $\Phi(2\pi + \varphi) = \Phi(\varphi)$

which tells us $m = 0, \pm 1, \pm 2, \pm 3 \dots$

so the azimuthal dependence of the wave is quantised.

Now we move onto the polar equation which is harder to solve. The equation is a type of diff. eqn. called a Legendre differential equation. The solutions are known to be of the form

$$\underline{\Theta(\theta)} = AP_l^m(\cos\theta) \text{ where } P_l^m \text{ are associated Legendre functions}$$

$$P_l^m(x) = (1-x^2)^{|m|/2} \left(\frac{d}{dx} \right)^{|m|} P_l(x)$$

$$\text{where } P_l(x) \text{ is a Legendre Polynomial : } P_l(x) = \frac{1}{2^l l!} \left(\frac{d}{dx} \right)^l (x^2 - 1)^l$$

Physical and normalisable solutions are only found when:

$$l \geq 0, m = -l, -l+1, -l+2 \dots l-1, l \quad \text{so} \quad -l \leq m \leq l$$

Remember that the argument of the Legendre polynomial for our case is $\cos\theta$.

What more information can we get from the angular eqn. Well, we expect the 3D wavefunction to be normalised so let's work with that.

$$\begin{aligned} \int |\psi|^2 dr &= \int_0^{\infty} \int_0^{2\pi} \int_0^{\pi} |\psi|^2 r^2 \sin\theta d\theta d\phi dr \\ &= \int_0^{\infty} |R|^2 r^2 dr \int_0^{2\pi} \int_0^{\pi} |Y|^2 \sin\theta d\theta d\phi \end{aligned}$$

The angular wave function normalises to be:

$$Y_l^m(\theta, \phi) = \underbrace{\epsilon \sqrt{\frac{2l+1}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}}}_{\text{normalisation constant}} e^{im\phi} P_l^{|m|}(\cos\theta)$$

where $\epsilon = (-1)^{|m|}$ for $m \geq 0$ and $\epsilon = 1$ for $m \leq 0$

$Y_l^m(\theta, \phi)$ is also orthonormal:

$$\int_0^{2\pi} \int_0^{\pi} Y_l^m * Y_{l'}^{m'} \sin\theta d\theta d\phi = \delta_{ll'} \delta_{mm'}$$

- Summary:
- We separated angular eqn into azimuthal and polar parts
 - We showed azimuthal part was quantised
 - Polar part also quantised (but we didn't show it)
 - Polar eqn solved by associated legendre polynomials which are different for different choices of l, m
 - Solution $Y_l^m(\theta, \phi)$ solves all problems where potential depends only on $|r|$ and not on a particular direction

The Radial Equation

$$\frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2mr^2}{\hbar^2} (V(r) - E) R = L(L+1)R$$

To make solving this eqn. enjoyable, we make a substitution

$$R = \frac{u}{r} \quad \frac{dR}{dr} = \frac{1}{r} \frac{du}{dr} + u \frac{d}{dr} \left(\frac{1}{r} \right) = \frac{1}{r} \frac{du}{dr} - \frac{u}{r^2}$$

$$\frac{dR}{dr} = \left(r \frac{du}{dr} - u \right) / r^2$$

$$\frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) = r \frac{d^2u}{dr^2} \quad \text{Prove this to yourself by doing } \frac{d}{dr} \left(r \frac{du}{dr} - u \right)$$

Making these substitutions, the radial equation becomes:

$$-\frac{\hbar^2}{2m} \frac{d^2u}{dr^2} + \left(V + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2} \right) u = Eu$$

which is now similar to the 1D TISE where $\Psi \rightarrow u$ and $V \rightarrow V + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2}$. This is the effective potential. The $\frac{\hbar^2}{2m} \frac{l(l+1)}{r^2}$ term is called the centrifugal term, we will talk about it later.

The radial wavefunction u is normalised as:

$$\int_0^\infty |R|^2 r^2 dr = \int_0^\infty |u|^2 dr = 1$$

For every physical solution, we will make a choice for V and solve the TISE. Remember, for the angular wave equation, as long as wavefn is spherically symmetric (ie V depends only on r), we have everything we need already.

The Hydrogen Atom

A Hydrogen atom is made up of a single proton and a single electron. The potential which describes the Hydrogen atom is the familiar Coulomb potential:

$$V(1/r) = V(r) = -\frac{e^2}{4\pi\epsilon_0 r} \quad \text{so we can write the radial eqn:}$$

$$-\frac{\hbar^2}{2m} \frac{d^2u}{dr^2} + \left[\underbrace{-\frac{e^2}{4\pi\epsilon_0}}_{\substack{\text{attractive} \\ \text{term pulling} \\ \text{electron to proton}}} + \underbrace{\frac{\hbar^2}{2m} \frac{l(l+1)}{r^2}}_{\substack{\text{repulsive} \\ \text{centrifugal term} \\ \text{keeping electron away}}} \right] u = Eu$$

depending on E ,
we can find scattering
and bound states.
We will only consider
bound states.

by introducing $K = \sqrt{-2mE}/\hbar$ we can simplify this:

$$\frac{1}{K^2} \frac{d^2u}{dr^2} = \left[1 - \frac{me^2}{2\pi\epsilon_0\hbar^2 K} \frac{1}{Kr} + \frac{l(l+1)}{(Kr)^2} \right] u$$

letting $P = kr$ and $P_0 = \frac{Me^2}{2\pi\epsilon_0 n^2 K}$:

$$\frac{d^2u}{dp^2} = \left[1 - \frac{P_0}{p} + \frac{l(l+1)}{p^2} \right] u$$

The hydrogen radial equation is nonlinear and no obvious solution exists. We will need to try a brute force technique.

Consider the limiting cases:

i) $p \rightarrow \infty$ $\frac{d^2u}{dp^2} = u \rightarrow u = Ae^{-p} + Be^p$ we set $B=0$ to make it normalisable

ii) $p \rightarrow 0$ $\frac{d^2u}{dp^2} = \frac{l(l+1)}{p^2}$ since this term dominates $\rightarrow u = Cp^{l+1} + Dp^{-l}$ for normalisability $D=0$

we combine the ansatz to be $u = p^{l+1}e^{-p}v(p)$

To plug this into the hydrogen radial eqn. (the TISE) we need $\frac{du}{dp}$

$$\begin{aligned} \frac{du}{dp} &= (l+1)p^le^{-p}v(p) - p^{l+1}e^{-p}v(p) + p^{l+1}e^{-p}\frac{dv}{dp} \\ &= p^le^{-p} \left[(l+1-p) + p\frac{dv}{dp} \right] \end{aligned}$$

$$\frac{d^2u}{dp^2} = p^le^{-p} \left\{ \left[-2l-2+p + \frac{l(l+1)}{p} \right] v(p) + 2(l+1-p)\frac{dv}{dp} + p\frac{d^2v}{dp^2} \right\}$$

so the SE is:

$$p^le^{-p} \left\{ \left[-2l-2+p + \frac{l(l+1)}{p} \right] v(p) + 2(l+1-p)\frac{dv}{dp} + p\frac{d^2v}{dp^2} \right\} = \left[1 - \frac{P_0}{p} + \frac{l(l+1)}{p^2} \right] \times p^{l+1}e^{-p}v(p)$$

which simplifies to:

$$p\frac{d^2v}{dp^2} + 2(l+1-p)\frac{dv}{dp} + [P_0 - 2(l+1)]v = 0$$

We say $v(p) = \sum_{j=0}^{\infty} c_j p^j$ so if we plug this expansion into the SE, we get a tower of linear equations, recursive relations for the c_j

$$c_{j+1} = \left\{ \frac{2(j+l+1) - p_0}{(j+1)(j+2l+2)} \right\} c_j$$

For normalisable solutions, the series expansion for $v(p)$ needs to be finite, i.e. there must be a maximum j after which all $c_j = 0$

$$\therefore 2(j_{\max} + l + 1) - p_0 = 0$$

$$j_{\max} + l + 1 = \frac{p_0}{2} \Rightarrow j_{\max} + l + 1 = n$$

we call n the
principal quantum number
where $p_0 = 2n$

The hydrogen wave function is thus:

$$\Psi_{nlm}(r, \theta, \varphi) = R_{nl}(r) Y_l^m(\theta, \varphi)$$

where $R_{nl} = \frac{1}{r} r^{l+1} e^{-p} v(p)$ with $v(p)$ a polynomial of degree $j_{\max} = n-l-1$

with $K = \sqrt{\frac{-2mE}{\pi}}$ and $p_0 = \frac{-me^2}{2\pi\epsilon_0\alpha^2 K}$ we get

$$E = \frac{-\alpha^2 K^2}{2m} = \frac{-me^4}{8\pi^2\epsilon_0^2\alpha^2 p_0^2}$$

Replacing $p_0 = 2n$ we get:

$$E_n = -\frac{me^4}{8\pi^2\epsilon_0^2\alpha^2} \cdot \frac{1}{4n^2}$$

$$\text{so } E_n = E_1 \frac{1}{n^2} \quad n=1, 2, 3 \dots$$

This is Bohr's formula where
 $E_1 = -13.6 \text{ eV}$, ground state energy

$$K = \frac{me^2}{4\pi\epsilon_0\alpha^2} \cdot \frac{1}{n} = \frac{1}{an}$$

which defines

$$a = \frac{4\pi\epsilon_0\alpha^2}{me^2}$$

this is the Bohr radius giving
the size of a hydrogen atom

The ground state wave function is for $n=1, l=0, m=0$ so

$$\Psi_{100}(r, \theta, \varphi) = R_{10}(r) Y_0^0(\theta, \varphi) \quad \text{where } R_{10}(r) = \frac{C_0}{a} e^{-r/a}$$

so there is no angular dependence in ground state

$\Psi_{100} = R_{10}(r) = \frac{C_0}{a} e^{-r/a}$ which can be normalized to find C_0 :

$$\int_0^{\infty} |R_{10}|^2 r^2 dr = \frac{|C_0|^2}{a^2} \int_0^{\infty} e^{-2r/a} r^2 dr = |C_0|^2 \frac{a}{4} = 1$$

$$\therefore C_0 = \frac{2}{\sqrt{a}}$$

$$\text{Using } Y_0^0 = \frac{1}{\sqrt{4\pi}}, \text{ we get: } \Psi_{100} = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$$

Let's consider the next energy state E_2 .

$$\text{we know } E_2 = E_1 \cdot \frac{1}{n^2} = \frac{-13.6}{4} = -3.4 \text{ eV}$$

Since $L \leq n$, and $-L \leq M \leq L$, the allowed quantum numbers are:

$L=0 \quad M=0$ $L=1 \quad M=-1, 0, 1$	so there is 4-fold degeneracy 00, 1-1, 10, 11
---	--

$$R_{20}(r) = \frac{C_0}{2a} \left(1 - \frac{r}{2a}\right) e^{-r/2a}$$

$$R_{21}(r) = \frac{C_0}{4a^2} r e^{-r/2a}$$

The complete set of wavefunctions for the Hydrogen atom is:

$$\boxed{\Psi_{nlm}(r, \theta, \phi) = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n((l+1)!)^3}} e^{-r/na} \left(\frac{2r}{na}\right)^l L_{n-l-1}^{2l+1} \left(\frac{2r}{na}\right) Y_l^m(\theta, \phi)}$$

How do we check whether our results from calculation do indeed describe nature?

Electrons when changing energy levels radiate off / absorb photons we can measure the photon energy and check our prediction.

The photons will have wavelength defined by:

$$\boxed{\frac{1}{\lambda} = R \left(\frac{1}{\lambda_f^2} - \frac{1}{\lambda_i^2} \right)}$$

where R is the Rydberg constant.

Angular Momentum

In classical mechanics we define angular momentum as $\vec{L} = \vec{r} \times \vec{p}$

We transition to quantum mechanics by replacing \vec{p} with the momentum operator $P_{x,y,z} = -i\hbar \frac{\partial}{\partial x,y,z}$

$$\text{so } \hat{L}_x = \hat{y}\hat{P}_z - \hat{z}\hat{P}_y$$

$$\hat{L}_y = \hat{z}\hat{P}_x - \hat{x}\hat{P}_z$$

$$\hat{L}_z = \hat{x}\hat{P}_y - \hat{y}\hat{P}_x$$

The angular momentum operator can be shown to be Hermitian and therefore represents a measurable quantity.

Let's find the commutation relations for \hat{L}_i :

$$\begin{aligned} [\hat{L}_x, \hat{L}_y] &= [y\hat{P}_z - z\hat{P}_y, z\hat{P}_x - x\hat{P}_z] && \text{Note I've dropped "^\wedge" for convenience but they are still operators} \\ &= [y\hat{P}_z, z\hat{P}_y] - [y\hat{P}_z, -x\hat{P}_z] - \underbrace{[z\hat{P}_y, x\hat{P}_z]}_{\substack{\text{we've added 0 to simplify} \\ \text{the whole expression}}} + [z\hat{P}_y, x\hat{P}_z] \\ &= -yz[\hat{P}_z, \hat{P}_z] + y[\hat{P}_z, z]\hat{P}_x + z[y, \hat{P}_z]\hat{P}_z \\ &\quad - [y, z]\hat{P}_x\hat{P}_z - zx[\hat{P}_y, \hat{P}_z] + z[z, \hat{P}_y]\hat{P}_z \\ &\quad + x[z, \hat{P}_z]\hat{P}_y - [z, x]\hat{P}_z\hat{P}_y \\ &= i\hbar[x\hat{P}_y - y\hat{P}_x] \quad \therefore [\hat{L}_x, \hat{L}_y] = i\hbar \underline{\hat{L}_z} \end{aligned}$$

$$\text{similarly } [\hat{L}_y, \hat{L}_z] = i\hbar \underline{\hat{L}_x} \quad [\hat{L}_z, \hat{L}_x] = i\hbar \underline{\hat{L}_y}$$

Since the operators do not commute, there is no joint eigenfunction.

but we still want to find L in QM so what do we do? Let's

$$\text{try } \hat{L}^2 \text{ instead where } \hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

Does it commute with \hat{L}_x ?

$$\begin{aligned} [\hat{L}^2, \hat{L}_x] &= [\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2, \hat{L}_x] \\ &= L_y [\hat{L}_y, \hat{L}_x] + [\hat{L}_y, \hat{L}_x] L_y + L_z [\hat{L}_z, \hat{L}_x] + [\hat{L}_z, \hat{L}_x] L_z \\ &= i\hbar (-L_y L_z - L_z L_y + L_z L_y + L_y L_z) = 0 \end{aligned}$$

so it does commute!

Similarly:

$$[L^2, \hat{L}_z] = [\hat{L}^2, \hat{L}_x] = [\hat{L}^2, \hat{L}_y] = 0$$

so we can use \hat{L}^2 instead! What is the joint eigenvalue equations of this pair?

$$\hat{L}^2 f = \lambda f ; \quad \hat{L}_z f = \mu f \quad \text{with eigenvalues } \lambda \text{ and } \mu \text{ and eigefunction } f$$

What remains is to find the form of f .

We can take inspiration from the harmonic oscillator solution and define angular-momentum ladder operators as:

$$\hat{L}_{\pm} = \hat{L}_x \pm i \hat{L}_y \quad \text{which commutes as follows}$$

$$\begin{aligned} [\hat{L}_z, \hat{L}_{\pm}] &= [\hat{L}_z, \hat{L}_x \pm i \hat{L}_y] = [L_z, L_x] \pm i [L_z, L_y] \\ &= i \hbar L_y \pm \hbar L_x = \pm \hbar (L_x \mp i L_y) \end{aligned}$$

$$\therefore \underbrace{[\hat{L}_z^2, \hat{L}_{\pm}]}_{= \pm \hbar \hat{L}_{\pm}} = \pm \hbar \hat{L}_{\pm}$$

$$\text{and } \underbrace{[\hat{L}^2, \hat{L}_{\pm}]}_{= 0} = 0$$

so $L_{\pm}f$ is an eigefunction of \hat{L}_z^2 and \hat{L}^2 with eigenvalues $(\mu \pm \hbar)$ and λ respectively. So L_{\pm} leaves the EV of L^2 untouched but raises or lowers the EV of \hat{L}_z^2 by \hbar .

So can we increase/decrease infinitely?

$$\text{Remember } L^2 f = \lambda f \quad L_z f = \mu f$$

$$\langle L^2 \rangle = \langle L_x^2 \rangle + \langle L_y^2 \rangle + \langle L_z^2 \rangle = \lambda$$

$$\therefore \lambda = \langle L^2 \rangle = \langle L_x^2 \rangle + \langle L_y^2 \rangle + \mu^2 \geq \mu^2$$

so there must be a limit such that $L_z f_{\max} = 0$

$$\text{Let } \hat{L}_z f_{\max} = \hbar f_{\max} \quad \hat{L}^2 f_{\max} = \lambda f_{\max}$$

we choose $\mu = \hbar$ for future convenience

Let's try and write \hat{L}^2 in terms of the ladder operators:

$$\begin{aligned}\hat{L}_{\pm}\hat{L}_{\mp} &= (\hat{L}_x \pm i\hat{L}_y)(\hat{L}_x \mp i\hat{L}_y) \\ &= \hat{L}_x^2 + \hat{L}_y^2 \mp i(\hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x) \\ &= \hat{L}^2 - \hat{L}_z^2 \mp i[\hat{L}_x, \hat{L}_y] \\ &= \hat{L}^2 - \hat{L}_z^2 \mp i(i\hbar\hat{L}_z)\end{aligned}$$

$$\therefore \hat{L}^2 = \hat{L}_{+}\hat{L}_{-} + \hat{L}_z^2 + \hbar\hat{L}_z$$

$$\begin{aligned}\text{so } \hat{L}^2 f_{\max} &= \lambda f_{\max} \Rightarrow (\hat{L}_{-}\hat{L}_{+} + \hat{L}_z^2 + \hbar\hat{L}_z) f_{\max} \\ &= (\hbar^2(l^2 + \hbar^2l)) f_{\max} \quad \text{since } \hat{L}_{-}\hat{L}_{+} f_{\max} = 0 \\ &= \hbar^2l(l+1) f_{\max} \quad \text{so only } \hat{L}_z \text{ and } \hat{L}_z^2 \text{ matter}\end{aligned}$$

$$\therefore \underline{\lambda = \hbar^2 l(l+1)}$$

similarly, for f_{\min} :

$$\underline{\lambda = \hbar^2 \bar{l}(\bar{l}-1)}$$

$$\text{so we have } l(l+1) = \bar{l}(\bar{l}-1)$$

The solutions are $\bar{l} = l+1$ which is not possible since then lower end is larger
or $\bar{l} = -l$

We therefore conclude eigenvalues of L_z lie between $-l$ and l and we call them m . This is where $-l \leq m \leq l$ comes from!

$$\hat{L}^2 f_l^m = \hbar^2 l(l+1) f_l^m \quad L_z f_l^m = \hbar m f_l^m$$

m covers $-l \dots l$ in integer steps. There are therefore $N = 2l$ steps from $-l$ to l . Therefore $l = \frac{N}{2}$ so l is either integer or half-integer. If there are $N = 2l$ steps, there are $2l+1$ number of values for m .

Angular Momentum Eigenfunctions

The remaining task is to find the simultaneous eigenfunctions f_i^m for the system of eigenvalue equations.

$$\hat{L}^2 f_i^m(\vec{r}) = -\hbar^2 (\vec{r} \times \vec{\nabla})^2 f_i^m = \hbar^2 l(l+1) f_i^m(\vec{r}) \quad [\lambda f_i^m]$$

$$\hat{L}_z f_i^m(\vec{r}) = \frac{\hbar}{i} (\vec{r} \times \vec{\nabla})_z f_i^m(\vec{r}) = \hbar m f_i^m(\vec{r}) \quad [mf_i^m]$$

but we found previously $\vec{\nabla} = \hat{e}_r \frac{\partial}{\partial r} + \hat{e}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \hat{e}_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi}$

where $\hat{e}_r = \sin \theta \cos \phi \hat{e}_x + \sin \theta \sin \phi \hat{e}_y + \cos \theta \hat{e}_z$

$$\hat{e}_\theta = \cos \theta \cos \phi \hat{e}_x + \cos \theta \sin \phi \hat{e}_y - \sin \theta \hat{e}_z$$

$$\hat{e}_\phi = -\sin \phi \hat{e}_x + \cos \phi \hat{e}_y$$

Cross products: $\hat{e}_r \times \hat{e}_r = 0$

$$\hat{e}_r \times \hat{e}_\theta = \hat{e}_\phi \quad \text{so we can write the angular}$$

$$\hat{e}_r \times \hat{e}_\phi = -\hat{e}_\theta \quad \text{momentum operator in spherical coordinates}$$

$$\hat{L} = \frac{\hbar}{i} (\vec{r} \times \vec{\nabla}) = \frac{\hbar}{i} r (\hat{e}_r \times \vec{\nabla})$$

$$= \frac{\hbar}{i} r \left(\hat{e}_\phi \frac{1}{r} \frac{\partial}{\partial \theta} - \hat{e}_\theta \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} \right)$$

$$\hat{L} = \frac{\hbar}{i} \left\{ \left(\begin{array}{c} -\sin \phi \\ \cos \phi \\ 0 \end{array} \right) \frac{\partial}{\partial \theta} - \left(\begin{array}{c} \cot \theta \cos \phi \\ \cot \theta \sin \phi \\ -1 \end{array} \right) \frac{\partial}{\partial \phi} \right\}$$

so we extract the result $L_z = \frac{\hbar}{i} \frac{\partial}{\partial \phi}$

This leads to the differential equation which we also found for the azimuthal wave function.

What about \hat{L}^2 ?

We previously found $\hat{L}^2 = L_+ L_- + L_z^2 + \hbar L_z$

We know what \hat{L}_z is here but how do we sub L_+ & L_- ?

We can write L_+ and L_- out as $L_\pm = L_x \pm i L_y$.

$$\text{where } L_x = \frac{\hbar}{i} \left\{ -\sin\varphi \frac{\partial}{\partial\theta} - \cot\theta \cos\varphi \frac{\partial}{\partial\varphi} \right\}$$

$$L_y = \frac{\hbar}{i} \left\{ \cos\varphi \frac{\partial}{\partial\theta} - \cot\theta \sin\varphi \frac{\partial}{\partial\varphi} \right\}$$

$$L_+ L_- = \hbar^2 \left[-\frac{\partial^2}{\partial\theta^2} - \cot^2\theta \frac{\partial^2}{\partial\varphi^2} - \cot\theta \frac{\partial}{\partial\theta} - i \frac{\partial}{\partial\varphi} \right] \text{ after a lot of simplification!}$$

$$\text{This leads us to: } L^2 = L_+ L_- + L_z^2 = \hbar^2 L_z$$

$$L^2 = L_+ L_- + \left(\frac{\hbar}{i} \frac{\partial}{\partial\varphi} \right)^2 - \frac{\hbar^2}{i^2} \frac{\partial^2}{\partial\varphi^2}$$

$$\underline{L^2} = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2} \right]$$

So in summary:

$$L^2 f_l^m = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\varphi^2} \right] f_l^m = \hbar^2 l(l+1) f_l^m$$

$$L_z f_l^m = \frac{\hbar}{i} \frac{\partial}{\partial\varphi} f_l^m = \hbar m f_l^m$$

In fact we find that $\underline{f_l^m} = Y_l^m$, the angular dependence function.

So the SE for spherically symmetric potentials is fully described by the simultaneous eigenvalue equations:

$$H\Psi = E\Psi, \quad L^2\Psi = \hbar^2 l(l+1)\Psi, \quad L_z\Psi = \hbar m\Psi$$

The Hamilton operator can be written as

$$\hat{H} = \left\{ \frac{1}{2mr^2} \left[-\hbar^2 \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + L^2 \right] + V \right\}$$

$$\text{giving SE: } \frac{1}{2mr^2} \left[-\hbar^2 \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + L^2 \right] \Psi + V\Psi = E\Psi$$

we have thus found a full understanding of the QM treatment of spherically symmetric potential in the SE.

Spin

For the hydrogen atom we found quantum numbers L and m describing angular momentum. In particular, the azimuthal equation

$$L_z \Phi(\varphi) = \frac{\hbar}{i} \frac{\partial \Phi}{\partial \varphi} = \hbar m \Phi \quad \text{where } \Phi = e^{im\varphi}$$

we said $m = 0, \pm 1, \pm 2 \dots$

$$\Phi \text{ is periodic with } 2\pi \text{ so } \Phi(\varphi) = \Phi(\varphi + 2\pi)$$

But in Quantum Mechanics we observe something weird. Particles appear to be the same, not after a rotation by 360° but after 720°

$$\text{Consider } \Phi = e^{im\varphi}, \text{ if } m = \frac{1}{2}: \Phi = e^{i\frac{1}{2}\varphi} = e^{i\frac{1}{2}(\varphi + 2\pi)} = e^{i\frac{1}{2}\varphi} e^{i\pi} = -e^{i\frac{1}{2}\varphi}$$

so we pick up a negative phase after 2π , so we need 4π .

In QM, properties of particles are mass, charge, angular momentum, spin.

Spin is not necessary to solve the Schrödinger equation we have considered so far. It is a kind of add-on which lives in its own Hilbert space

for an electron (which has half integer spin) there are two allowed states, spin up and spin down, represented by vectors:

$X_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ $X_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ which can be written together to define a Hilbert Space:

$$X = \begin{pmatrix} a \\ b \end{pmatrix} = aX_+ + bX_-$$

To make sure we know we aren't talking about angular momentum but spin, we replace L^2 and L_z by spin operators S^2 and S_z which are otherwise the same. So:

$$S^2 X_{\pm} = \hbar^2 s(s+1) X_{\pm} \stackrel{s=\frac{1}{2} \text{ for electron}}{=} \hbar^2 \frac{3}{4} X_{\pm}$$

We can represent S^2 with a matrix $S^2 = \begin{pmatrix} c & d \\ e & f \end{pmatrix}$

Its components can be determined from the EV equation.

for spin up: $\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$:

$$\begin{pmatrix} c & d \\ e & f \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 \\ 0 \end{pmatrix} \Rightarrow \begin{pmatrix} c \\ e \end{pmatrix} = \begin{pmatrix} 3/4\hbar^2 \\ 0 \end{pmatrix} \text{ so } c = \frac{3}{4}\hbar^2, e = 0$$

For spin down: $\chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$:

$$\begin{pmatrix} c & d \\ e & f \end{pmatrix} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{3}{4}\hbar^2 \begin{pmatrix} 0 \\ 1 \end{pmatrix} \Rightarrow \begin{pmatrix} d \\ f \end{pmatrix} = \begin{pmatrix} 0 \\ 3/4\hbar^2 \end{pmatrix} \text{ so } d = 0, f = \frac{3}{4}\hbar^2$$

$$\therefore S^2 = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

We can now work out S_z :

$$S_z \chi_+ = \frac{\hbar}{2} \chi_+ \quad S_z \chi_- = -\frac{\hbar}{2} \chi_-$$

from which we say

$$S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

We can now also define ladder operators

$S_{\pm} = S_x \pm iS_y$ and work out what S_x and S_y are from this.

$$\begin{cases} S_+ \chi_- = \hbar \chi_+, \quad S_- \chi_+ = \hbar \chi_- \\ S_- \chi_- = 0 \quad S_+ \chi_+ = 0 \end{cases}$$

we can combine these to find:

$$S_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}$$

$$S_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

$$\therefore S_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$S_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

These are the famous Pauli spin matrices, written $\vec{S} = \frac{\hbar}{2} \vec{\sigma}$

e.g.

Consider a system with $S = \frac{1}{2}$ represented by $\chi = a \chi_+ + b \chi_-$.

Measurement of S_z gives EV $\frac{\hbar}{2}$ with probability $|a|^2$ and $-\frac{\hbar}{2}$ with prob. $|b|^2$

What about S_x ?

To find EV, use characteristic polynomial $\det |A - \lambda I| = 0$:

$$\det |S_x - \lambda I| = \det \begin{pmatrix} -\lambda & \frac{\hbar}{2} \\ \frac{\hbar}{2} & -\lambda \end{pmatrix} = 0 \Rightarrow \lambda^2 - (\frac{\hbar}{2})^2 = 0 \text{ so } \lambda = \pm \frac{\hbar}{2}$$

Eigenstates given by solution to $S_x \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \pm \frac{\hbar}{2} \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$

these are
the eigenvalues

$$\frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \pm \frac{\hbar}{2} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \Rightarrow \begin{pmatrix} \beta \\ \alpha \end{pmatrix} = \pm \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \text{ so } \beta = \pm \alpha$$

We therefore choose $(1, 1)$ and $(1, -1)$, normalisation factor $\frac{1}{\sqrt{2}}$

The eigenvectors of S_z are therefore:

$$\text{For eigenvalue } \frac{\hbar}{2}: X_+ = \frac{1}{\sqrt{2}} (1) \quad \text{For eigenvalue } -\frac{\hbar}{2}: X_- = \frac{1}{\sqrt{2}} (-1)$$

We can therefore express $x = aX_+ + bX_-$ as:

$$x = \frac{a+b}{\sqrt{2}} X_+ + \frac{a-b}{\sqrt{2}} X_-$$

so the prob. of measuring $\pm \frac{\hbar}{2}$ is $\frac{1}{2}|a \pm b|^2$

Spin Precession

The electron's spin interacts with an external magnetic field and the strength of this interaction is given in terms of the magnetic dipole moment:

$$\vec{\mu} = \gamma \vec{S}$$

The electron acts like a little dipole magnet with poles along the direction of its spin. If we subject the electron to an external magnetic field, it will start to feel a torque proportional to $\vec{\mu} \times \vec{B}$

i.e. perpendicular to both external magnetic field and electron's spin.

The energy associated with this system is:

$$H = -\vec{\mu} \cdot \vec{B} \quad (\text{minimized for } \vec{\mu} \parallel \vec{B})$$

$$H = -\gamma B \vec{S} \cdot \vec{J}$$

If we assume \vec{B} is only in z direction: $\vec{B} = B \hat{e}_z$ then

$$H = -\gamma B S_z = -\frac{\gamma B \hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

The spin eigenvectors determine the energy eigenvalue:

$$X_+ \rightarrow E_+ = -\gamma B \frac{\hbar}{2} \quad \text{and} \quad X_- \rightarrow E_- = +\gamma B \frac{\hbar}{2}$$

The time-evolution of the stationary states can be determined using the SE

$$i\hbar \frac{dX}{dt} = H X : \quad X(t) = a X_+ e^{-iE_+ t/\hbar} + b X_- e^{-iE_- t/\hbar}$$

$$X(t) = \begin{pmatrix} a e^{-iE_+ t/\hbar} \\ b e^{-iE_- t/\hbar} \end{pmatrix} \quad \begin{matrix} (1) \\ (2) \end{matrix}$$

Now we need some initial conditions.

Let's take initial condition at $t=0$ $a = \cos \frac{\alpha}{2}$, $b = \sin \frac{\alpha}{2}$ so

$$\text{so } X(0) = \begin{pmatrix} a \\ b \end{pmatrix} = \begin{pmatrix} \cos \frac{\alpha}{2} \\ \sin \frac{\alpha}{2} \end{pmatrix}$$

$$\text{therefore: } X(t) = \begin{pmatrix} \cos(\frac{\alpha}{2}) e^{i\gamma B_1 t/2} \\ \sin(\frac{\alpha}{2}) e^{-i\gamma B_1 t/2} \end{pmatrix}$$

This is the evolution of the spinor over time.

We can now compute expectation values of S_x, S_y, S_z :

$$\langle S_x \rangle = \langle X | S_x X \rangle$$

$$= \frac{\hbar}{2} \begin{pmatrix} \cos \frac{\alpha}{2} e^{i\gamma B_1 t/2} \\ \sin \frac{\alpha}{2} e^{-i\gamma B_1 t/2} \end{pmatrix} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \begin{pmatrix} \cos \frac{\alpha}{2} e^{i\gamma B_1 t/2} \\ \sin \frac{\alpha}{2} e^{-i\gamma B_1 t/2} \end{pmatrix}$$

$$\langle S_x \rangle = \frac{\hbar}{2} \sin \alpha \cos(\gamma B_1 t)$$

similarly

$$\langle S_y \rangle = -\frac{\hbar}{2} \sin \alpha \sin(\gamma B_1 t)$$

$$\langle S_z \rangle = \frac{\hbar}{2} \cos \alpha$$

We have actually measured these to very high precisions!

Well done on finishing the course!