

Key Concepts

1. 3D QM: Hydrogen Atom
2. Intro to Orbital Angular Momentum

Example 3: Hydrogen Atom in QM

Recall the Spherical Box Problem with $V = \infty$ for $x \geq a$. We had 3 Diff. Eqs to solve:

1.
$$\frac{d^2\Phi}{d\phi^2} - m^2\Phi = 0$$
2.
$$-\frac{1}{\sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d\Theta}{d\theta} \right) + \frac{m^2\Theta}{\sin^2\theta} = l(l+1)\Theta$$
3.
$$\frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{2MEr^2R}{\hbar^2} = l(l+1)R$$

with solutions:

$$\psi(r, \theta, \phi) = A_{nl} j_l(kr) Y_l^m(\theta, \phi)$$

Look at form of $j_l(kr)$ and Energy Spectrum as shown in Text.

$$j_0(z) = \frac{\sin z}{z}$$

$$j_1(z) = \frac{\sin z}{z^2} - \frac{\cos z}{z}$$

$$j_2(z) = \left(\frac{3}{z^3} - \frac{1}{z} \right) \sin z - \frac{3}{z^2} \cos z,$$

Note: Form of $Y_l^m(\theta, \phi)$ solution requires l to be positive integers $l = 0, 1, 2, \dots$ and m to be integers between $-l$ and l , i.e.

$$m = -l, (-l + 1), \dots, 0, 1, \dots, (l - 1), l.$$

| | |
|--|--|
| $Y_0^0 = \left(\frac{1}{4\pi}\right)^{1/2}$ | $Y_2^{\pm 2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{\pm 2i\phi}$ |
| $Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$ | $Y_3^0 = \left(\frac{7}{16\pi}\right)^{1/2} (5\cos^3\theta - 3\cos\theta)$ |
| $Y_1^{\pm 1} = \mp \left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{\pm i\phi}$ | $Y_3^{\pm 1} = \mp \left(\frac{21}{64\pi}\right)^{1/2} \sin\theta (5\cos^2\theta - 1) e^{\pm i\phi}$ |
| $Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$ | $Y_3^{\pm 2} = \left(\frac{105}{32\pi}\right)^{1/2} \sin^2\theta \cos\theta e^{\pm 2i\phi}$ |
| $Y_2^{\pm 1} = \mp \left(\frac{15}{8\pi}\right)^{1/2} \sin\theta \cos\theta e^{\pm i\phi}$ | $Y_3^{\pm 3} = \mp \left(\frac{35}{64\pi}\right)^{1/2} \sin^3\theta e^{\pm 3i\phi}$ |

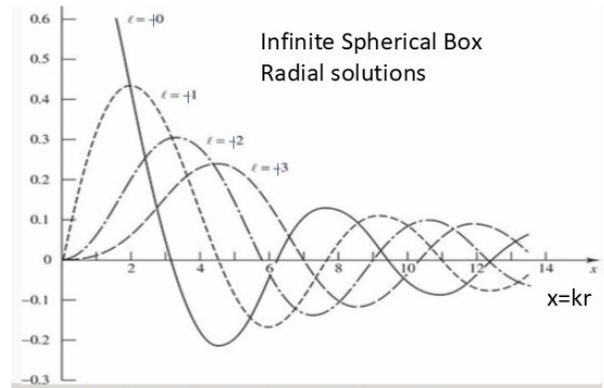
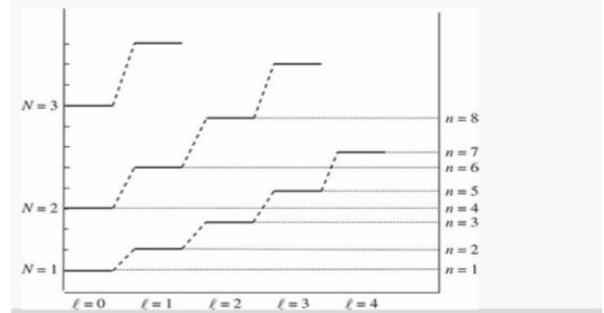


Figure 4.2: Graphs of the first four spherical Bessel functions.



Now let's consider the **Hydrogen Atom** - an electron bound by the Coulomb force to a proton with

$$V(r) = -\frac{1}{r} \left(\frac{e^2}{4\pi\epsilon_0} \right)$$

Since $V(r) < 0$ there are both scattering states (with $E > 0$) and bound states (with $E < 0$). We will consider only the bound states, which defines a **Hydrogen Atom**

To solve, we'll again look for separable solutions:

$$\psi(r, \theta, \phi) = A_{nl} \mathbb{R}(r) \Theta(\theta) \Phi(\phi)$$

Since $V = V(r)$ is a function of r only, the angular eigenstates are the same as the spherical box problem: $\Theta(\theta)\Phi(\phi) = Y_l^m(\theta, \phi)$, but the radial Differential Equation has a different $V(r)$.

The full solution (see text) has radial solutions composed of exponentials and polynomials in terms of r/a_0 :

$$\mathbb{R}_{nl}(r) = a_0^{\frac{-3}{2}} \left(\frac{2r}{na_0} \right)^l e^{-\frac{r}{na_0}} \mathbb{L}_{nl}(2r/na_0)$$

where \mathbb{L}_{nl} are the Laguerre Polynomials and

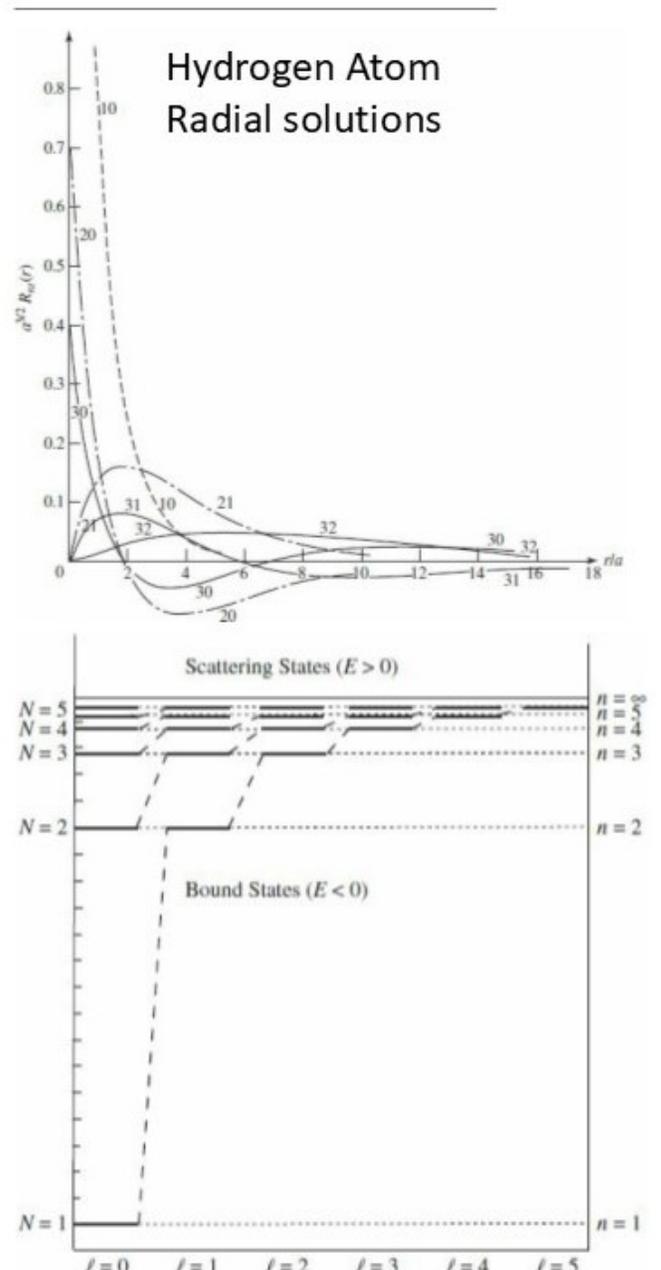
$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = \text{Bohr radius} = 5.29 \times 10^{-11} m$$

Plugging the radial solution into the differential equation #3 above gives the Eigenenergies:

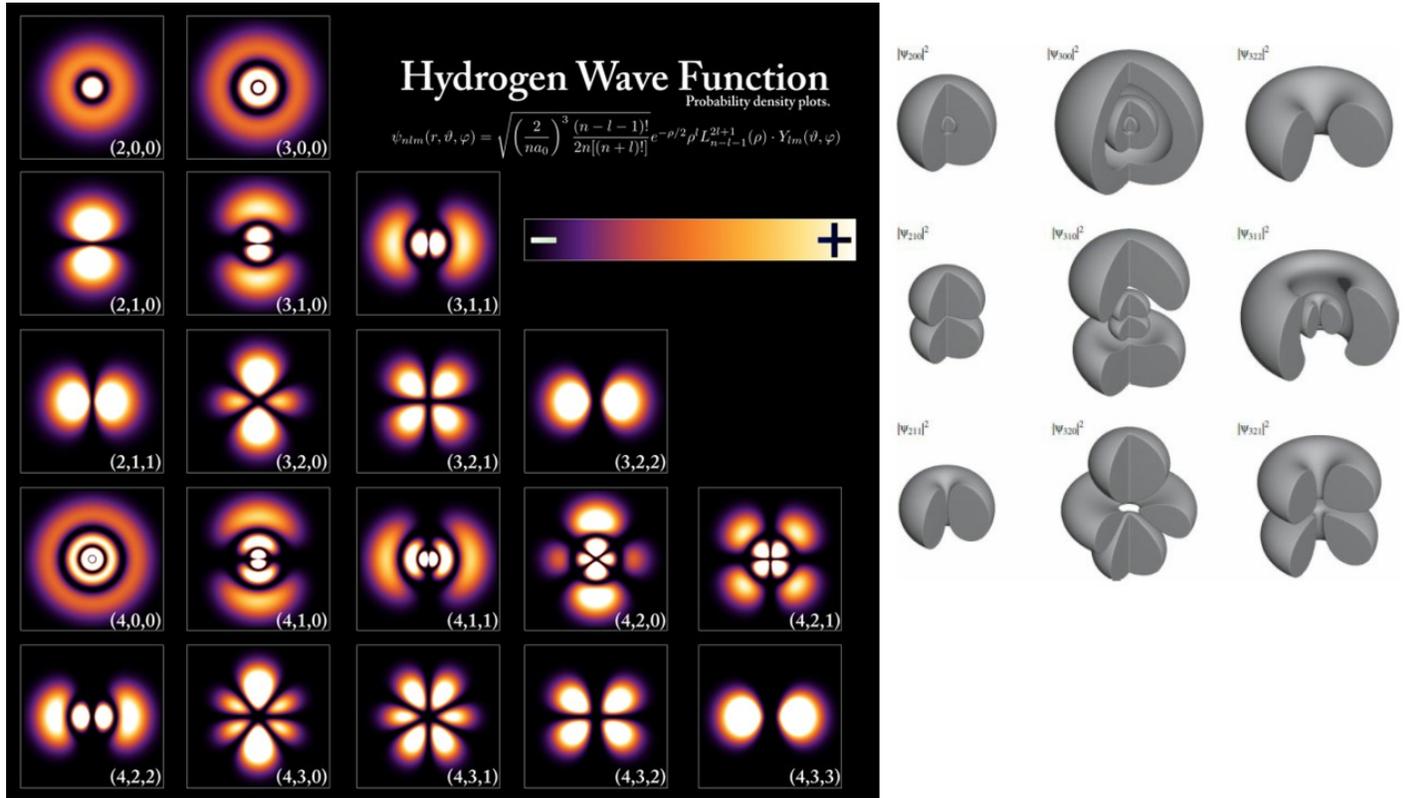
$$E_n = - \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{m}{2\hbar^2} \left(\frac{1}{n^2} \right) = \frac{-\hbar^2}{2a_0^2 m_e} \left(\frac{1}{n^2} \right)$$

\therefore Energy to remove an electron in the ground state is the Ionization Energy: $E_1 = -13.6eV$

The radial wave functions for Hydrogen and the energy levels are shown on the right. Note that the allowed l values are $0, 1, 2, \dots, n-1$



Now let's look at Hydrogen Solns. in both 2D and 3D:



Orbital Angular Momentum \hat{L}

Classically $\vec{L} = \vec{r} \times \vec{p}$ with e.g., $L_x = yp_z - zp_y$.

We can use the correspondence principle (“expectation values of Quantum operators obey classical eqs.”) to infer, e.g.:

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

or

$$\hat{L} = -i\hbar \hat{r} \times \hat{\nabla} = \hat{L}_x \hat{i} + \hat{L}_y \hat{j} + \hat{L}_z \hat{k}$$

where $\hat{i}, \hat{j}, \hat{k}$ are unit vectors in x, y, z direction. Can also show that \hat{L} is Hermitian since \hat{r} and \hat{p} are Hermitian

First let's find the Eigenstates of Orbital Angular Momentum

(skipped most of stuff between ***** in Lecture - just if you're interested in the "proof")

We will show that the 3-D Hamiltonian: $\hat{H} = \frac{\hat{p}^2}{2m} + V(|\vec{r}|)$ can be re-written in terms of \hat{L}^2
Starting with

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2 = (\hat{r} \times \hat{p})^2 \quad \text{can show that } \hat{L}^2 = \hat{r}^2 \hat{p}^2 - (\hat{r} \cdot \hat{p})^2 + i\hbar \hat{r} \cdot \hat{p} \quad \text{Eq A}$$

Then for middle term we can re-write it via

$$\hat{r} \cdot \hat{p} = -i\hbar \vec{r} \cdot \nabla$$

then noting that

$$\hat{r} = r \vec{a}_r \text{ and } \hat{\nabla} = \vec{a}_r \frac{\partial}{\partial r} + \vec{a}_\theta \frac{1}{r} \frac{\partial}{\partial \theta} + \vec{a}_\phi \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi}, \text{ where } \vec{a}_i \text{ are unit vectors}$$

we have

$$\hat{r} \cdot \hat{p} = -i\hbar r \frac{\partial}{\partial r} \text{ and then } (\vec{r} \cdot \vec{p})^2 = -\hbar^2 r \frac{\partial}{\partial r} \left(r \frac{\partial}{\partial r} \right) = -\hbar^2 r \left(\frac{\partial}{\partial r} + r \frac{\partial^2}{\partial r^2} \right)$$

Now using Eq. A above we can rewrite:

$$\hat{p}^2 = \frac{L^2 + (\hat{r} \cdot \hat{p})^2 - i\hbar \vec{r} \cdot \vec{p}}{r^2} = -\hbar^2 \left[\frac{r \frac{\partial}{\partial r} + r^2 \frac{\partial^2}{\partial r^2} + r \frac{\partial}{\partial r}}{r^2} \right] + \frac{\vec{L}^2}{r^2} = -\hbar^2 \left[\frac{2}{r} \frac{\partial}{\partial r} + \frac{\partial^2}{\partial r^2} \right] + \frac{\vec{L}^2}{r^2}$$

then recalling form for $\hat{\nabla}^2$ in spherical coordinates:

$$p^2 = -\hbar^2 \hat{\nabla}^2 = -\hbar^2 \left\{ \underbrace{\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right)} + \frac{1}{r^2} \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \right\}$$

and noting that the first term above can be rewritten as

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) = \frac{1}{r^2} \left(2r \frac{\partial}{\partial r} + r^2 \frac{\partial^2}{\partial r^2} \right) = \frac{2}{r} \frac{\partial}{\partial r} + \frac{\partial^2}{\partial r^2}$$

we then discover that

$$\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] !$$

Thus the eigenvalue equation for \hat{L}^2 is

$$\hat{L}^2 \psi_{L^2} = l(l+1)\hbar^2 \psi_{L^2}, \text{ where } B \text{ is some constant}$$

which is the same as the separated angular equation from last week, where we found that the eigenstates were the $Y_l^m(\theta, \phi)$ s.

Thus the eigenstates of \hat{L}^2 are clearly the $Y_l^m(\theta, \phi)$ s.

This also gives us for \hat{p}^2 :

$$\hat{p}^2 = -\frac{\hbar^2}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{\hat{L}^2}{r^2}$$

and finally we can express \hat{H} in terms of \hat{L}^2 which we implied earlier:

$$\hat{H} = -\frac{\hbar^2}{2Mr^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{\hat{L}^2}{2Mr^2} + V(|\vec{r}|) \quad \text{recall orbits from Ph1a}$$

Key Concepts

1. Physics of Angular Momentum in QM
2. Math of Angular Momentum in QM

Physics Facts

1. Angular momentum is a conserved quantity if $\hat{H} \neq \hat{H}(\theta, \phi)$
If space is isotropic then \hat{H} doesn't change if we rotate coordinate system by a small angle $\Delta\phi$ about some axis (say \hat{z}).
2. We can construct a rotation operator, \hat{R} , such that $\hat{R}(\Delta\phi)\psi(\phi) = \psi(\phi + \Delta\phi)$ where $\Delta\phi$ is a rotation about the z-axis.
 $\Rightarrow \hat{R}(\Delta\phi) = e^{-\frac{i\Delta\phi\hat{L}_z}{\hbar}}$; where \hat{L}_z is an angular momentum operator.
3. There exists two kinds of angular momentum: orbital (\hat{L}) and intrinsic spin (\hat{S}) [\hat{S} is intrinsic angular momentum \rightarrow a property of particles - more later].
We sometimes also refer to total angular momentum \hat{J} : $\hat{J} = \hat{L} + \hat{S}$
4. Lots of Commutation Relations for Angular Momentum

We can work out some of the relations for components of the \hat{L} , for example:

$$[\hat{L}_x, \hat{x}] = [\hat{y}\hat{p}_z - \hat{z}\hat{p}_y, \hat{x}] = 0 = [\hat{L}_y, \hat{y}] = [\hat{L}_z, \hat{z}]$$

while

$$[\hat{L}_x, \hat{y}] = [\hat{y}\hat{p}_z, \hat{y}] - [\hat{z}\hat{p}_y, \hat{y}] = -\hat{z}[\hat{p}_y, \hat{y}]$$

since \hat{y} clearly commutes with \hat{y} and \hat{p}_z . Thus we have:

$$[\hat{L}_x, \hat{y}] = i\hbar\hat{z} \quad , \quad \text{since } [\hat{y}, \hat{p}_y] = i\hbar$$

and similarly for \hat{L}_y, \hat{L}_z , e.g.

$$[\hat{L}_y, \hat{x}] = [\hat{z}\hat{p}_x, \hat{x}] - [\hat{x}\hat{p}_z, \hat{x}] = \hat{z}[\hat{p}_x, \hat{x}] = -i\hbar\hat{z}$$

Likewise for $[\hat{L}_x, \hat{p}_y] = i\hbar\hat{p}_z$; although clearly we have $[\hat{L}_x, \hat{p}_x] = 0$. Thus e.g.,

$$\begin{aligned} [\hat{L}_x, \hat{L}_y] &= [\hat{L}_x, \hat{z}\hat{p}_x] - [\hat{L}_x, \hat{x}\hat{p}_z] \\ &= \hat{p}_x[\hat{L}_x, \hat{z}] - \hat{x}[\hat{L}_x, \hat{p}_z] \\ &= \hat{p}_x(-i\hbar\hat{y}) - \hat{x}(-i\hbar\hat{p}_y) \\ &= i\hbar(\hat{x}\hat{p}_y - \hat{y}\hat{p}_x) = i\hbar\hat{L}_z \end{aligned}$$

and in general

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

where ϵ_{ijk} is the totally antisymmetric unit tensor, defined as

$$\epsilon_{xyz} = \epsilon_{zxy} = \epsilon_{yxz} = 1$$

$$\epsilon_{zyx} = \epsilon_{yxz} = \epsilon_{xzy} = -1$$

and all others are zero ... $\epsilon_{xxy} = \dots = 0$.

Thus we *can't* form simultaneous eigenstates of any 2 *components* of angular momentum since they don't commute.

What about Total Orbital Angular Momentum? (e.g. the magnitude of \hat{L}^2)

$$\text{we can define: } \hat{L}^2 \equiv \hat{\vec{L}} \cdot \hat{\vec{L}} = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

Now it is easy to show (from previous commutation relations) that

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

\hookrightarrow for example

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

\therefore We *can* find simultaneous eigenstates of \hat{L}^2 and *one* and only one component of $\hat{\vec{L}}$ (This is the Commutator Theorem).

Let's find eigenstates and eigenvalues for Angular Momentum, since \hat{L}^2 is in the Hamiltonian.

Math Facts:

1. Consider $\hat{\vec{J}}$ as a generalized angular momentum that, for example, could combine angular momentum via $\hat{\vec{J}} = \hat{\vec{L}}_1 + \hat{\vec{L}}_2$ or with additional *types* of angular momentum via $\hat{\vec{J}} = \hat{\vec{L}} + \hat{\vec{S}}$, where $\hat{\vec{S}}$ is intrinsic spin. Then if $[\hat{J}_i, \hat{J}_j] = \epsilon_{ijk}(i\hbar \hat{J}_k)$ we say that $\hat{\vec{J}}$ has the structure of a Lie Algebra in Group Theory (FYI).
2. We can find the eigenstates and eigenvalues of \hat{J}^2 and one component of \hat{J}_i (we choose \hat{J}_z) by using an algebraic trick:

first define:

$$\begin{aligned} \hat{J}_+ &= \hat{J}_x + i\hat{J}_y \\ \hat{J}_- &= \hat{J}_x - i\hat{J}_y \end{aligned}$$

then e.g.

$$[\hat{J}_z, \hat{J}_\pm] = [\hat{J}_z, \hat{J}_x] \pm i[\hat{J}_z, \hat{J}_y] = i\hbar \hat{J}_y \pm i(-i\hbar \hat{J}_x) = \pm \hbar \hat{J}_\pm$$

as well as

$$[\hat{J}^2, \hat{J}_\pm] = 0$$

To find the eigenvalues of \hat{J}_z, \hat{J}^2 . We will first search for eigenvalues of \hat{J}_z .

Let $|\phi_m\rangle$ be an eigenstate of \hat{J}_z (and thus also of \hat{J}^2), then we have $\hat{J}_z|\phi_m\rangle = \hbar m|\phi_m\rangle$; where $\hbar m$ is the eigenvalue and m is some dimensionless quantum number TBD.

Skipped the derivation in lecture (between the ****):

***** To begin consider:

$$\hat{J}_z(\hat{J}_+|\phi_m\rangle) = \hat{J}_z\hat{J}_+|\phi_m\rangle = (\hbar\hat{J}_+ + \hat{J}_+\hat{J}_z)|\phi_m\rangle = (\hbar\hat{J}_+ + \hat{J}_+\hbar m)|\phi_m\rangle = \hbar(m+1)(\hat{J}_+|\phi_m\rangle)$$

Above works by using commutator above the *****, namely; $[\hat{J}_z, \hat{J}_+] = \hbar\hat{J}_+$

$\therefore \hat{J}_+|\phi_m\rangle$ is an unnormalized eigenstate of \hat{J}_z with eigenvalue $(m+1)\hbar$ or $\hat{J}_+|\phi_m\rangle \propto |\phi_{m+1}\rangle$

Likewise:

$$\hat{J}_-|\phi_m\rangle \propto |\phi_{m-1}\rangle$$

The above are true unless $|\phi_m\rangle$ is the highest or lowest possible state; in that case:

$\hat{J}_+|\phi_{max}\rangle = \hat{J}_-|\phi_{min}\rangle = 0$. Here we assume $|\phi_{max}\rangle, |\phi_{min}\rangle$ exist. We can confirm at the end.

Now noting that we have also assumed that $|\phi_m\rangle$ is also an eigenstate of \hat{J}^2

Thus we must have

$$\hat{J}^2|\phi_m\rangle = \hbar^2 K^2|\phi_m\rangle$$

as well as

$$\hat{J}^2(\hat{J}_+|\phi_m\rangle) = \hat{J}_+\hat{J}^2|\phi_m\rangle = \hat{J}_+(\hbar^2 K^2|\phi_m\rangle) = \hbar^2 K^2(\hat{J}_+|\phi_m\rangle)$$

Therefore $\hat{J}_+|\phi_m\rangle$ is also an eigenstate of \hat{J}^2 with eigenvalue $\hbar^2 K^2$

(e. g. with the same eigenvalue as $|\phi_m\rangle$).

To find values for m and K we first note that

$$\hat{J}_-\hat{J}_+ = \hat{J}_x^2 + \hat{J}_y^2 + i(\hat{J}_x\hat{J}_y - \hat{J}_y\hat{J}_x) = \hat{J}_x^2 + \hat{J}_y^2 + i[\hat{J}_x, \hat{J}_y] = \hat{J}_x^2 + \hat{J}_y^2 - \hbar\hat{J}_z$$

Thus we can write

$$\hat{J}^2 = \hat{J}_\mp\hat{J}_\pm + \hat{J}_z^2 \pm \hbar\hat{J}_z$$

and then recalling that $\hat{J}_+|\phi_{max}\rangle = 0$ and $\hat{J}_-|\phi_{min}\rangle = 0$ we can see that

$$\begin{aligned} \hat{J}^2|\phi_{max}\rangle &= \hbar^2 K^2|\phi_{max}\rangle = \hat{J}_z^2|\phi_{max}\rangle + \hbar\hat{J}_z|\phi_{max}\rangle \\ &= \hbar^2 m_{max}^2|\phi_{max}\rangle + \hbar^2 m_{max}|\phi_{max}\rangle \end{aligned}$$

or

$$K^2 = m_{max}(m_{max} + 1)$$

Likewise for $|\phi_{min}\rangle$, we can calculate $\hat{J}^2|\phi_{min}\rangle$ which gives

$$K^2 = m_{min}(m_{min} - 1)$$

$\therefore m_{\max}(m_{\max} + 1) = m_{\min}(m_{\min} - 1)$ which requires that either

$$m_{\max} - m_{\min} = -1 \text{ or } m_{\max} = -m_{\min}$$

The first condition is inconsistent since m_{\max} can't be less than m_{\min} , so the second condition must be true.

If we now let $j \equiv m_{\max}$, then $K^2 = j(j + 1)$ and m runs from $-j$ to $+j$ in integer steps. Clearly the m values are symmetric about 0. \therefore we have two options for j :

Algebra and Commutator "games" thus show that

$$j = \text{integer, with } m = -j, -|j - 1| \dots 0, \dots |j - 1|, j$$

OR

$$j = \text{a half integer, with } m = -j, -|j - 1| \dots, |j - 1|, j \Rightarrow \text{Note: zero is skipped}$$

Thus the Math "predicts" 1/2 integer angular momentum is possible ... but is it realized in Nature??

\Rightarrow **YES!** - see next Lecture on "Intrinsic Spin"

Examples:

if $j = 2$, then $m = -2, -1, 0, 1, 2,$.

if $j = \frac{3}{2}$, then $m = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$

Summarizing what we have found; letting $|\phi_m\rangle \equiv |jm\rangle$. then $|jm\rangle$ is an eigenstate of both J^2 and J_z with

$$\hat{J}^2|jm\rangle = j(j + 1)\hbar^2|jm\rangle$$

$$\hat{J}_z|jm\rangle = m\hbar|jm\rangle$$

where j is any positive integer or $\frac{1}{2}$ integer ($j = 0, \frac{1}{2}, 1, \frac{3}{2}, \dots$) and m varies from $-j$ to j spaced by 1.