4. QUANTUM MECHANICS IN 3-D :

So far we have shown how quantum mechanics can be used to describe motion in one dimension. Although the one-dimensional case illustrates basic features of systems such as the quantization of energy, we need a full three-dimensional treatment for the applications to atomic, solid-state, and nuclear physics. In this chapter we extend the concepts of quantum mechanics from one to three-dimensions and explore the predictions of the theory for the simplest of real systems — the hydrogen atom.

4.1. Extending QM to two particles and three-dimensions :

4.1.1. QM for two particles :

Consider a system of two particles with mass m_1 and m_2. We can know the state of both the particles at the same time as the positions and momenta of one particle commute with the positions and momenta of another particle, i.e.,

$$[x_1, x_2] = [p_1, p_2] = [x_1, p_2] = [x_2, p_1] = 0$$

Any interaction between these two particles appears only in the potential energy term — the kinetic energy terms in the Hamiltonian are independent. The Hamiltonian for two particles can be easily written as:

$$H = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} + V(x_1, x_2)$$

We often encounter the scenarios where the potential will only depend on the difference in the positions of the two particles: $V(x_1, x_2) = V(x_1 - x_2)$. This means that, the overall Hamiltonian has a "translational symmetry", i.e. for $x_1 \to x_1 + dx$ and $x_2 \to x_2 + dx$, Hamiltonian remains the same.

Let us examine an infinitesimal translation in x. The original Schrödinger equation (assuming the time-independent case for simplicity)

$$H\psi(x_1, x_2) = E\psi(x_1, x_2)$$

transforms to

$$H\psi(x_1 + dx, x_2 + dx) = E\psi(x_1 + dx, x_2 + dx)$$

which can be Taylor expanded

$$H\left[\psi(x_1, x_2) + \frac{\partial\psi}{\partial x_1}dx + \frac{\partial\psi}{\partial x_2}dx\right] = E\left[\psi(x_1, x_2) + \frac{\partial\psi}{\partial x_1}dx + \frac{\partial\psi}{\partial x_2}dx\right]$$

We can write the derivatives in terms of the total momentum operator:

$$p = p_1 + p_2 = \frac{\hbar}{i}\left(\frac{\partial}{\partial x_1} + \frac{\partial}{\partial x_2}\right)$$

$$H\psi(x_1, x_2) + \frac{i}{\hbar} H p\, \psi(x_1, x_2)\, dx = E\psi(x_1, x_2) + \frac{i}{\hbar} E p\, \psi(x_1, x_2)\, dx$$

Now subtract the original Schrödinger eq" and use the fact that E and p commute

$$H p \psi(x_1, x_2) = p E \psi(x_1, x_2) = p H \psi(x_1, x_2)$$

$$\Rightarrow (Hp - pH)\psi(x_1, x_2) = 0$$

As this is true for any ψ, we can get $[H, p] = 0$. Now if we use the eq", $\frac{d\langle \hat{A} \rangle}{dt} = \left\langle \frac{\partial \hat{A}}{\partial t} \right\rangle + \frac{i}{\hbar}\langle [\hat{H}, \hat{A}] \rangle$ and as the total momentum p doesn't have an explicit time-dependence, $\frac{dp}{dt} = 0 \Rightarrow$ Thus if the Hamiltonian has translational symmetry, the "total momentum is a constant of the motion"; i.e. total momentum is "conserved". We can have "simultaneous eigenfunctions" of the total momentum and of energy.

[This is true for time-dependent cases as well and can also be shown from the eq": $\frac{d\langle \hat{p} \rangle}{dt} = \left\langle -\frac{dV}{dx} \right\rangle$.
if Hamiltonian has translational symmetry, the potential energy term also has the translational symmetry, i.e. $V(x+dx) = V(x)$, then $\frac{dV}{dx} = 0 \longrightarrow \frac{dp}{dt} = 0$.]

4.1.2. QM in 3-D:

We've generalized Quantum Mechanics to include more than one particle. We now wish to include more than one-dim. too.

Additional dimensions are essentially independent, although they may be coupled through the potential. The coordinates and momenta from different dimensions commute, e.g.

$$[x, p_y] = \left[x, \frac{\hbar}{i}\frac{\partial}{\partial y}\right] = 0$$

The kinetic energy can simply be added and the potential energy now depends on 3 coordinates. The Hamiltonian in 3D is then,

$$H = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} + V(\vec{r}) = \frac{\vec{p}^2}{2m} + V(\vec{r})$$

$$= -\frac{\hbar^2}{2m}\vec{\nabla}^2 + V(\vec{r})$$

4.1.3. Two particles in 3-D:

The generalization of the Hamiltonian for two particles in 3D is now,

$$H = \frac{\vec{p}_1^{\,2}}{2m_1} + \frac{\vec{p}_2^{\,2}}{2m_2} + V(\vec{r}_1 - \vec{r}_2) = -\frac{\hbar^2}{2m_1}\vec{\nabla}_1^2 - \frac{\hbar^2}{2m_2}\vec{\nabla}_2^2 + V(\vec{r}_1 - \vec{r}_2) \quad \text{--- (1)}$$

[as, most of the cases the potential only depends on the difference in the positions of the two particles]

Defining the vector difference between the coordinates of the particles:

$$\vec{r} = \vec{r}_1 - \vec{r}_2$$

also defining the vector position of the center of mass:

$$\vec{R} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1 + m_2}$$

Now we want to transform the Hamiltonian as a function of these two parameters ($\vec{r}$ and $\vec{R}$).

Using chain rule in 1-D:

$$\frac{\partial}{\partial x_1} = \frac{\partial r}{\partial x_1}\frac{\partial}{\partial r} + \frac{\partial R}{\partial x_1}\frac{\partial}{\partial R}$$

in 3-D, we would have:

$$\vec{\nabla}_1 = \vec{\nabla}_r + \frac{m_1}{m_1 + m_2}\vec{\nabla}_R$$

$$\& \quad \vec{\nabla}_2 = -\vec{\nabla}_r + \frac{m_2}{m_1 + m_2}\vec{\nabla}_R$$

Putting this into the Hamiltonian (in eq^n ①) we get:

$$H = -\frac{\hbar^2}{2m_1}\left[\vec{\nabla}_r^2 + \left(\frac{m_1}{m_1+m_2}\right)^2\vec{\nabla}_R^2 + \frac{2m_1}{m_1+m_2}\vec{\nabla}_r\cdot\vec{\nabla}_R\right]$$

$$-\frac{\hbar^2}{2m_2}\left[\vec{\nabla}_r^2 + \left(\frac{m_2}{m_1+m_2}\right)^2\vec{\nabla}_R^2 - \frac{2m_2}{m_1+m_2}\vec{\nabla}_r\cdot\vec{\nabla}_R\right] + V(\vec{r})$$

$$= -\hbar^2\left[\left(\frac{1}{2m_1} + \frac{1}{2m_2}\right)\vec{\nabla}_r^2 + \frac{m_1+m_2}{2(m_1+m_2)^2}\vec{\nabla}_R^2\right] + V(\vec{r})$$

$$= -\frac{\hbar^2}{2}\left(\frac{1}{m_1} + \frac{1}{m_2}\right)\vec{\nabla}_r^2 - \frac{\hbar^2}{2}\cdot\frac{1}{m_1+m_2}\vec{\nabla}_R^2 + V(\vec{r})$$

Defining the reduced mass (μ) as $\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$ and the total mass $M = m_1 + m_2$:

$$H = -\frac{\hbar^2}{2\mu}\vec{\nabla}_r^2 - \frac{\hbar^2}{2M}\vec{\nabla}_R^2 + V(\vec{r})$$

The Hamiltonian essentially separates into two problems: the motion of the center of mass as a free particle:

$$H_R = -\frac{\hbar^2}{2M}\vec{\nabla}_R^2$$

and the interaction between the two particles:

$$H_r = -\frac{\hbar^2}{2\mu}\vec{\nabla}_r^2 + V(\vec{r})$$

→ This is exactly the same separation that we would make in classical physics!

4.1.4. Identical Particles:

In classical mechanics, particles are always distinguishable, as the individual "trajectories" through phase-space can, in principle, be traced. In quantum mechanics, however, particles can be identical and indistinguishable (e.g. electrons in an atom or a metal). ~~The intrinsic uncertainty in position and momentum therefore demands separate consideration of distinguishable and indistinguishable quantum particles.~~

There are many systems in nature that are made of several particles of same species. These particles all have the same mass, charge and spin. For instance the electrons in an atom are identical particles. Identical particles cannot be distinguished by measuring their properties. This is also true for classical physics. particles. However, in classical mechanics we can always follow the trajectory of each individual particles ~~through~~ through phasespace, i.e. their time-evolution in ~~phase~~ space, making identical particles distinguishable.

But in QM, the concept of always trajectories doesn't exist and thus the identical particles are indistinguishable. Hence there is a clear symmetry in nature under the interchange of any two such indistinguishable particles, say two electrons for example.

We define the "interchange operator" P_{12} as:

$$P_{12}\,\psi(\vec{r}_1,\vec{r}_2) = \psi(\vec{r}_2,\vec{r}_1)$$

if we interchange twice, we get back to the original state,

$$P_{12}\,P_{12}\,\psi(\vec{r}_1,\vec{r}_2) = \psi(\vec{r}_1,\vec{r}_2)$$

~~$P_{12}^2 = 1 \Rightarrow P_{12} = \pm 1$~~

$$\Rightarrow P_{12}^2\,\psi(\vec{r}_1,\vec{r}_2) = \psi(\vec{r}_1,\vec{r}_2)$$

so, the possible eigenvalues of the interchange operators are just +1 and −1.

$$P_{12}\,\psi = \pm\psi$$

[This can also be obtained from the following argument. $|\psi(\vec{r}_1,\vec{r}_2)|^2$ represents the probability for finding one electron at $\vec{r}_1$ and the other electron at $\vec{r}_2$. The indistinguishability of electrons requires that a formal interchange of particles produce no observable effects. In particular, all probabilities are unaffected by the interchange, so that, $|\psi(\vec{r}_1,\vec{r}_2)|^2 = |\psi(\vec{r}_2,\vec{r}_1)|^2$. Then the wavefunction itself may be either even ($\psi(\vec{r}_1,\vec{r}_2) = \psi(\vec{r}_2,\vec{r}_1)$) or odd ($\psi(\vec{r}_1,\vec{r}_2) = -\psi(\vec{r}_2,\vec{r}_1)$) under particle exchange]

[* Remember, wavefunctions of two indistinguishable particles might be different, like $\psi(\vec{r}_1,\vec{r}_2) = -\psi(\vec{r}_2,\vec{r}_1)$, but all the observables like probability or energy or momentum will be same for both]

Both possibilities exist in nature. Some particles like electrons, (protons, neutrons) always have the −1 quantum number. They are "spin-half particles" and are called the "fermions". On the other hand, some particles, like the photons (and pions), always have the +1 quantum number. They are "integer-spin" particles and are called "bosons." [It is an experimental fact that integer-spin particles are bosons, but half-integer spin particles are fermions.]

An important distinction between fermions and bosons can be derived from the interchange symmetry.

Suppose particle 'a' is in the one-particle state $\psi_a(\vec{r}_1)$ and the particle 'b' is in the one-particle state $\psi_b(\vec{r}_2)$. Due to the indistinguishability, we cannot write $\psi(r_1, r_2)$ as a simple product of them: $\psi_{ab}(\vec{r}_1,\vec{r}_2) \neq \psi_a(\vec{r}_1)\,\psi_b(\vec{r}_2)$. Because we cannot know which particle is in state ψ_a and which is in state ψ_b. We have to write this as a combination of them (with both possibilities of bosons and fermions):

$$\psi_{ab}(\vec{r}_1,\vec{r}_2) = A\left[\psi_a(\vec{r}_1)\,\psi_b(\vec{r}_2) \pm \psi_a(\vec{r}_2)\,\psi_b(\vec{r}_1)\right]$$

('+' for bosons and '−' for fermions)

So, for fermions if both particles are in the same state i.e. $a = b$, then ψ_{ab} is identically zero — the theory allows no solution or description of the system. Thus "two identical fermions cannot occupy the same state" → This is the famous "Pauli exclusion principle."

(4.2) 3D problems Separable in Cartesian Coordinates:

If the potential energy term is separable in Cartesian coordinates, i.e. $V(\vec{r}) = V_1(x) + V_2(y) + V_3(z)$, then the total Hamiltonian can be written as:

$$H = H_x + H_y + H_z$$

Then we can use separation of variables to solve the Schrödinger Eqn. (time-independent case, for simplicity).

let, $\psi(\vec{r}) = u(x)v(y)w(z)$. $\psi(x,y,z) = \psi_1(x)\psi_2(y)\psi_3(z)$

Schrödinger eq^n: $H\psi = E\psi$

$$\Rightarrow (H_x + H_y + H_z)\, u(x)v(y)w(z) = E\, u(x)v(y)w(z)$$

$$\Rightarrow (H_x + H_y + H_z)\, \psi_1(x)\psi_2(y)\psi_3(z) = E\,\psi_1(x)\psi_2(y)\psi_3(z)$$

$$\Rightarrow \psi_2(y)\psi_3(z)\left[H_x\psi_1(x)\right] + \psi_1(x)\psi_3(z)\left[H_y\psi_2(y)\right] + \psi_1(x)\psi_2(y)\left[H_z\psi_3(z)\right] = E\,\psi_1(x)\psi_2(y)\psi_3(z)$$

[as H_x only operates on $\psi_1(x)$, rest will be considered as constant.]

Dividing by $\psi(x,y,z)$ or $\psi_1\psi_2\psi_3$.

$$\frac{1}{\psi_1(x)} H_x\psi_1(x) + \frac{1}{\psi_2(y)} H_y\psi_2(y) + \frac{1}{\psi_3(z)} H_z\psi_3(z) = E$$

To satisfy the equation everywhere, each of these terms must reduce to a constant.

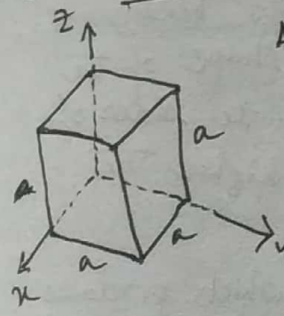
$$\frac{1}{\psi_1(x)} H_x\psi_1(x) = E_1 \Rightarrow H_x\psi_1(x) = E_1\psi_1(x)$$

similarly, $H_y\psi_2(y) = E_2\psi_2(y)$

$$H_z\psi_3(z) = E_3\psi_3(z)$$

The energies E_1, E_2, E_3 are separation constants and represent the energy of motion along the three Cartesian axes x, y, z. with total energy $E = E_1 + E_2 + E_3$.

4.2.1. Particle in a three-dimensional box:



A particle confined to move in a cubix box of sides 'a'. Inside the box potential energy $V = 0$, and outside it's infinite.

Inside the box, as $V=0$, the Hamiltonian can be written as: $H = H_x + H_y + H_z = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}$

So, we can use the separable sol^n.

$$E_{tot} = E_1 + E_2 + E_3$$

$$= \frac{\pi^2\hbar^2}{2ma^2}\left(n_1^2 + n_2^2 + n_3^2\right), \text{ with } n_1 = 1, 2, 3, \cdots$$
$$n_2 = 1, 2, 3, \cdots$$
$$n_3 = 1, 2, 3, \cdots$$

Energy is quantized.

Similarly, the magnitudes of particles momentum in all three directions are also quantized.

$$|p_x| = \hbar k_1 = n_1 \frac{\pi\hbar}{a}$$

$$|p_y| = \hbar k_2 = n_2 \frac{\pi\hbar}{a}$$

$$\& \; |p_z| = \hbar k_3 = n_3 \frac{\pi\hbar}{a}.$$

Note that, three quantum numbers (n_1, n_2, n_3) are needed to specify the quantization condition, corresponding to the three independent degrees of freedom i.e. 3-coordinates.

The wave-function for this particle will be:

$$\Psi(x,y,z,t) = A \sin(k_1 x) \sin(k_2 y) \sin(k_3 z)\, e^{-iE_{tot}t/\hbar}$$

for $0 < x, y, z < a$

$$= 0, \quad \text{otherwise.}$$

with the normalization constant $A = \left(\frac{2}{a}\right)^{3/2}$. [Check it!]

- The ground state, for which $n_1 = n_2 = n_3 = 1$, has energy

$$E_{111} = \frac{3\pi^2\hbar^2}{2ma^2}$$

- There are "three" first excited states, corresponding to the three different combinations of n_1, n_2, n_3, whose squares sum to 6.

$$E_{211} = E_{121} = E_{112} = \frac{6\pi^2\hbar^2}{2ma^2}$$

Note that each of the first excited states is characterized by a different wave-function, but they all have same energy eigenvalues. Whenever different states have the same energy, this energy level is said to be "degenerate."

In this example, the first excited state is three-fold (or triply) degenerate. This system has degenerate levels because of the high degree of symmetry associated with the cubic shape of the box. The degeneracy would be removed, or lifted, if the sides of the box were of unequal lengths. In fact, the higher the symmetry, the more degeneracy we find.

[Degeneracy is a direct result of symmetry which produces constant of motion. So, the existence of a constant of motion implies a degeneracy, and vice versa. This is true for classical Physics also. The classical dynamics of a particle moving in a spherically symmetric potential $V(r)$ possesses symmetry under rotations of the coordinate system. As a result, orbits differing only in their spacial orientation are degenerate, meaning that they all have the same energy. The symmetry and the degeneracy are associated with the property that the angular momentum $\vec{L}$ is a constant of the motion. The three constants L_i generate the symmetry by transforming a trajectory of a given energy into another trajectory of the same energy by means of a contact tranformation.]

For example, if we consider a particle confined in a rectangular box with edge lengths a_1, a_2, a_3, then the allowed energies will be

$$E = \frac{\pi^2\hbar^2}{2m}\left[\left(\frac{n_1}{a_1}\right)^2 + \left(\frac{n_2}{a_2}\right)^2 + \left(\frac{n_3}{a_3}\right)^2\right] \quad ; n_1, n_2, n_3 = 1, 2, 3, \cdots$$

The lowest energy occurs again for $n_1 = n_2 = n_3 = 1$. and the 1st excited level will be "non-degenerate". If a_2 or a_3 equals a_1, then the 1st excited level would be doubly degenerate and if all three are equal, the level would be triply degenerate. Thus, the higher the symmetry, the more degeneracy we find.

4.2.2 The 3D Harmonic Oscillator:

Consider a particle in 3D subject to a harmonic potential in x, y and z. Further, assume the force constants in each direction are different (this might be true for the vibrations of polyatomic molecules).

The general potential is given by

$$V(x,y,z) = \frac{1}{2}k_x x^2 + \frac{1}{2}k_y y^2 + \frac{1}{2}k_z z^2$$

$$= \frac{1}{2}m\left[\omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2\right]$$

Total Hamiltonian then can be written as $H = H_x + H_y + H_z$.

The problem separates nicely, giving us three independent harmonic oscillators.

We can write down the eigenfunctions and eigenvalues as:

$$\psi_{n_x,n_y,n_z}(x,y,z) = \left(\frac{m\omega_x}{\hbar\pi}\right)^{1/4}\left(\frac{m\omega_y}{\hbar\pi}\right)^{1/4}\left(\frac{m\omega_z}{\hbar\pi}\right)^{1/4}\cdot\frac{1}{\sqrt{2^{n_x+n_y+n_z}\,n_x!\,n_y!\,n_z!}}$$

$$\times\; H_{n_x}\left(\sqrt{\frac{m\omega_x}{\hbar}}\,x\right) H_{n_y}\left(\sqrt{\frac{m\omega_y}{\hbar}}\,y\right) H_{n_z}\left(\sqrt{\frac{m\omega_z}{\hbar}}\,z\right)$$

$$\times\; e^{-\frac{m}{2\hbar}(\omega_x x^2+\omega_y y^2+\omega_z z^2)}$$

$$E_{n_x n_y n_z} = \left(n_x+\tfrac{1}{2}\right)\hbar\omega_x + \left(n_y+\tfrac{1}{2}\right)\hbar\omega_y + \left(n_z+\tfrac{1}{2}\right)\hbar\omega_z$$

Note that, the oscillator is said to be "isotropic" if

$\omega_x = \omega_y = \omega_z = \omega$. (i.e. $k_x = k_y = k_z$)

then the energy looks like

$$E_{n_x n_y n_z} = \left(n_x+n_y+n_z+\frac{3}{2}\right)\hbar\omega.$$

- The ground state energy $E_{000} = \frac{3}{2}\hbar\omega$ is non-degenerate.
- The first excited state energy $E_{100} = E_{010} = E_{001} = \frac{5}{2}\hbar\omega$ is 3-fold degenerate.
- The 2nd excite state energy $E_{110} = E_{011} = E_{101} = E_{200} = E_{020} = E_{002} = \frac{7}{2}\hbar\omega$ is 6-fold degenerate.

In fact, we can find the degeneracy $= \frac{1}{2}(n+1)(n+2)$, where $n = n_x + n_y + n_z$.

$\Rightarrow$ Here also, if the symmetry is "broken" i.e. $k_x \neq k_y \neq k_z$, then all the states will be non-degenerate. It is possible to break some degeneracies but keep others. For example, if we choose: $\omega_x = \omega_y = \omega \neq \omega_z$, then

$$E_{n_x n_y n_z} = \hbar\omega\left(n_x+n_y+1\right) + \hbar\omega_z\left(n_z+\tfrac{1}{2}\right)$$

and we find,

$E_{000} = \hbar\omega + \frac{1}{2}\hbar\omega_z$ (non-degenerate)

$E_{100} = E_{010} = 2\hbar\omega + \frac{1}{2}\hbar\omega_z$ (2-fold degenerate)

$E_{001} = \hbar\omega + \frac{3}{2}\hbar\omega_z$ (non-degenerate)

Depending on the values of ω & ω_z, one of E_{100} (E_{010}) or E_{001} will be 1st excite state.

4.3 Angular Momentum in Quantum Mechanics:

In QM, angular momentum plays a central role in understanding the structure of atoms, as well as other quantum problems that involve rotational symmetry.

Like other observable quantities, angular momentum is described in QM by an operator (infact, a vector operator). There are several angular momentum operators in Q.M.: the total angular momentum ($\vec{J}$), the orbital angular momentum ($\vec{L}$) and the intrinsic, or spin angular momentum ($\vec{S}$). The last one has no classical analogue.

- Orbital angular momentum in QM has the same definition as the classical: $\vec{L} = \vec{r} \times \vec{p}$ where $\vec{r}$ and $\vec{p}$ are interpreted as the operators associated with position and linear momentum.
- The spin operator, $\vec{S}$, represents another type of angular momentum, associated with "intrinsic rotation" of a particle around an axis. Spin is an intrinsic property of a particle (nearly all elementary particles have spin), that is unrelated to its spatial motion. The existence of spin angular momentum is inferred from experiments, such as the "Stern-Gerlach" experiment, in which particles are observed to possess a (total) angular momentum that cannot be accounted for by orbital angular momentum alone.
- The total angular momentum $\vec{J}$ combines the both, $\vec{J} = \vec{L} + \vec{S}$.

4.3.1. Orbital angular momentum:

Consider a particle of mass m, momentum $\vec{p}$ and position vector ($\vec{r}$). In classical mechanics, we write

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

first, recall that the components of a vector cross-product can be written as:

$$(\vec{a} \times \vec{b})_i = \epsilon_{ijk} a_j b_k$$

where repeated indices are summed over and the "Levi-Civita" permutation symbol has the property:

$$\epsilon_{ijk} \epsilon_{klm} = \delta_{il}\delta_{jm} - \delta_{im}\delta_{jl}$$

and it is defined as:

$$\epsilon_{ijk} = \begin{cases} +1 & \text{if } (i,j,k) \text{ is } (1,2,3) \text{ or any even permutation of this (e.g. 2,3,1 or 3,1,2)} \\ -1 & \text{if in odd permutation of } (1,2,3) \text{ (e.g. 3,2,1 or 1,3,2)} \\ 0 & \text{if } i=j \text{ or } j=k \text{ or } k=i. \end{cases}$$

So, $\hat{L}_i = (\hat{\vec{r}} \times \hat{\vec{p}})_i$

$= \epsilon_{ijk} \hat{r}_j \hat{p}_k$

$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$

$\hat{L}_y = \hat{z}\hat{p}_x - \hat{x}\hat{p}_z = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$

$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$

In a more compact form, this can be written as a vector operator,

$$\hat{\vec{L}} = -i\hbar\left(\hat{\vec{r}} \times \hat{\vec{\nabla}}\right)$$

$\Rightarrow$ It is easy to verify that $\hat{\vec{L}}$ is Hermitian. (Check it!)

We can easily find the commutator relations between the different components of $\hat{\vec{L}}$!

$$[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z$$
$$[\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x$$
$$[\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y$$

or in general, $[\hat{L}_i, \hat{L}_j] = i\hbar\epsilon_{ijk}\hat{L}_k$

(*) As the different components of angular momentum do not commute, it is impossible to obtain definite values for all components of the angular momentum when measured simultaneously. Thus, if the system is in eigenstate of one component of the angular momentum, it will in general not be an eigenstate of either of the other two components.

Now define the operator representing the square of the magnitude of the orbital angular momentum by

$$\hat{L}^2 = \hat{\vec{L}} \cdot \hat{\vec{L}} = \hat{L}_i\hat{L}_i \quad (= \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2)$$

then

$[\hat{L}^2, \hat{L}_j] = [\hat{L}_i\hat{L}_i, \hat{L}_j]$

$= \hat{L}_i[\hat{L}_i, \hat{L}_j] + [\hat{L}_i, \hat{L}_j]\hat{L}_i$

$= i\hbar\epsilon_{ijk}\hat{L}_i\hat{L}_k + i\hbar\epsilon_{ijk}\hat{L}_k\hat{L}_i$

But, $\epsilon_{ijk}\hat{L}_k\hat{L}_i = \epsilon_{kji}\hat{L}_i\hat{L}_k$ (interchanging i and k, as there is a summation involved, interchanging them won't change the result)

$= -\epsilon_{ijk}\hat{L}_i\hat{L}_k$ (antisymmetry property of Levi-Civita)

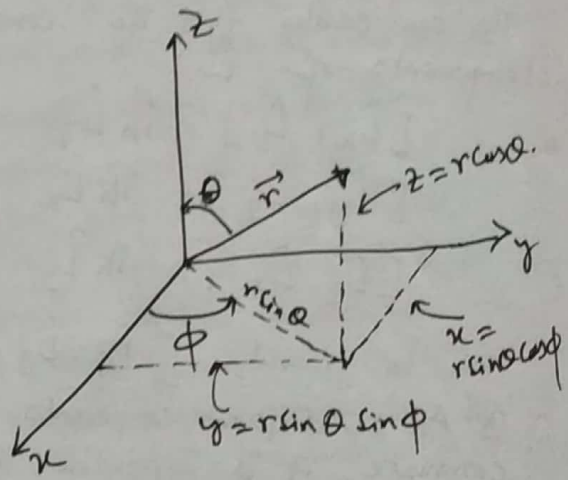
So, $[\hat{L}^2, \hat{L}_j] = 0$.

This means that one can find simultaneous eigenfunctions of $\hat{L}^2$ and each one of the components of $\vec{L}$, implying that both the magnitude of the angular momentum and one of its components can be precisely determined. Once there are known, they fully specify the angular momentum. The mutually commutating set of operators are $\hat{H}$, $\hat{L}^2$, and one component of $\hat{L}$ (typically $\hat{L}_z$, due to its simplicity in standard definition of spherical coordinates).

4.3.2. Eigenvalues and eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$:

In order to obtain the eigenvalues of $\hat{L}^2$ and $\hat{L}_z$, it is convenient to express the angular momentum operators in spherical polar coordinates: r, θ, ϕ, rather than the Cartesian coordinates. They are related as:

$$x = r\sin\theta\cos\phi$$
$$y = r\sin\theta\sin\phi$$
$$z = r\cos\theta$$



so that,

$$r = (x^2+y^2+z^2)^{1/2}$$
$$\theta = \cos^{-1} z/r$$
$$\phi = \tan^{-1} y/x$$

we have,

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

$$= \frac{x}{r}\frac{\partial}{\partial r} + \frac{xz}{r^3\sin\theta}\frac{\partial}{\partial\theta} - \frac{y}{x^2}\cos^2\phi\frac{\partial}{\partial\phi}$$

$$= \sin\theta\cos\phi\frac{\partial}{\partial r} + \frac{\cos\theta\cos\phi}{r}\frac{\partial}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi}$$

with similar expressions for $\frac{\partial}{\partial y}$ and $\frac{\partial}{\partial z}$, we can get:

$$L_x = -i\hbar\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)$$
$$L_y = -i\hbar\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$$
$$L_z = -i\hbar\frac{\partial}{\partial\phi}.$$

$r^2 = x^2+y^2+z^2$

$2r\frac{\partial r}{\partial x} = 2x$

$\Rightarrow \frac{\partial r}{\partial x} = \frac{x}{r}$

$\cos\theta = z/r$

$\Rightarrow -\sin\theta\cdot\frac{\partial\theta}{\partial x} = z\left(-\frac{1}{r^2}\right)\frac{\partial r}{\partial x}$

$\Rightarrow \sin\theta\frac{\partial\theta}{\partial x} = \frac{xz}{r^3}$

$\Rightarrow \frac{\partial\theta}{\partial x} = \frac{xz}{r^3\sin\theta}$

$\tan\phi = y/x$

$\Rightarrow \sec^2\phi\frac{\partial\phi}{\partial x} = -\frac{y}{x^2}$

$\Rightarrow \frac{\partial\phi}{\partial x} = -\frac{y}{x^2}\cos^2\phi$

$$\frac{\partial}{\partial y} = \sin\theta\sin\phi\frac{\partial}{\partial r} + \frac{1}{r}\sin\phi\cos\theta\frac{\partial}{\partial\theta} + \frac{1}{r}\frac{\cos\phi}{\sin\theta}\frac{\partial}{\partial\phi}$$
$$\frac{\partial}{\partial z} = \cos\theta\frac{\partial}{\partial r} - \frac{1}{r}\sin\theta\frac{\partial}{\partial\theta}.$$

Another way to get this:

writing the gradient in spherical coordinates:

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

Now, write the unit vectors of spherical coordinates in terms of their Cartesian components:

The radius vector is

$$\vec{r} = r\sin\theta\cos\phi\,\hat{i} + r\sin\theta\sin\phi\,\hat{j} + r\cos\theta\,\hat{k}$$

unit vectors are:

$$\hat{r} = \frac{\frac{d\vec{r}}{dr}}{\left|\frac{d\vec{r}}{dr}\right|} = \sin\theta\cos\phi\,\hat{i} + \sin\theta\sin\phi\,\hat{j} + \cos\theta\,\hat{k}$$

$$\hat{\theta} = \frac{\frac{d\vec{r}}{d\theta}}{\left|\frac{d\vec{r}}{d\theta}\right|} = \cos\theta\cos\phi\,\hat{i} + \cos\theta\sin\phi\,\hat{j} - \sin\theta\,\hat{k}$$

$$\hat{\phi} = \frac{\frac{d\vec{r}}{d\phi}}{\left|\frac{d\vec{r}}{d\phi}\right|} = \frac{1}{\left|\frac{d\vec{r}}{d\phi}\right|}\cdot\left(-r\sin\theta\sin\phi\,\hat{i} + r\sin\theta\cos\phi\,\hat{j}\right)$$

$$= \frac{-r\sin\theta\sin\phi\,\hat{i} + r\sin\theta\cos\phi\,\hat{j}}{\sqrt{r^2\sin^2\theta\sin^2\phi + r^2\sin^2\theta\cos^2\phi}}$$

$$= -\sin\phi\,\hat{i} + \cos\phi\,\hat{j}$$

Then,

$$\vec{L} = \vec{r}\times\vec{p} = -i\hbar\left(\vec{r}\times\vec{\nabla}\right)$$

$$= -i\hbar r\left(\hat{r}\times\vec{\nabla}\right)$$

$$= -i\hbar r\left[\hat{r}\times\hat{r}\frac{\partial}{\partial r} + \hat{r}\times\hat{\theta}\frac{1}{r}\frac{\partial}{\partial\theta} + \hat{r}\times\hat{\phi}\frac{1}{r\sin\theta}\frac{\partial}{\partial\phi}\right]$$

$$= -i\hbar\left[\hat{\phi}\frac{\partial}{\partial\theta} - \hat{\theta}\frac{1}{\sin\theta}\frac{\partial}{\partial\phi}\right]$$

$$\Rightarrow \vec{L} = -i\hbar\left[\hat{i}\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right) + \hat{j}\left(\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right) + \hat{k}\frac{\partial}{\partial\phi}\right]$$

So, we get,

$$\left.\begin{aligned} L_x &= -i\hbar\left(-\sin\phi\frac{\partial}{\partial\theta} - \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right) \\ L_y &= -i\hbar\left(-\cos\phi\frac{\partial}{\partial\theta} - \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right) \\ L_z &= -i\hbar\frac{\partial}{\partial\phi} \\ \vec{L}^2 &= -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \end{aligned}\right\} \quad (1)$$

- Eigenvalues of L_z :

Since, in spherical coordinates L_z depends only on ϕ, we can denote its eigenvalue by $m\hbar$ and the corresponding eigenfunctions by $\Phi_m(\phi)$. We thus have,

$$L_z\Phi_m(\phi) = m\hbar\Phi_m(\phi)$$

$$\Rightarrow -i\frac{\partial}{\partial\phi}\Phi_m(\phi) = m\Phi_m(\phi)$$

sol^n : $\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}}e^{im\phi}$, for any m.

Although the above sol^n is satisfied for any value of m, physically we require the wave function to be single valued (or continuous), namely $\Phi_m(2\pi) = \Phi_m(0)$, from which we find

$$e^{i2\pi m} = 1$$

$$\Rightarrow m = 0, \pm1, \pm2, \pm3, \cdots$$

The number m is called the "magnetic quantum number", due to the role it plays in the motion of charged particle in magnetic fields.

→ This means that, when measuring the z-component of an orbital angular momentum, one can only obtain $0, \pm\hbar, \pm2\hbar, \cdots$ Since the choice of the z-direction was arbitrary, we see that the component of the orbital angular momentum about any axis is quantized.

The wavefunctions $\Phi_m(\phi)$ are orthonormal :

$$\int_0^{2\pi}\Phi_n^*(\phi)\Phi_m(\phi)\,d\phi = \delta_{nm}$$

and they form a complete set, i.e. every function $f(\phi)$ can be written as : $f(\phi) = \sum_{m=-\infty}^{+\infty} a_m\Phi_m(\phi)$,

where the coefficients a_m are complex numbers,

• Simultaneous eigenvalues of $\vec{L}^2$ and L_z:

Let us denote simultaneous eigenfunctions of the operator $\vec{L}^2$ and L_z as $Y_{lm}(\theta, \phi)$.

We'll write the eigenvalues of $\vec{L}^2$ as $l(l+1)\hbar^2$ [the reason behind this will be clear shortly]

$$\vec{L}^2 Y_{lm}(\theta,\phi) = l(l+1)\hbar^2 Y_{lm}(\theta,\phi)$$

and $L_z Y_{lm}(\theta,\phi) = m\hbar\, Y_{lm}(\theta,\phi)$

as L_z only depends on ϕ, we can separate $Y_{lm}(\theta,\phi)$ as:

$$Y_{lm}(\theta,\phi) = \Theta_{lm}(\theta)\,\Phi_m(\phi)$$

where the functions $\Phi_m(\phi)$ are given as we found earlier,

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

So, $Y_{lm}(\theta,\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}\,\Theta_{lm}(\theta)$

Now, using the expression of $\vec{L}^2$ in spherical coordinates (eqⁿ ①'):

$$\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] Y_{lm}(\theta,\phi) = -l(l+1)\,Y_{lm}(\theta,\phi)$$

$$\Rightarrow \left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\cdot\frac{\partial^2}{\partial\phi^2}\right]\frac{1}{\sqrt{2\pi}} e^{im\phi}\,\Theta_{lm}(\theta) = -l(l+1)\frac{1}{\sqrt{2\pi}} \cdot e^{im\phi}\cdot\Theta_{lm}(\theta)$$

$$\Rightarrow \left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right] e^{im\phi}\,\Theta_{lm}(\theta) + \frac{1}{\sin^2\theta}\cdot(-m^2)\cdot e^{im\phi}\,\Theta_{lm}(\theta) = -l(l+1)\,e^{im\phi}\,\Theta_{lm}(\theta)$$

$$\Rightarrow \left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \left\{l(l+1) - \frac{m^2}{\sin^2\theta}\right\}\right]\Theta_{lm}(\theta) = 0 \quad \text{——— ②}$$

[as $e^{im\phi} \neq 0$, for $m = 0, \pm1, \pm2, \ldots$]

This eqⁿ is not easy to solve!

Now, change the variable $w = \cos\theta$ and $F_{lm}(w) = \Theta_{lm}(\theta)$

So that, $dw = -\sin\theta\, d\theta$.

and $\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) = \frac{\partial}{\partial(\cos\theta)}\left(\sin^2\theta\cdot\frac{\partial}{\partial(\cos\theta)}\right) = \frac{d}{dw}\left((1-w^2)\frac{d}{dw}\right)$

$$= (1-w^2)\frac{d^2}{dw^2} - 2w\cdot\frac{d}{dw}.$$

the eq^n becomes:

$$\left[(1-w^2)\frac{d^2}{dw^2} - 2w\frac{d}{dw} + l(l+1) - \frac{m^2}{1-w^2}\right] F_{lm}(w) = 0 \quad \text{— (3)}$$

This equation is known as the "Legendre's associated differential equation". The $m=0$ case is simply called Legendre's differential equation.

The solutions to this eq^n are given by the "associated Legendre's function," $P_l^m(w)$:

$$F_{lm}(w) = A\,P_l^m(w)$$

$$\Rightarrow \Theta_{lm}(\theta) = A\,P_l^m(\cos\theta)$$

where, $P_l^m(w)$ is defined by:

$$P_l^m(w) \equiv (1-w^2)^{|m|/2}\left(\frac{d}{dw}\right)^{|m|} P_l(w) \quad \left[\text{with } P_l^{-m} = P_l^m\right]$$

where $P_l(w)$ is known as the l^{th} Legendre polynomial, which is defined by the "Rodrigues formula":

$$P_l(w) = \frac{1}{2^l\, l!}\left(\frac{d}{dw}\right)^l (w^2-1)^l$$

[Note that, for $m=0$, $P_l^0(w) = P_l(w)$]

In order for Rodrigues formula to make sense, l must be non-negative integer! Moreover, if $|m| > l$, then we will get, $P_l^m = 0$. So, the physically accepted values of l and m are:

$$l = 0, 1, 2, \ldots$$

$$m = -l, -l+1, \ldots, -2, -1, 0, 1, 2, \ldots, l-1, l$$

for any given l, there are $(2l+1)$ possible values of m.

Wait! Eq^n (2) is a second-order differential equation, it should have two linearly-independent sol'n's. The most general solution of eq^n (3) should be:

$$F_{lm}(w) = A_1 P_l^m(w) + A_2 Q_l^m(w)$$

where, $Q_l^m(w)$ is called "Legendre function of the second kind." But they are physically unacceptable because they blow up at $\theta = 0$ and/or $\theta = \pi$ and do not yeild yield normalizable wavefunctions.

Ex: $Q_0(w) = \frac{1}{2}\ln\left(\frac{1+w}{1-w}\right)$

This result can also be understood physically. Since $\vec{L}^2 = L_x^2 + L_y^2 + L_z^2$, the expectation value of $\vec{L}^2$ in a given state ψ is $\langle \vec{L}^2 \rangle = \langle L_x^2 \rangle + \langle L_y^2 \rangle + \langle L_z^2 \rangle$. Since, L_x and L_y are Hermitian, $\langle L_x^2 \rangle \geq 0$ and $\langle L_y^2 \rangle \geq 0$, and therefore,

$$\langle \vec{L}^2 \rangle \geq \langle L_z^2 \rangle$$

$$\Rightarrow l(l+1) \geq m^2$$

$$\Rightarrow |m| \leq l.$$

The quantum number 'l' is called the "orbital angular quantum number".

- First few Legendre Polynomials: (using Rodrigues formula)

$$P_0(\omega) = 1$$

$$P_1(\omega) = \omega$$

$$P_2(\omega) = \frac{1}{2}(3\omega^2 - 1)$$

$$P_3(\omega) = \frac{1}{2}(5\omega^3 - 3\omega) \quad \ldots$$

and the first few associated Legendre's functions P_l^m are (putting $\omega = \cos\theta$)

$$P_0^0 = 1$$

$$P_1^0 = \cos\theta \qquad P_1^1 = \sin\theta$$

$$P_2^0 = \frac{1}{2}(3\cos^2\theta - 1) \qquad P_2^1 = 3\sin\theta\cos\theta. \qquad P_2^2 = 3\sin^2\theta.$$

$$P_3^0 = \frac{1}{2}(5\cos^3\theta - 3\cos\theta) \qquad P_3^1 = \frac{3}{2}\sin\theta(5\cos^2\theta - 1) \qquad P_3^2 = 15\sin^2\theta\cos\theta \ldots$$

$$\Rightarrow \text{So,} \quad \Theta_{lm}(\theta) = A P_l^m(\cos\theta)$$

$$\Rightarrow Y_{lm}(\theta,\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi} \Theta_{lm}(\theta)$$

$$= A \cdot \frac{1}{\sqrt{2\pi}} e^{im\phi} P_l^m(\cos\theta)$$

- The normalized $Y_{lm}(\theta,\phi)$ is called "spherical harmonics".

$$Y_{lm}(\theta,\phi) = (-1)^m \sqrt{\frac{(2l+1)}{4\pi} \cdot \frac{(l-|m|)!}{(l+|m|)!}}\, e^{im\phi} P_l^m(\cos\theta)$$

for $m \geq 0$

with $Y_{l,-m}(\theta,\phi) = (-1)^m Y_{lm}(\theta,\phi)$

It can be shown that,

$$\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \left[Y_{lm}(\theta,\phi)\right]^* \left[Y_{l'm'}(\theta,\phi)\right] = \delta_{ll'}\,\delta_{mm'}$$

↳ "orthonormality"

They further form a "complete set", namely, every arbitrary function $f = f(\theta,\phi)$ can be expanded as:

$$f(\theta,\phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} a_{lm}\, Y_{lm}(\theta,\phi)$$

- first few spherical harmonics:

l	m	$Y_{lm}(\theta,\phi)$
0	0	$Y_{00} = \frac{1}{\sqrt{4\pi}}$
1	0	$Y_{10} = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$
	± 1	$Y_{1,\pm1} = \mp\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta\, e^{\pm i\phi}$
2	0	$Y_{20} = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$
	± 1	$Y_{2,\pm1} = \mp\left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta\, e^{\pm i\phi}$
	± 2	$Y_{2,\pm2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta\, e^{\pm 2i\phi}$

4.3.3. The angular momentum ladder operators:

Let us study the effect of the operator L_x and L_y on the eigenfunctions Y_{lm}. For this purpose, it is convenient to introduce the two new operators:

$$L_\pm = L_x \pm iL_y$$

- These operators are "not Hermitian", but are "mutually adjoint".

$$\left.\begin{aligned} L_+^\dagger &= L_x - iL_y = L_- \\ \& \; L_-^\dagger &= L_x + iL_y = L_+ \end{aligned}\right\} \text{(We used the fact that } L_x \text{ and } L_y \text{ are Hermitian).}$$

Since both L_x and L_y commute with $\vec{L}^2$,

$$[\vec{L}^2, L_\pm] = 0$$

$$\begin{aligned} L_\pm L_\mp &= (L_x \pm iL_y)(L_x \mp iL_y) \\ &= L_x^2 + L_y^2 \mp iL_xL_y \pm iL_yL_x \\ &= \vec{L}^2 - L_z^2 \mp i(L_xL_y - L_yL_x) \\ &= \vec{L}^2 - L_z^2 \mp i.[L_x, L_y] \\ &= \vec{L}^2 - L_z^2 \mp i.i\hbar L_z \\ &= \vec{L}^2 - L_z^2 \pm \hbar L_z . \end{aligned}$$

$$\begin{aligned} [L_+, L_-] &= L_+L_- - L_-L_+ \\ &= \vec{L}^2 - L_z^2 + \hbar L_z - \vec{L}^2 + L_z^2 + \hbar L_z . \\ &= 2\hbar L_z . \end{aligned}$$

$$\begin{aligned} [L_z, L_\pm] &= [L_z, L_x] \pm i[L_z, L_y] \\ &= i\hbar L_y \pm i(-i\hbar L_x) \\ &= i\hbar L_y \pm \hbar L_x \\ &= \pm\hbar(L_x \pm iL_y) \\ &= \pm\hbar L_\pm \end{aligned}$$

We had earlier, $L_z Y_{lm}(\theta, \phi) = m\hbar Y_{lm}(\theta, \phi)$.

and $\vec{L}^2 Y_{lm}(\theta, \phi) = l(l+1)\hbar^2 Y_{lm}(\theta, \phi)$

So, $$\begin{aligned} L_z(L_\pm Y_{lm}) &= (L_zL_\pm - L_\pm L_z)Y_{lm} + L_\pm L_z Y_{lm} \\ &= \pm\hbar L_\pm Y_{lm} + m\hbar L_\pm Y_{lm} \\ &= (m \pm 1)\hbar (L_\pm Y_{lm}) \end{aligned}$$

and, $\vec{L}^2 (L_\pm Y_{lm}) = L_\pm (\vec{L}^2 Y_{lm})$ [as $L_\pm$ commute with $\vec{L}^2$]

$= l(l+1)\hbar^2 (L_\pm Y_{lm})$.

Thus, $L_\pm Y_{lm}$ is a simultaneous eigenfunction of $\vec{L}^2$ and L_z with eigenvalues $l(l+1)\hbar^2$ and $(m\pm1)\hbar$ respectively. This explains their names — "raising" and "lowering" operators.

As the raising and lowering operators change the value of m by one unit, we can write:

$$L_\pm Y_{lm} = C^{\pm}_{lm} Y_{l,m\pm1}$$

where $C^{\pm}_{lm}$ are constants, whose value we want to find. To determine this value, write $L_\pm$ in spherical polar coordinates (eqn ①):

$$L_\pm = L_x \pm iL_y$$

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

$$= \hbar (\cos\phi \pm i\sin\phi) \left(\pm \frac{\partial}{\partial\theta} \right) + i\hbar (\cos\phi \pm i\sin\phi) \times \left(\cot\theta \frac{\partial}{\partial\phi} \right)$$

$$= \hbar e^{\pm i\phi} \left[\pm \frac{\partial}{\partial\theta} + i \cot\theta \frac{\partial}{\partial\phi} \right]$$

This can be applied to $Y_{lm}(\theta,\phi)$ functions derived above.
[You might need, $(1-x^2)\frac{dP_l^m(x)}{dx} = (l+m)P_{l-1}^m(x) - lxP_l^m(x)$]
The result is:

$$L_\pm Y_{lm}(\theta,\phi) = \hbar \left[l(l+1) - m(m\pm1) \right]^{1/2} Y_{l,m\pm1}(\theta,\phi)$$

However, this calculation is not trivial! Another way to achieve this is as follows.

We have, $L_\pm L_\mp = \vec{L}^2 - L_z^2 \pm \hbar L_z$

$$\Rightarrow L_\mp L_\pm = \vec{L}^2 - L_z^2 \mp \hbar L_z .$$

Now, calculate the expectation value of $L_{\mp}L_{\pm}$ for wavefunction Y_{lm}

$$\int Y_{lm}^{*}\left(L_{\mp}L_{\pm}Y_{lm}\right)d\tau = \int Y_{lm}^{*}\left(\vec{L}^{2}-L_{z}^{2}\mp\hbar L_{z}\right)Y_{lm}\,d\tau$$

$$= \int Y_{lm}^{*}\left[\hbar^{2}l(l+1)-\hbar^{2}m^{2}\mp\hbar^{2}m\right]Y_{lm}\,d\tau$$

$$= \hbar^{2}\left[l(l+1)-m(m\pm1)\right]\int Y_{lm}^{*}Y_{lm}\,d\tau$$

$$= \hbar^{2}\left[l(l+1)-m(m\pm1)\right] \quad (\text{as } Y_{lm} \text{ are normalized})$$

$$\Rightarrow \int\left(L_{\pm}Y_{lm}\right)^{*}L_{\pm}Y_{lm}\,d\tau = \hbar^{2}\left[l(l+1)-m(m\pm1)\right]$$

$$(\text{as } (L_{\pm})^{\dagger} = L_{\mp})$$

$$\Rightarrow |C_{lm}^{\pm}|^{2}\int Y_{lm}^{*}Y_{lm}\,d\tau = \hbar^{2}\left[l(l+1)-m(m\pm1)\right]$$

$$\Rightarrow C_{lm}^{\pm} = \hbar\sqrt{l(l+1)-m(m\pm1)}$$

So, $$L_{\pm}Y_{lm} = \hbar\sqrt{l(l+1)-m(m\pm1)}\;Y_{l,m\pm1}$$

- The expectation values of $L_{\pm}$ are zero.

proof: $$\int Y_{lm}^{*}L_{\pm}Y_{lm}\,d\tau$$

$$= \hbar\sqrt{l(l+1)-m(m\pm1)}\int Y_{lm}^{*}Y_{l,m\pm1}\,d\tau$$

$$= 0 \quad \left[\text{as } \int Y_{lm}^{*}Y_{l'm'}\,d\tau = \delta_{ll'}\delta_{mm'}\right]$$

- Using $L_{x} = \frac{1}{2}(L_{+}+L_{-})$ and $L_{y} = \frac{1}{2i}(L_{+}-L_{-})$, this result implied that, $\langle L_{x}\rangle = \langle L_{y}\rangle = 0$

- Prove that, for a particle in a potential $V(\vec{r})$,

$$\frac{d}{dt}\langle\vec{L}\rangle = \langle\vec{N}\rangle \Longleftarrow \text{rotational analog to Ehrenfest's theorem.}$$

where, $\vec{N}$ is the torque, $\vec{N} = \vec{r}\times\vec{F} = \vec{r}\times(-\vec{\nabla}V)$

From that, show that, $\frac{d\langle\vec{L}\rangle}{dt} = 0$ for any spherically symmetric potential $\longrightarrow$ quantum statement of conservation of angular momentum.

Proof: from $\frac{d\langle A\rangle}{dt} = \frac{i}{\hbar}\langle [H, A]\rangle$, where A doesn't have any explicit time dependence,

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

Now, $[H, L_x] = \frac{1}{2m}[\vec{p}^2, L_x] + [V, L_x]$

$$[\vec{p}^2, L_x] = [p_x^2, L_x] + [p_y^2, L_x] + [p_z^2, L_x]$$

$$= [p_x^2, (yp_z - zp_y)] + [p_y^2, (yp_z - zp_y)] + [p_z^2, (yp_z - zp_y)]$$

($[p_x^2, (yp_z - zp_y)] = 0$)

$$= p_y[p_y, (yp_z - zp_y)] + [p_y, (yp_z - zp_y)]p_y + p_z[p_z, (yp_z - zp_y)] + [p_z, (yp_z - zp_y)]p_z$$

$$= p_y[p_y, y]p_z + [p_y, y]p_y p_z + p_z[p_z, z]p_y + [p_z, z]p_y p_z$$

(as $[p_i, p_j] = 0$)

$$= -i\hbar p_y p_z - i\hbar p_y p_z + i\hbar p_y p_z + i\hbar p_y p_z$$

$\Longleftarrow$ Similarly, $[\vec{p}^2, L_z] = [\vec{p}^2, L_y] = 0$.

$$= 0$$

Now $[V, L_x] = 0$ only for central potential, i.e. $V(\vec{r}) = V(r)$.

but in general,

$$[V, L_x] = [V, (yp_z - zp_y)]$$

$$= y[V, p_z] - z[V, p_y]$$

Now, $[V, p_z]\psi = [V, \frac{\hbar}{i}\frac{\partial}{\partial z}]\psi$

$$= V\cdot\frac{\hbar}{i}\frac{\partial\psi}{\partial z} - \frac{\hbar}{i}\frac{\partial}{\partial z}(V\psi)$$

$$= V\frac{\hbar}{i}\frac{\partial\psi}{\partial z} - V\frac{\hbar}{i}\frac{\partial\psi}{\partial z} - \frac{\hbar}{i}\frac{\partial V}{\partial z}\psi$$

$$= i\hbar\frac{\partial V}{\partial z}\psi$$

So, $[V, p_z] = i\hbar\frac{\partial V}{\partial z}$.

similarly, $[V, p_y] = i\hbar\frac{\partial V}{\partial y}$.

So, $[V, L_x] = i\hbar\left(y\frac{\partial V}{\partial z} - z\frac{\partial V}{\partial y}\right) = i\hbar[\vec{r}\times(\vec{\nabla}V)]_x$

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

$= -\langle [\vec{r} \times \vec{\nabla} V]_x \rangle$

and the same goes for other components also.

So, $\frac{d\langle \vec{L}\rangle}{dt} = \langle \vec{N}\rangle$

where, $\vec{N} = \vec{r} \times (-\vec{\nabla} V)$

Now, if $V(\vec{r}) = V(r)$, then $\vec{\nabla} V = \frac{\partial V}{\partial r}\hat{r}$

and then, $\vec{r} \times (-\vec{\nabla} V) = \vec{r} \times \left(\frac{\partial V}{\partial r}\hat{r}\right)$

$= 0$ [as $\vec{r} \times \hat{r} = 0$]

So, $\frac{d\langle \vec{L}\rangle}{dt} = 0$ for $V(\vec{r}) = V(r)$.

$\Rightarrow$ This also implies that, if the system has a rotational symmetry i.e. its potential is spherically symmetric, then the orbital angular momentum will be conserved.

4.3.4. Spin:

It is an experimental fact that many particles, and the electrons in particular, have an intrinsic angular momentum. This was originally deduced by Goudsmit and Uhlenbeck (1925) in their analysis of the famous sodium D line (arises by the transition from the $1s^2 2s^2 2p^6 3p$ excited state to the ground state) by the Zeeman effect. To explain this "fine structure" of atomic spectra, they proposed that the electron possesses an intrinsic angular momentum in addition to the orbital angular momentum (motion about the nucleus). It was originally thought that this was due to the electron spinning on its axis, and hence this intrinsic angular momentum was called "spin". However, this is not the case! A number of arguments can be put forth to disprove that classical model, and we must assume that spin is a purely quantum phenomena, without a classical analogue. This spin must be viewed as an intrinsic property like mass and charge which is particular to a given type of particle. Note that, unlike mass and charge, there is no classical analog to spin.

Spin can be described by the usual angular momentum theory. We postulate a spin operator $\vec{S}$ and corresponding eigenstates $|s\ m_s\rangle$ such that,

[Note that, I am switching to the more abstract notation for the eigenstates]

$$[S_i, S_j] = i\hbar\epsilon_{ijk} S_k$$

$$\vec{S}^2 |s\ m_s\rangle = s(s+1)\hbar^2 |s\ m_s\rangle$$

$$S_z |s\ m_s\rangle = \hbar m_s |s\ m_s\rangle$$

like,
$[L_i, L_j] = i\hbar\epsilon_{ijk} L_k$
$\vec{L}^2 |l\ m_l\rangle = l(l+1)\hbar^2 |l\ m_l\rangle$
$L_z |l\ m_l\rangle = \hbar m_l |l\ m_l\rangle$

and,

$$S_\pm |s\ m_s\rangle = \hbar\sqrt{s(s+1) - m_s(m_s \pm 1)}\ |s\ m_s \pm 1\rangle$$

where, $S_\pm = S_x \pm iS_y$

But this time, the eigenstates $|s\ m_s\rangle$ are NOT spherical harmonics, infact they are not functions of θ and ϕ at all. The s and m_s can have half-integer values as well:

$$s = 0, \frac{1}{2}, 1, \frac{3}{2}, \cdots ; \quad m_s = -s, -s+1, \cdots, s-1, s$$

Every elementary particle has a specific value of s, like π mesons have spin $s=0$, electrons, neutrons, protons have spin $\frac{1}{2}$, photons have spin 1, deltas have spin $3/2$, gravitons have spin 2 and so on. For a given particle, the quantum number s is fixed, unlike the orbital angular momentum (l).

- **Spin $\frac{1}{2}$:** All quarks, all leptons and protons, neutrons & are spin $\frac{1}{2}$ particles.

For, $s = \frac{1}{2}$, $m_s = -\frac{1}{2}, \frac{1}{2}$.

So, there are two eigenstates: $|\frac{1}{2}\ \frac{1}{2}\rangle$, which is called "spin up" ($\uparrow$)
and $|\frac{1}{2}\ -\frac{1}{2}\rangle$, which is called "spin down" ($\downarrow$).

Using these as basis vectors, the general state of a spin $\frac{1}{2}$ particle can be expressed as a two-element column matrix (known as "spinor"):

$$\chi = \begin{pmatrix} a_+ \\ a_- \end{pmatrix} = a_+\chi_+ + a_-\chi_-$$

with $\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$ [spin-up] and $\chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ [spin-down]

With this choice of basis, we can now construct the 2×2 matrix representation of the spin operator $\vec{S}$.

Note that, the states $\chi_\pm$ were specifically constructed to be the eigenstates of S_z and hence the matrix representation of S_z is diagonal with diagonal elements are precisely the eigenvalues $\pm\hbar/2$. In other words, we have: $S_z\chi_+ = \frac{\hbar}{2}\chi_+$ and $S_z\chi_- = -\frac{\hbar}{2}\chi_-$.

So, we get,

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

(We are being somewhat sloppy with notation and using the same symbol S_z to denote both the operators and its matrix representation.)

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

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

$$S_+\chi_+ = S_+\left|\tfrac{1}{2}\ \tfrac{1}{2}\right\rangle$$
$$= \hbar\sqrt{\tfrac{1}{2}\left(\tfrac{1}{2}+1\right) - \tfrac{1}{2}\left(\tfrac{1}{2}+1\right)}\ \left|\tfrac{1}{2}\ \tfrac{3}{2}\right\rangle$$
$$= 0.$$

$$S_-\chi_- = S_-\left|\tfrac{1}{2}\ -\tfrac{1}{2}\right\rangle$$
$$= \hbar\sqrt{\tfrac{1}{2}\left(\tfrac{1}{2}+1\right) + \tfrac{1}{2}\left(-\tfrac{1}{2}-1\right)}\ \left|\tfrac{1}{2}\ -\tfrac{3}{2}\right\rangle$$
$$= 0.$$

$$S_+\chi_- = S_+\left|\tfrac{1}{2}\ -\tfrac{1}{2}\right\rangle$$
$$= \hbar\sqrt{\tfrac{1}{2}\left(\tfrac{1}{2}+1\right) + \tfrac{1}{2}\left(-\tfrac{1}{2}+1\right)}\ \left|\tfrac{1}{2}\ \tfrac{1}{2}\right\rangle$$
$$= \hbar\sqrt{\tfrac{3}{4}+\tfrac{1}{4}}\ \left|\tfrac{1}{2}\ \tfrac{1}{2}\right\rangle$$
$$= \hbar\left|\tfrac{1}{2}\ \tfrac{1}{2}\right\rangle = \hbar\chi_+$$

and $S_-\chi_+ = S_-\left|\tfrac{1}{2}\ \tfrac{1}{2}\right\rangle$
$$= \hbar\sqrt{\tfrac{1}{2}\left(\tfrac{1}{2}+1\right) - \tfrac{1}{2}\left(\tfrac{1}{2}-1\right)}\ \left|\tfrac{1}{2}\ -\tfrac{1}{2}\right\rangle$$
$$= \hbar\sqrt{\tfrac{3}{4}+\tfrac{1}{4}}\ \left|\tfrac{1}{2}\ -\tfrac{1}{2}\right\rangle$$
$$= \hbar\left|\tfrac{1}{2}\ -\tfrac{1}{2}\right\rangle = \hbar\chi_-$$

Now, $S_x = \frac{1}{2}(S_+ + S_-)$ and $S_y = \frac{1}{2i}(S_+ - S_-)$

From previous relations, we can construct

$$S_+ = \hbar \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} \quad \text{and} \quad S_- = \hbar \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}$$

So, $$S_x = \frac{\hbar}{2}\left[\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}\right]$$

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

and $$S_y = \frac{\hbar}{2i}\left[\begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} - \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix}\right]$$

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

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

From these, it is easy to calculate, $\tilde{S}^2 = \tilde{S}_x^2 + \tilde{S}_y^2 + \tilde{S}_z^2$

$$\Rightarrow \tilde{S}^2 = \frac{\hbar^2}{4}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} + \frac{\hbar^2}{4}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} + \frac{\hbar^2}{4}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

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

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

It is conventional to write $\vec{S}$ in terms of the "Pauli spin matrices" $\vec{\sigma}$, defined by

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

where, $$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Notice that, S_x, S_y, S_z and S^2 are all Hermitian (as they should be, since they represent observables). On the other hand, S_+ and S_- are NOT Hermitian — evidently they are not observables.

Ex: verify Pauli matrices obey following relations:

$$[\sigma_i, \sigma_j] = 2i\epsilon_{ijk}\sigma_k \qquad \| \; [\sigma_i, \sigma_j]_+ = 2I\delta_{ij}$$

($[\,,\,]_+$ → anticommutator.)

$$\sigma_i\sigma_j = i\epsilon_{ijk}\sigma_k \quad \text{for } i \neq j$$

$$\sigma_i\sigma_j = I\delta_{ij} + i\epsilon_{ijk}\sigma_k$$

We've seen, $\chi = \begin{pmatrix} a_+ \\ a_- \end{pmatrix} = a_+\chi_+^{(z)} + a_-\chi_-^{(z)}$

From the standpoint of physics, this means that, if we have an electron (or any spin $\frac{1}{2}$ particle) in an arbitrary spin state χ, then the probability that a measurement of the z-component of spin will result in $+\hbar/2$ is $|a_+|^2$ and the probability that a measurement of the z-component of spin will yield $-\hbar/2$ is $|a_-|^2$. We can say this because we expressed χ as a linear superposition of eigenvectors of S_z.

But, we could equally well describe χ in terms of eigenvectors of S_x. How to do that?

To do so, we have to diagonalize S_x and use its eigenvectors as a new set of basis vectors for our two-dimensional spin space.

solve: $S_x\vec{v} = \lambda\vec{v}$ (λ = eigenvalue, $\vec{v}$ = eigenvectors)

characteristic eq^n:

$$\det(S_x - \lambda I) = 0$$

$$\Rightarrow \left| \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} - \lambda\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \right| = 0$$

$$\Rightarrow \begin{vmatrix} -\lambda & \hbar/2 \\ \frac{\hbar}{2} & -\lambda \end{vmatrix} = 0$$

$$\Rightarrow \lambda^2 - \hbar^2/4 = 0$$

$\lambda_\pm = \pm\hbar/2$. (as we should expect)

eigenvector corresponding to $\lambda_+ = +\hbar/2$,

$$(S_x - \lambda_+ I)\vec{v} = 0$$

$$\Rightarrow \frac{\hbar}{2}\begin{pmatrix} -1 & 1 \\ 1 & -1 \end{pmatrix}\begin{pmatrix} a \\ b \end{pmatrix} = 0 \qquad \left[\text{say } \vec{v} = \begin{pmatrix} a \\ b \end{pmatrix}\right]$$

$\Rightarrow -a+b=0 \Rightarrow a=b$

So, the normalized eigenvector is: (denote as $\chi_+^{(x)}$)

$$\chi_+^{(x)} = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix}$$

for $\lambda_- = -\hbar/2$, we have similarly,

$$(S_x - \lambda_- I)\vec{v} = 0$$

$$\Rightarrow \frac{\hbar}{2}\begin{pmatrix}1 & 1\\ 1 & 1\end{pmatrix}\begin{pmatrix}c\\ d\end{pmatrix} = 0$$

$$\Rightarrow c = -d$$

normalized eigenvector (denote as $\chi_-^{(x)}$):

$$\chi_-^{(x)} = \frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix}$$

Now we can express any arbitrary spin state χ in this new (S_x basis) basis as:

$$\chi = \begin{pmatrix}b_+\\ b_-\end{pmatrix} = b_+\chi_+^{(x)} + b_-\chi_-^{(x)}$$

in the S_z basis, we had,

$$\chi = \begin{pmatrix}a_+\\ a_-\end{pmatrix} = a_+\chi_+^{(z)} + a_-\chi_-^{(z)}$$

So, there should be a relation between those coefficients:

$$\chi = \begin{pmatrix}a_+\\ a_-\end{pmatrix} = \begin{pmatrix}b_+\\ b_-\end{pmatrix} = b_+\frac{1}{\sqrt{2}}\begin{pmatrix}1\\1\end{pmatrix} + b_-\frac{1}{\sqrt{2}}\begin{pmatrix}1\\-1\end{pmatrix}$$

(as they represent the same state)

$$= \begin{pmatrix}\frac{b_+}{\sqrt{2}} + \frac{b_-}{\sqrt{2}}\\ \frac{b_+}{\sqrt{2}} - \frac{b_-}{\sqrt{2}}\end{pmatrix}$$

So, $a_+ = \frac{b_+}{\sqrt{2}} + \frac{b_-}{\sqrt{2}}$ and $a_- = \frac{b_+}{\sqrt{2}} - \frac{b_-}{\sqrt{2}}$

Solving b_+ and b_- in terms of a_+ and a_- gives:

$$b_+ = \frac{1}{\sqrt{2}}(a_+ + a_-) \text{ and } b_- = \frac{1}{\sqrt{2}}(a_+ - a_-)$$

so that, $\chi = \left(\frac{a_+ + a_-}{\sqrt{2}}\right)\chi_+^{(x)} + \left(\frac{a_+ - a_-}{\sqrt{2}}\right)\chi_-^{(x)}$.

$\Rightarrow$ Thus, the probability of measuring the x-component of spin to be $+\hbar/2$ is $|a_+ + a_-|^2/2$ and the probability of getting the value to be $-\hbar/2$ is $|a_+ - a_-|^2/2$.

4.4 Schrödinger Equation in Spherical Coordinates

The generalized 3D Schrödinger eq^n:

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

where, $\Psi \equiv \Psi(\vec{r},t)$ with $\int |\Psi|^2 d^3\vec{r} = 1$

where, $d^3\vec{r} = dx\,dy\,dz$

If the potential is independent of time, there will be a complete set of stationary states,

$$\Psi_n(\vec{r},t) = \psi_n(\vec{r})\, e^{-iE_n t/\hbar}$$

with the spacial part ψ_n satisfies the time-independent Schrödinger eq^n:

$$-\frac{\hbar^2}{2m}\vec{\nabla}^2\psi_n + V\psi_n = E_n\psi_n$$

The general solution to the time-dependent Schrödinger eq^n is:

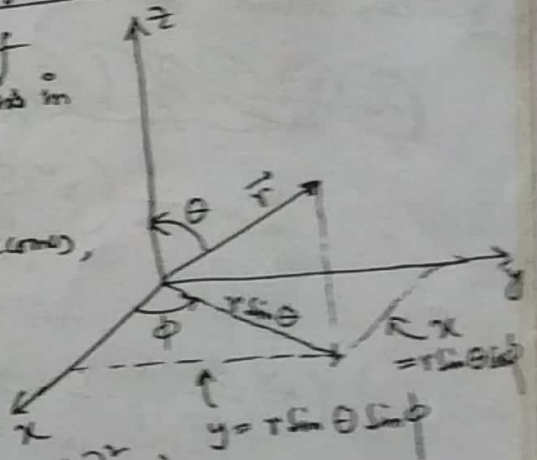
$$\Psi(\vec{r},t) = \sum C_n \psi_n(\vec{r})\, e^{-iE_n t/\hbar}$$

with constant C_n determined by the initial wave function $\Psi(\vec{r},0)$

If the potential admits continuum states, then this sum becomes an integral.

In 3-D cartesian, $\vec{\nabla}^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$.

Now, if the potential is "central", namely $V(\vec{r}) = V(r)$, this means that the potential is spherically symmetric and is not a function of θ or ϕ. In this type of systems, the best way to represent it is in spherical coordinates (r, θ, ϕ).



In spherical coordinates, the Laplacian becomes,

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

Comparing to the representation of $\vec{L}^2$ in spherical coordinates (eq^n ①) in the previous section, we can write:

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

Thus, we can write the Hamiltonian as:

$$\hat{H}=-\frac{\hbar^2}{2m}\vec{\nabla}^2+V(r)$$

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

Note that, all the angular momentum operators L_x, L_y, L_z and $\vec{L}^2$ do not operate on the radial variable r. (see eq^n ①).

This means that, $\left[\hat{L}_i, \hat{V}(r)\right]=0$

and $\left[\hat{H}, \hat{L}_i\right]=\left[\hat{H}, \hat{\vec{L}}^2\right]=0$

Thus, it is possible to obtain solutions to the Schrödinger eq^n which are common eigenfunctions of $\hat{H}$, $\vec{L}^2$ and L_z.

We already know simultaneous eigenfunctions of $\vec{L}^2$ and L_z, they are the spherical harmonics $Y_{lm}(\theta,\phi)$. So, we can now apply the seperation of variable technique to solve the Schrödinger eq^n: $\psi(r,\theta,\phi)=R(r)\,Y_{lm}(\theta,\phi)$

Using the fact that, $\vec{L}^2Y_{lm}(\theta,\phi)=l(l+1)\hbar^2Y_{lm}(\theta,\phi)$, we can obtain the radial equation:

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

($E \equiv$ seperation const.)

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

This eq^n simplifies if we change variables: $u(r)=rR(r)$

so that, $R=u/r$

$$\frac{dR}{dr}=-\frac{u}{r^2}+\frac{1}{r}\frac{du}{dr}=\frac{1}{r^2}\left[r\frac{du}{dr}-u\right]$$

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

Hence,

$$\frac{r\,d^2u}{dr^2} - \frac{2mr^2}{\hbar^2}V(r)\frac{u}{r} + \frac{2mr^2}{\hbar^2}E\cdot\frac{u}{r} = l(l+1)\cdot\frac{u}{r}$$

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

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

This is called the radial equation, which is identical in form to the one-dimensional Schrödinger eq^n, except that the effective potential,

$$V_{eff}(r) = V(r) + \frac{\hbar^2}{2mr^2}l(l+1)$$

The extra term $\frac{\hbar^2}{2mr^2}l(l+1)$ is called "centrifugal term". It tends to throw the particle outward (away from the origin), just like the repulsive centrifugal pseudo-force in classical mechanics.

We cannot proceed further until a specific potential is provided.

To be physically acceptable, the whole wave function must be square-integrable and normalized to 1:

$$\int_0^\infty dr\, r^2 \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi\, |\psi(r,\theta,\phi)|^2 = 1.$$

We already know that, the spherical part $Y_{lm}(\theta,\phi)$ is normalized, i.e. $\int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi\, |Y_{lm}(\theta,\phi)|^2 = 1$.

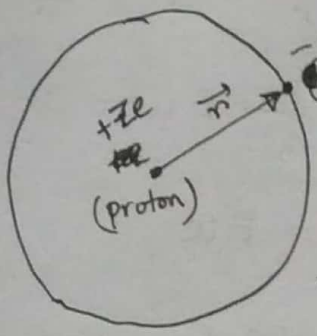
Thus, the radial part must satisfy:

$$\int_0^\infty dr\, r^2 |R(r)|^2 = 1$$

or, $$\int_0^\infty dr\, |u(r)|^2 = 1.$$

Now, we must provide the boundary condition at $r=0$. But, $R(r) = u(r)/r$ and $R(r)$ must remain finite at $r=0$ for a physically acceptable solution, so this implies that, we must have, $u(r=0) = 0$. as our boundary condition.

4.5. The Hydrogen-like Atom :



The object of interest is the orbiting electron, with its mass m_e and charge $-e$, bound by the force of electrostatic attraction to the nucleus, with its much larger mass M and charge $+Ze$, where Z is the atomic number.

$Z = 1$ describes the hydrogen atom, while for singly ionized helium (He^+) and doubly ionized lithium (Li^{++}), we take $Z = 2$ and $Z = 3$ respectively, and so on.

Ions with only one electron are called "Hydrogenlike atoms" (e.g. He^+, Li^{++} etc.).

As $M \gg m_e$, we will assume that the nucleus does not move by simply exerts the attractive force that binds the electron. This force is the Coulomb force, with its associated potential energy :

$$V(r) = \frac{k(+Ze)(-e)}{r} = -\frac{kZe^2}{r}$$

where k is the coulomb constant ($= \frac{1}{4\pi\varepsilon_0}$ in SI unit)

We've already seen for two-particle system, Hamiltonian in 3D can be written as: $H = -\frac{\hbar^2}{2\mu}\vec{\nabla}_r^2 - \frac{\hbar^2}{2m_{tot}}\vec{\nabla}_R^2 + V(\vec{r})$

where $\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{M}$ & $m_{tot} = m_e + M$

But in this case, as $M \gg m_e$ & the centre of mass doesn't move, we have, $\mu = m_e$ & $H \approx -\frac{\hbar^2}{2m_e}\vec{\nabla}_r^2 + V(\vec{r})$

The hydrogen atom constitutes a central force problem, so the the stationary states can be described as :

$$\Psi(r, \theta, \phi) = R(r)\, Y_{lm_l}(\theta, \phi)$$

where $Y_{lm_l}(\theta, \phi)$ are the spherical harmonics and the radial wavefunction $R(r)$ satisfies :

$$-\frac{\hbar^2}{2m}\frac{d^2u(r)}{dr^2} + V_{eff}(r)\,u(r) = E\,u(r)$$

where, $u(r) = r\,R(r)$ & the effective potential energy,

$$V_{eff} = \frac{l(l+1)\hbar^2}{2mr^2} + V(r) = \frac{l(l+1)\hbar^2}{2mr^2} - \frac{kZe^2}{r}$$

Our problem is to solve this eq^n for $U(r)$ and determine the allowed electron energy E. This eq^n can be solved using the series-solution method we used for Harmonic oscillator. Incidentally, the Coulomb potential admits the continuum states ($E>0$), describing electron-proton scattering, as well as discrete bound state ($E<0$), representing the hydrogen-like atoms. We will only consider the bound state solution for our purposes.

The solution to this eq^n can be found in terms of "associated Laguerre polynomial" and it is beyond the scope of this lecture note.

Acceptable wavefunctions can be found only if the energy E is restricted to be one of the following values:

$$E_n = -\frac{ke^2}{2a_0}\left[\frac{Z^2}{n^2}\right] = -13.6\ eV\left[\frac{Z^2}{n^2}\right], \quad \boxed{n = 1, 2, 3, \cdots}$$

$a_0 = \dfrac{\hbar^2}{m_e k e^2}$ is the "Bohr radius", $0.529\ \text{Å}$

and $\dfrac{ke^2}{2a_0}$ is the "Rydberg energy", $13.6\ eV$.

The integer n is called the "principal quantum number". Although, n can be any positive integer, the orbital quantum number (L) now is limited to values less than n, i.e.,

$$\boxed{l = 0, 1, 2, \cdots, (n-1)}$$

The quantum numbers n, l and m_l are associated with the observables E, $|\vec{L}|$, and L_z respectively.

$\Rightarrow$ For each l, there are $(2l+1)$ possible values of m_l, so the total degeneracy of the energy level E_n is:

$$d(n) = \sum_{l=0}^{n-1}(2l+1) = n^2$$

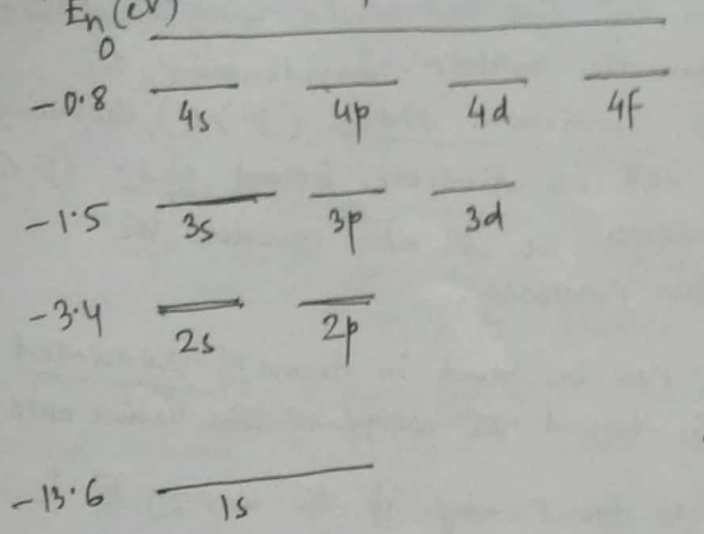
e.g., for $n=2$, $l=0$ & 1. Then we've: (for hydrogen atom; $Z=1$)

$n=2,\ l=0,\ m_l=0$
$l=1,\ m_l=-1$
$m_l=0$
$m_l=+1$

} total $2^2 = 4$ no. of states. but they all have same energy $E_2 = -13.6\left[\frac{1}{2^2}\right]eV = -3.4\ eV$.

In the spectroscopic notation, the letters K, L, M, ... are assigned to denote the states with $n=1, 2, 3, \cdots$ and the letters s, p, d, f, ... are used to denote states with $l = 0, 1, 2, 3, \cdots$

Energy-level diagram of atomic hydrogen:



- The radial wavefunction $R(r)$ for hydrogen-like atoms can be calculated as the products of exponentials with polynomials in r/a_0:

n	l	$R_{nl}(r)$
1	0	$\left(\frac{Z}{a_0}\right)^{3/2} 2e^{-Zr/a_0}$ → ground-state
2	0	$\left(\frac{Z}{2a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right)e^{-Zr/2a_0}$
2	1	$\left(\frac{Z}{2a_0}\right)^{3/2}\frac{Zr}{\sqrt{3}\,a_0}e^{-Zr/2a_0}$

- Ground-state of hydrogen-like atoms:

$n=1,\ l=0,\ m_l=0$

$E_1 = (-13.6\ \text{eV})Z^2$

wavefunction for ground state

$$\psi_{100} = R_{10}(r)\,Y_{00} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$$

(as $Y_{00} = \frac{1}{\sqrt{4\pi}}$)

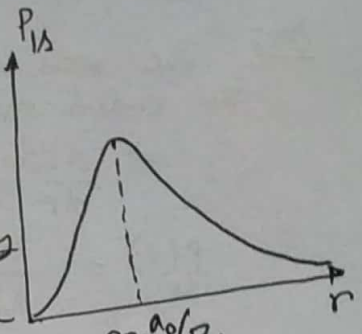
as ψ_{100} doesn't depend on angle, since $Y_{00} = \frac{1}{\sqrt{4\pi}}$, $l=0$ waves or all s-state waves are spherically symmetric ($R(r)$ doesn't depend on angle, as we know).

⇒ radial probability distribution, with its associated density $P(r)$, is defined such that $P(r)dr$ is the probability of finding the electron anywhere in the spherical shell of radius r and thickness dr, so we have:

$P(r)\,dr = |\psi|^2 4\pi r^2 dr$ [as the shell volume is its surface area $4\pi r^2$, multiplied by the shell thickness dr]

for the hydrogen-like 1s state,

$$P_{1s}(r) = |\psi_{100}|^2 4\pi r^2$$
$$= \frac{4Z^3}{a_0^3} r^2 e^{-2Zr/a_0}$$



$P(r)$ may be loosely interpreted as the probability of finding the electron at distance r from the center, i.e. nucleus, irrespective of its angular position. Thus the peak of the curve for P_{1s} vs r represents the most probable distance of the 1s electron from nucleus.

Furthermore, the normalization condition becomes,

$$\int_0^\infty P(r)\,dr = 1$$ ← integral is taken over all possible values of r from 0 to ∞.

The average distance of the electron from the nucleus is found by weighting each possible distance with the probability density at that distance:

$$\langle r \rangle = \int_0^\infty r\,P(r)\,dr.$$

[infact, the average value of any function of distance $F(r)$ is obtained from $\langle f \rangle = \int_0^\infty f(r)\,P(r)\,dr$

Problem 1: Calculate the probability that the electron in the ground state of hydrogen atom will be found outside the 1st Bohr radius.

Ans: with $Z = 1$ for hydrogen atom, the required probability will be:

$$P = \frac{4}{a_0^3} \int_{a_0}^\infty r^2 e^{-2r/a_0} dr$$

put the integral in dimensionless form by substituting

$z = 2r/a_0 \Rightarrow dr = \frac{a_0}{2} dz$ and $z = 2$, when $r = a_0$.

$$P = \frac{4}{a_0^3} \int_2^\infty \frac{a_0^2}{4} \cdot z^2 e^{-z} \cdot \left(\frac{a_0}{2}\right) dz = \frac{1}{2} \int_2^\infty z^2 e^{-z} dz$$

$$= \frac{1}{2}\left[\left(-z^2 e^{-z}\right)\Big|_2^\infty + \int_2^\infty 2z\,e^{-z}\right] = \frac{1}{2}\left[\left(-z^2 e^{-z}\right)\Big|_2^\infty - 2\left(z e^{-z}\right)\Big|_2^\infty + 2\int_2^\infty e^{-z}\right]$$

$$= -\frac{1}{2}\left[z^2 + 2z + 2\right] e^{-z}\Big|_2^\infty = 5e^{-2} \simeq 0.677 \text{ or } 67.7\%.$$

● **Problem 2**: Calculate the most probable distance of electron from the nucleus in the ground state of hydrogen, and compare this with the average distance.

Ans: The most probable distance is the value of r for which the radial probability $P(r)$ is maximum.

$$\Rightarrow \frac{dP(r)}{dr} = 0$$

$$P_{1s}(r) = \frac{4}{a_0^3} r^2 e^{-2r/a_0}$$

$$\frac{dP(r)}{dr} = \frac{4}{a_0^3} \frac{d}{dr}\left[r^2 e^{-2r/a_0}\right]$$

$$= \frac{4}{a_0^3} e^{-2r/a_0}\left[2r - \frac{2r^2}{a_0}\right] = 0$$

$$\Rightarrow \frac{4}{a_0} e^{-2r/a_0} \cdot 2r\left(1 - \frac{r}{a_0}\right) = 0$$

Now for $r=0$, we get $P_{1s}(r=0) = 0$, so it is a minimum of $P_{1s}(r)$

So, the most probable distance, $r = a_0$.

The average distance is obtained from:

$$\langle r \rangle = \frac{4}{a_0^3} \int_0^\infty r^3 e^{-2r/a_0} dr$$

again, substitute $z = 2r/a_0$

$$\langle r \rangle = \frac{a_0}{4} \int_0^\infty z^3 e^{-z} dz$$

One can use the formula: $\int_0^\infty z^n e^{-z} dz = n!$

[or more general case: $\int_0^\infty z^n e^{-az} dz = \frac{n!}{a^{n+1}}$]

So, $\langle r \rangle = \frac{a_0}{4}(3!) = \frac{3}{2} a_0 = 1.5\, a_0$

So, the average distance is 1.5 × the Bohr radius.

[The most probable and average distance is not the same, as the curve for $P(r)$ is not symmetric about a_0]

Similarly, it can be shown that, $\langle r^2 \rangle = 3a_0^2$