Chap 4 - Quantum Mechanics in 3 Dimensions

We will start by first doing two dimensions. This will let us sneak up on 3-D. The most important question is "How to write Schrodinger Equation for 2 D?"

Always $i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = \hat{H} |\Psi(t)\rangle$

The question is "what is $\hat{H}$ in 2D?" $\hat{H} = \frac{\hat{p}^2}{2m} + V(\hat{x}, \hat{y}, t)$

$$\hat{H} = \frac{1}{2m}\left(\hat{P}_x^2 + \hat{P}_y^2\right) + V(\hat{x}, \hat{y}, t)$$

A very common representation $\hat{P}_x^2 + \hat{P}_y^2 = \left(\frac{\hbar}{i}\frac{\partial}{\partial x}\right)^2 + \left(\frac{\hbar}{i}\frac{\partial}{\partial y}\right)^2 = -\hbar^2\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)$

A Schr. Eq. representation

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

Just like the 1D case you can find eigenstates with the form

$$\Psi(x,y,t) = \psi_n(x,y)\, e^{-iE_n t/\hbar}$$

The ψ_n are solutions of $H\psi_n = E_n \psi_n$

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2 \psi_n(x,y)}{\partial x^2} + \frac{\partial^2 \psi_n(x,y)}{\partial y^2}\right) + V(x,y)\,\psi_n(x,y) = E_n \psi_n(x,y)$$

For a general $V(x,y)$, the $\psi_n(x,y)$ does not have special symmetry and the eigenfunctions can be numbered by a single index. If the potential is separable, it is often more useful to have 2 indices.

Special Case: $V(x,y) = V^{(1)}(x) + V^{(2)}(y)$

Separation of variables in spatial coordinates:

$$\psi_n(x,y) = f_{n_x}(x)\, g_{n_y}(y)$$

Substitute into Sch. Eq.

$$g_{n_y}(y)\left(-\frac{\hbar^2}{2m}\frac{d^2 f_{n_x}(x)}{dx^2} + V^{(1)}(x) f_{n_x}(x)\right) + f_{n_x}(x)\left(-\frac{\hbar^2}{2m}\frac{d^2 g_{n_y}(y)}{dy^2} + V^{(2)}(y) g_{n_y}(y)\right) = E_n f_{n_x}(x) g_{n_y}(y)$$

Set $E_n = E^{(1)}_{n_x} + E^{(2)}_{n_y}$

$$-\frac{\hbar^2}{2m}\frac{d^2 f_{n_x}}{dx^2} + V^{(1)}(x) f_{n_x}(x) = E^{(1)}_{n_x} f_{n_x}(x) \qquad -\frac{\hbar^2}{2m}\frac{d^2 g_{n_y}}{dy^2} + V^{(2)}(y) g_{n_y}(y) = E^{(2)}_{n_y} g_{n_y}(y)$$

If $V^{(1)} = V^{(2)}$, then the Hamiltonian has the property $H(x,y) = H(y,x)$. This means the $\psi_n(x,y)$ <u>can</u> have the property $\psi_n(x,y) = \pm\psi_n(y,x)$. Does our solution have this property? No! Unless $n_x = n_y$.

Example ∞ square well $V(x,y) = 0$ for $0 \le x \le a$ <u>and</u> $0 \le y \le a$

$$\psi_{n_x n_y}(x,y) = \sqrt{\tfrac{2}{a}}\sin\left(\frac{n_x \pi x}{a}\right)\sqrt{\tfrac{2}{a}}\sin\left(\frac{n_y \pi x}{a}\right)$$

$$\psi_{3,4}(x,y) = \frac{2}{a}\sin\left(\frac{3\pi x}{a}\right)\sin\left(\frac{4\pi y}{a}\right) \neq \psi_{3,4}(y,x) = \frac{2}{a}\sin\left(\frac{3\pi y}{a}\right)\sin\left(\frac{4\pi x}{a}\right)$$

The combinations
$$\left.\begin{aligned}\psi^{\pm}_{3,4}(x,y) &= \frac{1}{\sqrt{2}}\left(\psi_{3,4}(x,y) \pm \psi_{3,4}(y,x)\right)\\ &= \frac{1}{\sqrt{2}}\left(\psi_{3,4}(x,y) \pm \psi_{4,3}(x,y)\right)\end{aligned}\right]$$
have the symmetry property

$$\psi^{\pm}_{3,4}(x,y) = \pm\psi_{3,4}(y,x)$$

When the eigenstates have the form $f_{n_x}(x)\, g_{n_y}(y)$, the nodal lines are a grid in x and y.

Cylindrical coordinates : $x = \rho\cos\phi \quad y = \rho\sin\phi$

$\rho = \sqrt{x^2+y^2} \quad \tan\phi = y/x$

Useful when $V(x,y) = V(\rho)$

When V is only a function of ρ, the classical angular momentum

$$L_z = (\vec{r}\times\vec{p})\cdot\hat{z} = xP_y - yP_x$$

is a conserved quantity. To see this first get the form of the force

$$F_x = -\frac{\partial V(\rho)}{\partial x} = -\frac{\partial\rho}{\partial x}\frac{dV}{d\rho} = -\frac{x}{\rho}\frac{dV}{d\rho} \qquad F_y = -\frac{y}{\rho}\frac{dV}{d\rho}$$

$$\frac{dL_z}{dt} = \frac{dx}{dt}P_y + x\frac{dP_y}{dt} - \frac{dy}{dt}P_x - y\frac{dP_x}{dt}$$

$$= V_x P_y - V_y P_x + xF_y - yF_x = 0 + \frac{-xy}{\rho}\frac{dV}{d\rho} - \frac{yx}{\rho}\frac{dV}{d\rho} = 0$$

In Q.M. we need to show $[\hat{L}_z, \hat{H}] = 0$

$$[L_z, V] = [xP_y, V] - [yP_x, V] = x[P_y, V] - y[P_x, V]$$

$$= \frac{\hbar}{i}\left(x\frac{\partial V}{\partial y} - y\frac{\partial V}{\partial x}\right) = \frac{\hbar}{i}\left(x\frac{y}{\rho}\frac{dV}{d\rho} - y\frac{x}{\rho}\frac{dV}{d\rho}\right) = 0$$

$$[L_z, P_x^2+P_y^2] = [xP_y, P_x^2+P_y^2] - [yP_x, P_x^2+P_y^2] = [x, P_x^2]P_y - [y, P_y^2]P_x$$

$$= 2i\hbar P_x P_y - 2i\hbar P_y P_x = 0 \qquad \underline{\text{Yes!}}$$

Since $[\hat{L}_z, \hat{H}] = 0$, every energy eigenstate <u>can</u> also be an eigenstate of L_z. Very important!!

Can we find an expression for $\hat{L}_z$ in terms of ρ, ϕ?

$$L_z = \frac{\hbar}{i}\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right) = \frac{\hbar}{i}\left(x\frac{\partial\rho}{\partial y}\frac{\partial}{\partial\rho} + x\frac{\partial\phi}{\partial y}\frac{\partial}{\partial\phi} - y\frac{\partial\rho}{\partial x}\frac{\partial}{\partial\rho} - y\frac{\partial\phi}{\partial x}\frac{\partial}{\partial\phi}\right)$$

$$= \frac{\hbar}{i}\left(x\frac{y}{\rho}\frac{\partial}{\partial\rho} + x\frac{x}{x^2+y^2}\frac{\partial}{\partial\phi} - y\frac{x}{\rho}\frac{\partial}{\partial\rho} - y\left(\frac{-y}{x^2+y^2}\right)\frac{\partial}{\partial\phi}\right) = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$$

Find the eigenstates of L_z.

$$\frac{\hbar}{i}\frac{\partial}{\partial\phi}F_m(\phi) = \lambda_m F_m(\phi) \quad \Rightarrow \quad F_m(\phi) = e^{i\lambda_m\phi/\hbar}$$

m is an unfortunate index, but standard. Don't confuse w/ mass!

How to figure out which λ_m allowed?

$$F_m(\phi+2\pi) = F_m(\phi) \quad \Rightarrow \quad e^{i\lambda_m 2\pi/\hbar} = 1 \qquad \lambda_m = m\hbar$$

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

Stop and recognize what this means. The allowed eigenvalues of L_z are integer times $\hbar$! (Reminder of Bohr quantization cond.)

From many different sources $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho} + \frac{1}{\rho^2}\frac{\partial^2}{\partial\phi^2}$

$$\hat{H} = -\frac{\hbar^2}{2M}\left(\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho}\right) - \frac{\hbar^2}{2M\rho^2}\frac{\partial^2}{\partial\phi^2} + V(\rho)$$

$$= -\frac{\hbar^2}{2M}\left(\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho}\right) + \frac{1}{2M\rho^2}\hat{L}_z^2 + V(\rho)$$

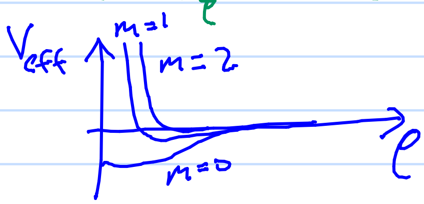
The time independent Schr. Eq. can have solutions of the form.

$$\Psi_n(\rho,\phi) = F_{n_\rho,m}(\rho)\, e^{im\phi}$$

$$-\frac{\hbar^2}{2M}\left(\frac{d^2F_{n_\rho,m}}{d\rho^2} + \frac{1}{\rho}\frac{dF_{n_\rho,m}}{d\rho}\right)e^{im\phi} + \frac{\hbar^2 m^2}{2M\rho^2}F_{n_\rho,m}\, e^{im\phi} + V(\rho)F_{n_\rho m}e^{im\phi} = E_{n_\rho m}F_{n_\rho m}\, e^{im\phi}$$

$$-\frac{\hbar^2}{2M}\left(\frac{d^2F_{n_\rho m}}{d\rho^2} + \frac{1}{\rho}\frac{dF_{n_\rho m}}{d\rho}\right) + V_{eff}(\rho)F_{n_\rho m} = E_{n_\rho m}F_{n_\rho m} \qquad V_{eff} = V + \frac{\hbar^2 m^2}{2M\rho^2}$$

It is very important to realize what is going on. For each m (eig val of L_z), there are an ∞ number of solutions that have $n_\rho - 1$ nodes in the function $F_{n_\rho,m}$



Useful energy relations: $E_{n_\rho,m} = E_{n_\rho,-m}$

$$E_{n_\rho+1,m} > E_{n_\rho,m}$$

$$E_{n_\rho,|m|+1} > E_{n_\rho,|m|}$$

The orthonormality relation for the two special cases have a special form.

$$\iint \psi^*_{n_x n_y}(x,y)\,\psi_{n'_x n'_y}(x,y)\,dx\,dy = \delta_{n_x n'_x}\,\delta_{n_y n'_y}$$

$$\iint \psi^*_{n_\rho m}(\rho,\phi)\,\psi_{n'_\rho m'}(\rho,\phi)\,d\phi\,\rho\,d\rho = \delta_{n_\rho n'_\rho}\,\delta_{m m'}$$

Now let's look at the 3D case $\quad H\psi_n(x,y,z) = E_n\psi_n(x,y,z)$

As with the 2D case, the H for the 3D case is extended in the obvious way.

$$H = \frac{1}{2M}\left(P_x^2 + P_y^2 + P_z^2\right) + V(x,y,z) = -\frac{\hbar^2}{2M}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + V(x,y,z)$$

As with the 2D case, the generic $V(x,y,z)$ does not give any special symmetry to $\psi_n(x,y,z)$ so can just number them with n. To have bound state, $V(x,y,z) > E$ as $x,y,z \to \infty$ in <u>every</u> direction is obvious restriction but is too strong. Example $V = \frac{1}{2}m\omega^2(x^2+y^2) - \alpha\,\delta(z)$ could give bound state $E>0$.

We will focus on special cases where E_n and ψ_n can be found analytically.

Special Case: $V = V^{(1)}(x) + V^{(2)}(y) + V^{(3)}(z)$

Use separation of variables $\quad \psi(x,y,z) = \psi^{(1)}_{n_x}(x)\,\psi^{(2)}_{n_y}(y)\,\psi^{(3)}_{n_z}(z)$

Plug into Sch. Eq.

$$\left(H^{(1)}_{(x)}\psi^{(1)}_{n_x}(x)\right)\psi^{(2)}_{n_y}(y)\,\psi^{(3)}_{n_z}(z) + \psi^{(1)}_{n_x}(x)\left(H^{(2)}_{(y)}\psi^{(2)}_{n_y}(y)\right)\psi^{(3)}_{n_z}(z) + \psi^{(1)}_{n_x}(x)\,\psi^{(2)}_{n_y}(y)\left(H^{(3)}_{(z)}\psi^{(3)}_{n_z}(z)\right)$$

$$= E^{(1)}_{n_x}\psi^{(1)}_{n_x}\psi^{(2)}_{n_y}\psi^{(3)}_{n_z} + E^{(2)}_{n_y}\psi^{(1)}_{n_x}\psi^{(2)}_{n_y}\psi^{(3)}_{n_z} + E^{(3)}_{n_z}\psi^{(1)}_{n_x}\psi^{(2)}_{n_y}\psi^{(3)}_{n_z}$$

$$\Rightarrow E_{n_x n_y n_z} = E^{(1)}_{n_x} + E^{(2)}_{n_y} + E^{(3)}_{n_z}$$

Example ∞ "cube" well $V(x,y,z)=0$ if $0\le x\le a_x$ and $0\le y\le a_y$ and $0\le z\le a_z$
$=\infty$ otherwise

$$\psi_{n_x n_y n_z}(x,y,z) = \sqrt{\frac{2}{a_x}}\sin\left(\frac{n_x\pi x}{a_x}\right)\sqrt{\frac{2}{a_y}}\sin\left(\frac{n_y\pi y}{a_y}\right)\sqrt{\frac{2}{a_z}}\sin\left(\frac{n_z\pi z}{a_z}\right)$$

$$E_{n_x n_y n_z} = \frac{\hbar^2\pi^2}{2M}\left(\frac{n_x^2}{a_x^2}+\frac{n_y^2}{a_y^2}+\frac{n_z^2}{a_z^2}\right)$$

Special-special case $V^{(1)} = V^{(2)} = V^{(3)} = V$
For this case most states are degenerate.
$n_x = n_y = n_z$ degeneracy 1
2 n's same, other different degeneracy 3 (example 2,2,5 ; 2,5,2 ; 5 2 2)
all n's different degeneracy 6

Special case $V = V^{(1)}(\rho) + V^{(2)}(z) \Rightarrow H = H^{(1)}(\rho,\phi) + H^{(2)}(z)$

Use separation of variables $\psi_{n_\rho,m,n_z} = F^{(1)}_{n_\rho,m}(\rho)\, e^{im\phi}\, \psi^{(2)}_{n_z}(z)$

$$H\psi_{n_\rho m n_z} = \left(H^{(1)}(\rho,\phi)\, F^{(1)}_{n_\rho m}(\rho) e^{im\phi}\right)\psi^{(2)}_{n_z}(z) + F_{n_\rho m}(\rho)e^{im\phi}\left(H^{(2)}(z)\,\psi^{(2)}_{n_z}(z)\right)$$

$$= E^{(1)}_{n_\rho m} F^{(1)}_{n_\rho m} e^{im\phi}\psi^{(2)}_{n_z} + E^{(2)}_{n_z} F^{(1)}_{n_\rho m} e^{im\phi}\psi^{(2)}_{n_z}$$

$$E_{n_\rho m n_z} = E^{(1)}_{n_\rho m} + E^{(2)}_{n_z}$$

These eigenstates are also eigenstates of L_z $L_z\psi_{n_\rho m n_z} = \hbar m\,\psi_{n_\rho m n_z}$

One of the most common form for V is that it only depends on distance from the origin: $V(x,y,z) = V(r)$

Classically this gives a force with magnitude that only depends on r and direction $\pm\hat{r}$

Classically $\frac{dL_z}{dt} = 0$ and $\frac{dL_x}{dt} = 0$ and $\frac{dL_y}{dt} = 0$

In Q.M. can show $[\hat{L}_i, \hat{H}] = 0$ which means $\langle \hat{L}_i \rangle =$ constant

Very important: this does not mean can find eigenstates of $\hat{H}$, $\hat{L}_x$, $\hat{L}_y$, and $\hat{L}_z$. Reason: the different L's do not commute!

To see how this works, work out the different commutators:

$L_x = yP_z - zP_y \qquad L_y = zP_x - xP_z \qquad L_z = xP_y - yP_x$

$[L_x, x] = 0 \qquad [L_x, y] = i\hbar z \qquad [L_x, z] = -i\hbar y$

$[L_y, x] = -i\hbar z \qquad [L_y, y] = 0 \qquad [L_y, z] = i\hbar x$

$[L_z, x] = i\hbar y \qquad [L_z, y] = -i\hbar x \qquad [L_z, z] = 0$

$[L_x, P_x] = 0 \qquad [L_x, P_y] = i\hbar P_z \qquad [L_x, P_z] = -i\hbar P_y$

$[L_y, P_x] = -i\hbar P_z \qquad [L_y, P_y] = 0 \qquad [L_y, P_z] = i\hbar P_x$

$[L_z, P_x] = i\hbar P_y \qquad [L_z, P_y] = -i\hbar P_x \qquad [L_z, L_z] = 0$

$[L_x, L_x] = 0 \qquad [L_x, L_y] = i\hbar L_z \qquad [L_x, L_z] = -i\hbar L_y$

$[L_y, L_x] = -i\hbar L_z \qquad [L_y, L_y] = 0 \qquad [L_y, L_z] = i\hbar L_x$

$[L_z, L_x] = i\hbar L_y \qquad [L_z, L_y] = -i\hbar L_x \qquad [L_z, L_z] = 0$

$[L_a, Q_b] = i\hbar \varepsilon_{abc} Q_c \qquad Q = P$ or X or L

$\varepsilon_{123} = \varepsilon_{312} = \varepsilon_{231} = 1 \qquad \varepsilon_{213} = \varepsilon_{132} = \varepsilon_{321} = -1$ all else $= 0$

Can show that L_i commutes with any scalar combination of $\vec{P}$, $\vec{r}$, $\vec{L}$

$$\begin{aligned}[L_x, xP_x + yP_y + zP_z] &= [L_x, yP_y] + [L_x, zP_z] \\ &= y[L_x, P_y] + [L_x, y]P_y + z[L_x, P_z] + [L_x, z]P_z \\ &= i\hbar\, yP_z + i\hbar\, zP_y + z(-i\hbar P_y) + -i\hbar y P_z \\ &= 0\end{aligned}$$

$[L_z, L_x^2 + L_y^2 + L_z^2] = [L_z, L^2] = 0$ Very important.

$[L_i, H] = 0$ means $[L^2, H] = 0$

We can find states that are simultaneously eigenstates of H, L^2, and L_z $\boxed{\psi_{n_r,\ell,m}}$

m – quantum number for L_z
ℓ – " " " L^2
n_r – " " " H_r

From many places $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$

Spherical coordinates

$$\left.\begin{aligned} x &= r\sin\theta\cos\phi \\ y &= r\sin\theta\sin\phi \\ z &= r\cos\theta \end{aligned}\right]$$

many math books interchange θ and ϕ

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial\theta^2} + \frac{1}{r^2}\cot\theta\frac{\partial}{\partial\theta} + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

$$= \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\left[\frac{\partial^2}{\partial\phi^2}\right]\right)$$

Try a separation of variables $\psi_{n\ell m}(r,\theta,\phi) = R_{n_r\ell}(r)\,\Theta_{\ell m}(\theta)\,\Phi_m(\phi)$

$$H\psi = -\frac{\hbar^2}{2M}\left(\frac{d^2R_{n\ell}}{dr^2} + \frac{2}{r}\frac{dR_{n\ell}}{dr}\right)\Theta_{\ell m}\Phi_m - \frac{\hbar^2}{2Mr^2}\left(\frac{d^2\Theta_{\ell m}}{d\theta^2} + \cot\theta\frac{d\Theta_{\ell m}}{d\theta} - \frac{m^2}{\sin^2\theta}\Theta_{\ell m}\right)R_{n_r\ell}\Phi_m$$

$$+ V(r)R_{n_r\ell}\Theta_{\ell m}\Phi_m = E_{n_r\ell m}R_{n_r\ell}\Theta_{\ell m}\Phi_m$$

used $\frac{d^2\Phi_m}{d\phi^2} = -m^2\Phi_m$

The equation in θ gives $\frac{d^2\Theta_{\ell m}}{d\theta^2} + \cot\theta\frac{d\Theta_{\ell m}}{d\theta} - \frac{m^2}{\sin^2\theta}\Theta_{\ell m} = -\ell(\ell+1)\Theta_{\ell m}$

with $\ell = |m|, |m|+1, |m|+2, \ldots$

The equation in r gives

$$-\frac{\hbar^2}{2m}\left(\frac{d^2R_{n_r\ell}}{dr^2} + \frac{2}{r}\frac{dR_{n_r\ell}}{dr}\right) + \frac{\hbar^2\ell(\ell+1)}{2Mr^2}R_{n_r\ell} + V(r)R_{n_r\ell} = E_{n_r\ell}R_{n_r\ell}$$

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

Important: Notice E does not depend on the m-quantum number.
Why??

Since the equation in Θ is the same for all $V(r)$, look at its properties first.

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\,\frac{d\Theta_{\ell m}}{d\theta}\right) - \frac{m^2}{\sin^2\theta}\Theta_{\ell m} + \ell(\ell+1)\Theta_{\ell m} = 0$$

$$\frac{d}{d(\cos\theta)}\left(\sin^2\theta\,\frac{d\Theta_{\ell m}}{d(\cos\theta)}\right) - \frac{m^2}{\sin^2\theta}\Theta_{\ell m} + \ell(\ell+1)\Theta_{\ell m} = 0 \qquad \text{set } x=\cos\theta$$

$$\frac{d}{dx}\left((1-x^2)\frac{d\Theta_{\ell m}}{dx}\right) - \frac{m^2}{1-x^2}\Theta_{\ell m} + \ell(\ell+1)\Theta_{\ell m} = 0 \qquad -1\le x\le 1$$

The solutions of this equation are well known: associated Legendre function: $P_\ell^m(x)$
Important to note that there are different sign conventions for $m<0$. Griffiths uses $P_\ell^m(x) = P_\ell^{-m}(x)$

The Legendre polynomial $P_\ell(x) = P_\ell^0(x)$ $\qquad \ell = 0,1,2,3,\ldots$

Rodrigues formula: $P_\ell(x) \equiv \frac{1}{2^\ell \ell!}\frac{d^\ell}{dx^\ell}(x^2-1)^\ell$

The number of nodes of $P_\ell(x)$ is ℓ, $P_\ell^m(x)$ is $\ell-|m|$

$P_0(x)=1 \qquad P_1(x)=x \qquad P_2(x)=\frac{3}{2}x^2-\frac{1}{2} \qquad P_3(x)=\frac{5}{2}x^3-\frac{3}{2}x \quad \ldots$

Some properties of the $P_\ell(x)$

1. $P_\ell(x) = (-1)^\ell P_\ell(-x)$
2. $P_\ell(1) = 1$ and $P_\ell(-1) = (-1)^\ell$
3. $|P_\ell(x)| < 1$ for $\ell>0$ and $|x|<1$
4. $\int_{-1}^{1} P_\ell(x)P_{\ell'}(x)\,dx = 2\delta_{\ell\ell'}/(2\ell+1)$

The associated Legendre function $P_\ell^m(x) = (1-x^2)^{|m|/2}\frac{d^{|m|}}{dx^{|m|}}P_\ell(x)$

Since the highest power of $P_\ell(x)$ is x^ℓ, $P_\ell^m(x)=0$ if $|m|>\ell$

The normalized combination $\Theta_{\ell m}(\theta)\,\Phi_m(\phi)$ is called the spherical harmonics and is the symbol $Y_{\ell m}$

$$Y_\ell^m(\theta,\phi) = \epsilon\sqrt{\frac{2\ell+1}{4\pi}\,\frac{(\ell-|m|)!}{(\ell+|m|)!}}\;P_\ell^m(\cos\theta)\,e^{im\phi} \qquad \begin{aligned}\epsilon &= 1 \quad \text{if } m<0\\ &= -1 \quad \text{if } m\geq 0\end{aligned}$$

The ϵ is the result of convention and must be followed!

Another common notation is $Y_{\ell m}(\theta,\phi)$

The volume element in spherical coordinates is $\sin\theta\, d\theta\, d\phi\, r^2 dr$

The normalization is $\displaystyle\int_0^\pi\int_0^{2\pi} Y_{\ell'}^{m'*}(\theta,\phi)\,Y_\ell^m(\theta,\phi)\,d\phi\,\sin\theta\,d\theta = \delta_{\ell\ell'}\,\delta_{mm'}$

Look at the Y_ℓ^m and discuss generic properties.
As $|m|$ increases, less probability near $\cos\theta \sim \pm 1$

Now look at the radial part of the Schr. Eq.

$$-\frac{\hbar^2}{2m}\left[\frac{d^2R_{n,\ell}}{dr^2}+\frac{2}{r}\frac{dR_{n\ell}}{dr}\right]+\frac{\hbar^2\ell(\ell+1)}{2Mr^2}R_{n,\ell}+V(r)R_{n\ell}=E_{n,\ell}R_{n\ell}$$

You get a somewhat simpler equation if you substitute $R(r)=\frac{u(r)}{r}$

$$R'=\frac{u'}{r}-\frac{u}{r^2}\qquad R''=\frac{u''}{r}-\frac{2u'}{r^2}+\frac{2u}{r^3}$$

$$R''+\frac{2}{r}R=\frac{u''}{r}-\frac{2u'}{r}+\frac{2u}{r^3}+\frac{2u'}{r^2}-\frac{2u}{r^3}=\frac{u''}{r}$$

$$-\frac{\hbar^2}{2M}\frac{d^2u}{dr^2}+\left(V(r)+\frac{\hbar^2\ell(\ell+1)}{2Mr^2}\right)u=E\,u \longleftarrow$$ looks like the 1D Sch. Eq.

The normalization condition $\int_0^\infty |R(r)|^2 r^2 dr=\int_0^\infty |u(r)|^2 dr$

Must have $u(0)=0$ Why?

Not obvious but the $u(r)$ has to have a specific power law as $r\to 0$ (not necessarily linear) when $r^2V(r)\to 0$ as $r\to 0$

At small r, need to satisfy

$$-\frac{\hbar^2}{2M}\frac{d^2u}{dr^2}+\frac{\hbar^2\ell(\ell+1)}{2Mr^2}u(r)=0 \to \frac{d^2u}{dr^2}=\frac{\ell(\ell+1)}{r^2}u$$

Try $u(r)=Ar^b$

$$Ab(b-1)r^{b-2}=A\ell(\ell+1)r^{b-2}$$

$$\Rightarrow b(b-1)=\ell(\ell+1)$$

$b=\ell+1$ or $b=-\ell$ why not allowed?

There are not alot of potentials where you can find the u analytically: infinite spherical well, harmonic oscillator, $-c/r$, ...

Example: <u>Infinite spherical well</u>

$$V(r)=0 \text{ if } r<a \qquad =\infty \text{ if } r>a$$

$$-\frac{\hbar^2}{2M}\frac{d^2u}{dr^2}+\frac{\hbar^2\ell(\ell+1)}{2Mr^2}u=E\,u$$

Change variables $r = x/k$ $\quad E = \frac{\hbar^2 k^2}{2m}$

$$\frac{d^2u}{dx^2} + \left(1 - \frac{\ell(\ell+1)}{x^2}\right) u = 0$$

The two linearly independent solutions are $x\, j_\ell(x)$ and $x\, n_\ell(x)$
These are spherical Bessel functions (the n_ℓ is often called the Neumann function).

$$j_\ell(x) = (-x)^\ell \left(\frac{1}{x}\frac{d}{dx}\right)^\ell \left(\frac{\sin x}{x}\right) \qquad n_\ell(x) = -(-x)^\ell \left(\frac{1}{x}\frac{d}{dx}\right)^\ell \left(\frac{\cos x}{x}\right)$$

$$j_{\ell+1}(x) = \frac{2\ell+1}{x} j_\ell(x) - j_{\ell-1}(x)$$ and similar n_ℓ

$$j_0(x) = \frac{\sin x}{x} \qquad j_1(x) = \frac{\sin x}{x^2} - \frac{\cos x}{x} \qquad j_2(x) = \left(\frac{3}{x^3} - \frac{1}{x}\right)\sin x - \frac{3\cos x}{x^2}$$

$$n_0(x) = -\frac{\cos x}{x} \qquad n_1(x) = -\frac{\cos x}{x^2} - \frac{\sin x}{x} \qquad n_2(x) = -\left(\frac{3}{x^3} - \frac{1}{x}\right)\cos x - \frac{3\sin x}{x^2}$$

It is not obvious from the functions but

$x\, j_\ell(x) \rightarrow \text{const}\ x^{\ell+1}$ $\qquad x\, n_\ell(x) \rightarrow \text{const}/x^\ell$

Undo the change of variable $u(r) = A r j_\ell(kr) + B r n_\ell(kr)$

Apply the boundary condition at $r=0$ What is it? $\Rightarrow B = 0$

Apply the boundary condition at $r=a$ What is it? $\Rightarrow j_\ell(ka) = 0$

Define $\beta_{n\ell}$ so that $j_\ell(\beta_{n\ell}) = 0$ $\quad \beta_{n\ell}$ is the n^{th} 0 of $j_\ell(x)$.

$$k_{n\ell} = \beta_{n\ell}/a \longrightarrow E_{n\ell} = \frac{\hbar^2}{2Ma^2}\beta_{n\ell}^2$$

The $\beta_{n0} = n\pi$ All others are found numerically (See online calc.)

$\beta_{11} = 4.493\ldots$ $\beta_{21} = 7.725\ldots$ $\beta_{31} = 10.90\ldots$ $\beta_{12} = 5.763$ $\beta_{22} = 9.095\ldots$ $\beta_{32} = 12.32$

The full, normalized wave function is

$$\psi_{n\ell m}(r,\theta,\phi) = A_{n\ell}\, j_\ell(k_{n\ell} r)\, Y_\ell^m(\theta,\phi) \qquad A_{n\ell}^2 \int_0^a j_\ell^2(k_{n\ell} r)\, r^2 dr = 1$$

normalization

Special case: Harmonic oscillator $V(x) = \frac{1}{2}M\omega^2x^2 + \frac{1}{2}M\omega^2y^2 + \frac{1}{2}M\omega^2z^2$
$= \frac{1}{2}M\omega^2r^2$

You can solve using cartesian coords

$$E_{n_xn_yn_z} = (n_x + n_y + n_z + \tfrac{3}{2})\hbar\omega$$

Allowed energies: $\frac{3}{2}\hbar\omega$, $\frac{5}{2}\hbar\omega$, $\frac{7}{2}\hbar\omega$, ...
Degeneracy 1 3 6

You can solve using spherical coords

$$-\frac{\hbar^2}{2M}\frac{d^2u}{dr^2} + \left[\frac{1}{2}M\omega^2r^2 + \frac{\hbar^2 \ell(\ell+1)}{2Mr^2}\right]u(r) = E_{n_r,\ell}\,u(r)$$

Use transformation variable $\xi = \sqrt{\frac{M\omega}{\hbar}}\,r$ and factor out the small r, $\xi^{\ell+1}$, and large r, $e^{-\xi^2/2}$, behaviors

$$u = h(\xi)e^{-\xi^2/2}$$

Follow the same steps as Sec 2.3.2. The $h(\xi)$ turn out to be associated Laguerre polynomials times $\xi^{\ell+1}$

Substitute ξ $\quad -\frac{1}{2}\hbar\omega\frac{d^2u}{d\xi^2} + \frac{1}{2}\hbar\omega\left(\xi^2 + \frac{\ell(\ell+1)}{\xi^2}\right)u = Eu$

$K = 2E/\hbar\omega$

$$\frac{d^2u}{d\xi^2} + \left(K - \xi^2 - \frac{\ell(\ell+1)}{\xi^2}\right)u = 0$$

Now take out the large ξ behavior $u(\xi) = h(\xi) e^{-\xi^2/2}$

$$u' = h' e^{-\xi^2/2} - \xi h e^{-\xi^2/2}$$
$$u'' = h'' e^{-\xi^2/2} - \xi h' e^{-\xi^2/2} - h e^{-\xi^2/2} - \xi h' e^{-\xi^2/2} + \xi^2 h e^{-\xi^2/2}$$
$$= (h'' - 2\xi h' + (\xi^2 - 1) h) e^{-\xi^2/2}$$

$$h'' - 2\xi h' + \left(K - 1 - \frac{\ell(\ell+1)}{\xi^2}\right) h = 0$$

Write $h(\xi) = \xi^{\ell+1} (a_0 + a_1 \xi + a_2 \xi^2 + \ldots)$

From bdry condition at $r = 0$

Terms with $\xi^{\ell-1}$ $\quad (\ell+1)\ell a_0 - 0 - \ell(\ell+1) a_0 = 0$

" " ξ^{ℓ} $\quad (\ell+2)(\ell+1) a_1 - 0 - \ell(\ell+1) a_1 = 0 \Rightarrow \boxed{a_1 = 0}$

" " $\xi^{\ell+1}$ $\quad (\ell+3)(\ell+2) a_2 - 2(\ell+1) a_0 + (K-1) a_0 - \ell(\ell+1) a_2 = 0$

" " $\xi^{\ell+2}$ $\quad (\ell+4)(\ell+3) a_3 - 2(\ell+2) a_1 + (K-1) a_1 - \ell(\ell+1) a_3 = 0 \Rightarrow \boxed{a_3 = 0}$

Only the <u>even</u> $a_j \neq 0$. <u>All</u> odd $a_j = 0$.

$$\left[(\ell+3+j)(\ell+2+j) - \ell(\ell+1)\right] a_{j+2} = \left[2(\ell+j+1) - K + 1\right] a_j$$

Just as with the cartesian derivation, there is a solution for any value of K (which is proportional to E). Must have the series truncate so $\psi \to 0$ as $r \to \infty$

$$K_{n_r,\ell} = \frac{2E_{n_r,\ell}}{\hbar\omega} = 2n_r + 2\ell + 3$$

$$E_{n_r,\ell} = \left(n_r + \ell + \tfrac{3}{2}\right)\hbar\omega$$

Remember that for each n_r, ℓ there are $2\ell+1$ m-states

$m = -\ell, -\ell+1, \ldots 0 \ldots \ell-1, \ell$

$$\psi_{n_r,\ell,m} = A_{n_r,\ell}\, h_{n_r,\ell}\left(\sqrt{\frac{M\omega}{\hbar}}\, r\right) e^{-\frac{M\omega r^2}{2\hbar}}\, Y_\ell^m(\theta,\phi)/r$$

The $n_r/2$ is the number of radial nodes

The $h_{n_r,\ell}\left(\sqrt{\frac{M\omega}{\hbar}}\,r\right)/r = C\, r^\ell L_{n_r}^{\ell+1/2}\left(\frac{M\omega}{\hbar}r^2\right)$

Associated Laguerre function

Special Case: The "non relativistic" Hydrogen atom $V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}$

You can generalize to He^+, Li^{2+}, ... by changing $e^2 \to Ze^2$ in <u>all</u> subsequent equations.

The radial equation $-\frac{\hbar^2}{2M}\frac{d^2u}{dr^2} + \left(-\frac{e^2}{4\pi\varepsilon_0 r} + \frac{\hbar^2\ell(\ell+1)}{2Mr^2}\right)u(r) = E\,u$

See the book for the derivation. Similar to the Harmonic oscillator case.

What range of energies correspond to bound states?

The small r and large r turning points defined by the quadratic eq.

$$-\frac{e^2}{4\pi\varepsilon_0 r} + \frac{\hbar^2\ell(\ell+1)}{2Mr^2} = E$$

For a quick and dirty estimate of the "size" of an atom, ignore the $1/r^2$ term

$$r \sim -\frac{e^2}{4\pi\varepsilon_0 E}$$ (size scales like $1/|E|$)

For a given ℓ, the smallest E must be larger than the value of V_{eff} at its minimum

$$V_{eff}' = 0 = \frac{e^2}{4\pi\varepsilon_0 r_m^2} - \frac{\hbar^2\ell(\ell+1)}{Mr_m^3} \qquad r_m = \frac{\hbar^2\ell(\ell+1)4\pi\varepsilon_0}{Me^2}$$

$$V_{eff}(r_m) = -M\left(\frac{e^2}{4\pi\varepsilon_0\hbar}\right)^2\frac{1}{2\ell(\ell+1)} = -Mc^2\underbrace{\left(\frac{e^2}{4\pi\varepsilon_0\hbar c}\right)^2}_{\alpha^2}\frac{1}{2\ell(\ell+1)}$$

$$= -\frac{e^2}{4\pi\varepsilon_0}\frac{1}{\underbrace{\left(\frac{4\pi\varepsilon_0\hbar^2}{me^2}\right)}_{a_0}}\frac{1}{2\ell(\ell+1)}$$

α = fine structure constant $= \frac{e^2}{4\pi\varepsilon_0\hbar c} = 1/137.035999\ldots$

a_0 = Bohr radius $= \frac{4\pi\varepsilon_0\hbar^2}{Me^2} = 0.52917721\ldots \times 10^{-10}$ m

αc = velocity unit $= 2.187691 \times 10^6$ m/s

$a_0/\alpha c$ = time unit $= 2.418884 \times 10^{-17}$ s = 24.19 attosec.

See book for derivation of energies and wave functions.

$E_{n_r,\ell} = -\frac{1}{2} M(\alpha c)^2/n^2$ with $n = n_r + \ell + 1$ (n_r starts from 0)

$\psi_{n\ell m}(r,\theta,\varphi) = R_{n\ell}(r)\, Y_\ell^m(\theta,\phi)$

notice change in notation (standard due to history: Blame Bohr)

$R_{n\ell}(r) = \frac{1}{r}\left(\frac{r}{a_0 n}\right)^{\ell+1} e^{-r/a_0 n}\, v(r/a_0 n)$

$v(r/a_0 n) = c_0 + c_1 \frac{r}{a_0 n} + c_2 (r/a_0 n)^2 + \ldots$

$c_{j+1} = 2\, \frac{j+\ell+1-n}{(j+1)(j+2\ell+2)}\, c_j$

As you might expect, these functions are well known. They are also Associated Laguerre polynomials.

$L_q(x) \equiv e^x \left(\frac{d}{dx}\right)^q (x^q e^{-x})$ $\qquad L^p_{q-p}(x) = (-1)^p \frac{d^p}{dx^p} L_q(x)$

$\psi_{n\ell m} = \left(\frac{2}{n a_0}\right)^{3/2} \left(\frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}\right)^{1/2} \left(\frac{2r}{n a_0}\right)^{\ell} L^{2\ell+1}_{n-\ell-1}\left(\frac{2r}{n a_0}\right) e^{-r/n a_0}\, Y_\ell^m(\theta,\phi)$

These are the normalized $\psi_{n\ell m}$ $\qquad \int \psi^*_{n\ell m} \psi_{n'\ell'm'}\, r^2 \sin\theta\, dr\, d\theta\, d\phi = \delta_{nn'}\delta_{\ell\ell'}\delta_{mm'}$

Visualizing the $\psi_{n\ell m}$.

Important notation: States with $\ell = 0$ called "s"-states, $\ell = 1$ are "p" states, $\ell = 2$ are "d" states, $\ell = 3$ are "f" states, $\ell = 4$ are "g" states...

Important multiplicity and naming.

$n=1$ can only be $n_r=0, \ell=0$ 1s state (1 state)
$n=2$ can be $n_r=1, \ell=0$ or $n_r=0, \ell=1$ (2s and 2p) ($1+3=4$ states)
$n=3$ can be $n_r=2, \ell=0$; $n_r=1, \ell=1$; $n_r=0, \ell=2$ (3s, 3p, 3d) ($1+3+5=9$ states)
$n=4$ can be (3,0); (2,1); (1,2); (0,3) (4s, 4p, 4d, 4f) ($1+3+5+7=16$ states)

The degeneracy of level n is n^2 spatial states (spin coming!)

Transitions caused by photons have selection rules. If light is
linearly polarized along z $\ell_{fin} = \ell_{init} \pm 1$, $m_{fin} = m_{init}$, $\Delta n \neq 0$
circularly polarized along z " " $m_{fin} = m_{init}+1$ or $m_{init}-1$
depending on direction, $\Delta n \neq 0$

These are called electric dipole transitions because the transition operator is proportional to ez or $e(x \pm iy)$ where e is charge.

The energy of the photon emitted or absorbed is

$$hf = |E_f - E_i| = E_{1,0} \left| \frac{1}{n_f^2} - \frac{1}{n_i^2} \right| = hc/\lambda$$

$$\frac{1}{\lambda} = R \left| \frac{1}{n_f^2} - \frac{1}{n_i^2} \right| \qquad R = \frac{E_{1,0}}{hc} = 1.097 \times 10^7 \, \frac{1}{m}$$ Rydberg constant

Is $n_f > n_i$ or $n_f < n_i$ for photon emitted?
" " " " " absorbed?

Can a photon be absorbed where $hf > E_{1,0}\left(\frac{1}{n_i^2} - \frac{1}{\infty^2}\right)$?
What does it mean?

Show plots of different $R_{n,\ell}$ and discuss trends.

Now do a formal approach to angular momenta.

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

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

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

These relations mean the eigenstates of $\hat{L}^2$ can also be eigenstates of $\hat{L}_z$ (Going to use slightly different notation from book.)

$\hat{L}^2 |\psi_{\lambda,\mu}\rangle = \hbar^2\lambda(\lambda+1)|\psi_{\lambda,\mu}\rangle \qquad \hat{L}_z^2 |\psi_{\lambda,\mu}\rangle = \hbar^2\mu^2 |\psi_{\lambda,\mu}\rangle$

Why must $\langle\psi_{\lambda\mu}| \hat{L}^2 - \hat{L}_z^2 |\psi_{\lambda\mu}\rangle = \hbar^2(\lambda(\lambda+1) - \mu^2) \geq 0$?

Define the raising and lowering operators $\hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y$

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

Use this to see how the raising/lowering works
Show $\hat{L}_\pm|\psi_{\lambda,\mu}\rangle$ is also eigenstate of $\hat{L}^2$ and $\hat{L}_z$

$\hat{L}^2\hat{L}_\pm|\psi_{\lambda\mu}\rangle = \hat{L}_\pm\hat{L}^2|\psi_{\lambda\mu}\rangle + \cancelto{0}{[\hat{L}^2, \hat{L}_\pm]}|\psi_{\lambda\mu}\rangle$
$= \hbar^2\lambda(\lambda+1)\hat{L}_\pm|\psi_{\lambda\mu}\rangle \longrightarrow$ The λ doesn't change

$\hat{L}_z\hat{L}_\pm|\psi_{\lambda\mu}\rangle = \hat{L}_\pm\hat{L}_z|\psi_{\lambda\mu}\rangle + [\hat{L}_z, \hat{L}_\pm]|\psi_{\lambda\mu}\rangle$
$= \hbar\mu\hat{L}_\pm|\psi_{\lambda\mu}\rangle \pm \hbar\hat{L}_\pm|\psi_{\lambda\mu}\rangle = \hbar(\mu\pm1)\hat{L}_\pm|\psi_{\lambda\mu}\rangle$

This means $\hat{L}_\pm|\psi_{\lambda\mu}\rangle = \hbar A^\pm_{\lambda\mu}|\psi_{\lambda,\mu\pm1}\rangle$

The eigenvalues of $\hat{L}_z$ are a series of values separated by $\hbar$.

We can find the $A^\pm_{\lambda\mu}$ using a similar procedure to when we found $\hat{a}_+\psi_n = C_n\psi_{n+1}$ for the Harmonic oscillator.

$\hat{L}_+ |\Psi_{\lambda\mu}\rangle = \hbar A^+_{\lambda\mu} |\Psi_{\lambda,\mu+1}\rangle$ $\quad A^+_{\lambda\mu} = \frac{1}{\hbar} \langle \Psi_{\lambda,\mu+1} | \hat{L}_+ | \Psi_{\lambda\mu}\rangle$

Write as Hermitian Conj. $A^+_{\lambda\mu} = \frac{1}{\hbar} \langle \hat{L}_+^\dagger \Psi_{\lambda,\mu+1} | \Psi_{\lambda\mu}\rangle$

Do Hermitian Conj. $(\hat{L}_x + i\hat{L}_y)^\dagger = \hat{L}_x^\dagger - i\hat{L}_y^\dagger = \hat{L}_x - i\hat{L}_y = \hat{L}_-$

Now use L_- $\quad A^+_{\lambda\mu} = \frac{1}{\hbar} \langle \hat{L}_- \Psi_{\lambda,\mu+1} | \Psi_{\lambda\mu}\rangle = A^-_{\lambda,\mu+1}$

The "trick" is to do L_+ then L_- so you get back

$$\hat{L}_-\hat{L}_+ |\Psi_{\lambda\mu}\rangle = \hbar A^+_{\lambda\mu} \hat{L}_- |\Psi_{\lambda,\mu+1}\rangle = \hbar^2 A^+_{\lambda\mu} A^-_{\lambda,\mu+1} |\Psi_{\lambda\mu}\rangle = \hbar^2 (A^+_{\lambda\mu})^2 |\Psi_{\lambda\mu}\rangle$$

The $|\Psi_{\lambda\mu}\rangle$ is an eigenstate of L_-L_+. What is L_-L_+???

$$\hat{L}_-\hat{L}_+ = (\hat{L}_x - i\hat{L}_y)(\hat{L}_x + i\hat{L}_y) = \hat{L}_x^2 + \hat{L}_y^2 + i(\hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x)$$

$$= \hat{L}_x^2 + \hat{L}_y^2 - \hbar\hat{L}_z = \hat{L}^2 - (\hat{L}_z^2 + \hbar\hat{L}_z)$$

Since the $|\Psi_{\lambda\mu}\rangle$ is an eigenstate of $\hat{L}^2$ and $\hat{L}_z$, we're done

$$\hat{L}_-\hat{L}_+ |\Psi_{\lambda\mu}\rangle = \left[\hbar^2\lambda(\lambda+1) - \hbar^2\mu(\mu+1)\right] |\Psi_{\lambda\mu}\rangle$$

$$A^{\pm}_{\lambda\mu} = \sqrt{\lambda(\lambda+1) - \mu(\mu\pm1)}$$

Remember the point! This lets us get the different eigenstates.

$$|\Psi_{\lambda,\mu\pm1}\rangle = \frac{1}{\hbar A^{\pm}_{\lambda\mu}} \hat{L}_\pm |\Psi_{\lambda\mu}\rangle$$

It also lets us find the <u>allowed</u> values of λ, μ. The state that corresponds to the maximum μ must have

$$L_+ |\Psi_{\lambda\mu_{max}}\rangle = 0 = \hbar A^+_{\lambda\mu_{max}} |\Psi_{\lambda,\mu+1}\rangle$$

This gives $\mu_{max} = \lambda$. Similar treatment of μ_{min} gives $\mu_{min} = -\lambda$.

Since the $\mu_{min} = -\mu_{max}$ and $\mu_{max} - \mu_{min}$ = integer, the

$\lambda = \mu_{max}$ = integer/2

Allowed values $(\lambda=0, \mu=0)$; $(\lambda=1, \mu=-1,0,1)$; $(\lambda=2, \mu=-2,-1,0,1,2)$...
These are just the values we found earlier, but we use l, m

Representation: For λ, μ = integer $\langle\theta,\phi|\psi_{l,m}\rangle \equiv Y^{l}_{m}(\theta,\phi)$

But we've missed some. The condition was $\lambda = \frac{\text{integer}}{2}$
What do we do with $\lambda = 1/2, 3/2, 5/2, \ldots$

Allowed values: $(\lambda=\frac{1}{2}, \mu=-\frac{1}{2},\frac{1}{2})$, $(\lambda=\frac{3}{2}, \mu=-\frac{3}{2},-\frac{1}{2},\frac{1}{2},\frac{3}{2})$ ...

We did not find these cases when we did the differential equation.
They are not allowed for orbital angular momentum. All the different λ are allowed for spins.

$[\hat{S}_a, \hat{S}_b] = i\hbar\varepsilon_{abc}\hat{S}_c \Rightarrow$ Same logic will give allowed values

$\hat{S}^2|s,m_s\rangle = \hbar^2 s(s+1)|s,m_s\rangle$ and $\hat{S}_z|s,m_s\rangle = \hbar m_s|s,m_s\rangle$

$\hat{S}_\pm|s,m_s\rangle = \hbar\sqrt{s(s+1)-m_s(m_s\pm1)}\;|s,m_s\pm1\rangle$

For spins, the representation of $\hat{S}_a$ and states $|s,m_s\rangle$ are taken to be $(2s+1)\times(2s+1)$ matrices and $2s+1$ length vector.

Every particle has a well defined spin. Electrons, quarks $s=\frac{1}{2}$
photons, gluons $s=1$
Composite particles can have several s depending on state

H-atom ground state (proton $[s=\frac{1}{2}]$ and electron $[s=\frac{1}{2}]$) $s_{tot} = 0$ or 1
" " $n=2$ states $s_{tot} = 0$ or 1 or 2

Representation of spin ½ $\quad |1\rangle = |\tfrac{1}{2}, \tfrac{1}{2}\rangle$ and $|2\rangle = |\tfrac{1}{2}, -\tfrac{1}{2}\rangle$

$\langle 1|\hat{S}^2|1\rangle = \hbar^2 \frac{1}{2}\frac{3}{2}\langle 1|1\rangle = \frac{3}{4}\hbar^2 \qquad \langle 1|\hat{S}^2|2\rangle = \frac{3}{4}\hbar^2\langle 1|2\rangle = 0$

$\langle 2|\hat{S}^2|1\rangle = \frac{3}{4}\hbar^2\langle 2|1\rangle = 0 \qquad \langle 2|\hat{S}^2|2\rangle = \frac{3}{4}\hbar^2\langle 2|2\rangle = \frac{3}{4}\hbar^2$

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

Representation of $\hat{S}^2$ is $\hbar^2 s(s+1)\underline{\underline{1}}$

$\langle 1|\hat{S}_z|1\rangle = \frac{1}{2}\hbar\langle 1|1\rangle = \frac{\hbar}{2} \qquad \langle 1|\hat{S}_z|2\rangle = -\frac{\hbar}{2}\langle 1|2\rangle = 0$

$\langle 2|\hat{S}_z|1\rangle = \frac{\hbar}{2}\langle 2|1\rangle = 0 \qquad \langle 2|\hat{S}_z|2\rangle = -\frac{\hbar}{2}\langle 2|2\rangle = -\frac{\hbar}{2}$

$$\underline{\underline{S}}_z = \frac{\hbar}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$$

Representation of $\hat{S}_z$ is diagonal matrix

$\langle 1|\hat{S}_+|1\rangle = \langle 1|0|1\rangle = 0 \qquad \langle 1|\hat{S}_+|2\rangle = \hbar\sqrt{\frac{3}{4} - (-\frac{1}{2})\frac{1}{2}}\,\langle 1|1\rangle = \hbar$

$\langle 2|\hat{S}_+|1\rangle = \langle 2|0|1\rangle = 0 \qquad \langle 2|\hat{S}_+|2\rangle = \hbar\langle 2|1\rangle = 0$

$$\underline{\underline{S}}_+ = \hbar\begin{pmatrix}0 & 1\\ 0 & 0\end{pmatrix} \qquad \hat{S}_+^{\dagger} = \hat{S}_- \Rightarrow \underline{\underline{S}}_- = \hbar\begin{pmatrix}0 & 0\\ 1 & 0\end{pmatrix}$$

$$\hat{S}_x = \frac{1}{2}(\hat{S}_+ + \hat{S}_-) \qquad \underline{\underline{S}}_x = \frac{\hbar}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}$$

$$\hat{S}_y = -\frac{i}{2}(S_+ - S_-) \qquad \underline{\underline{S}}_y = \frac{\hbar}{2}\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix}$$

The $\underline{\underline{S}}_x$, $\underline{\underline{S}}_y$, $\underline{\underline{S}}_z$ are written in terms of the Pauli spin matrices when $S = 1/2$

$$\underline{\underline{S}}_i = \frac{\hbar}{2}\underline{\underline{\sigma}}_i \qquad \sigma_x = \begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} \qquad \sigma_y = \begin{pmatrix}0 & -i\\ i & 0\end{pmatrix} \qquad \sigma_z = \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$$

Every Pauli Spin matrix has the property $\underline{\underline{\sigma}}_a^2 = \underline{\underline{1}}$

$$\underline{\underline{S}}^2 = \underline{\underline{S}}_x^2 + \underline{\underline{S}}_y^2 + \underline{\underline{S}}_z^2 = \left(\frac{\hbar}{2}\right)^2\underline{\underline{\sigma}}_x^2 + \left(\frac{\hbar}{2}\right)^2\underline{\underline{\sigma}}_y^2 + \left(\frac{\hbar}{2}\right)^2\underline{\underline{\sigma}}_z^2 \overset{\checkmark}{=} \frac{3}{4}\hbar^2\underline{\underline{1}}$$

The eigenvalues of $\underline{\underline{\sigma}}_z$ are ± 1. By symmetry the eigenvectors of $\underline{\underline{\sigma}}_x$ and $\underline{\underline{\sigma}}_y$ must also be ± 1.

Example: Find the eigenvalues of $\underline{\underline{S}}_y$

$\underline{\underline{S}}_y |\psi_\alpha\rangle = g_\alpha |\psi_\alpha\rangle$ $\quad \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} \psi_{1,\alpha} \\ \psi_{2,\alpha} \end{pmatrix} = g_\alpha \begin{pmatrix} \psi_{1\alpha} \\ \psi_{2\alpha} \end{pmatrix}$

$-\frac{i\hbar}{2}\psi_{2,\alpha} = g_\alpha \psi_{1\alpha}$ and $\frac{i\hbar}{2}\psi_{1\alpha} = g_\alpha \psi_{2\alpha} = \left(g_\alpha^2 / \left(-\frac{i\hbar}{2}\right)\right)\psi_{1\alpha}$

$g_\alpha^2 = \frac{i\hbar}{2}\left(-\frac{i\hbar}{2}\right) = \frac{\hbar^2}{4} \Rightarrow g_+ = \frac{\hbar}{2} \quad g_- = -\frac{\hbar}{2}$

$-\frac{i\hbar}{2}\psi_{2+} = \frac{\hbar}{2}\psi_{1+} \Rightarrow \psi_+ = \begin{pmatrix} 1/\sqrt{2} \\ i/\sqrt{2} \end{pmatrix}$

$-\frac{i\hbar}{2}\psi_{2-} = -\frac{\hbar}{2}\psi_{1-} \Rightarrow \psi_- = \begin{pmatrix} 1/\sqrt{2} \\ -i/\sqrt{2} \end{pmatrix}$

$\langle\psi_-|\psi_+\rangle = \begin{pmatrix} \frac{1}{\sqrt{2}} & \frac{i}{\sqrt{2}} \end{pmatrix}\begin{pmatrix} 1/\sqrt{2} \\ i/\sqrt{2} \end{pmatrix} = \frac{1}{2} - \frac{1}{2} = 0$

Make sure look at eigenvalues and eigenvectors of $\underline{\underline{S}}_x$ and $\underline{\underline{S}}_z$

Example: Spin precession in a magnetic field

Remember that the energy for a dipole moment in a magnetic field is $U = -\vec{\mu}\cdot\vec{B}$ and $\vec{\mu} \propto g\vec{S}/m$

$H \equiv -\gamma \vec{B}\cdot\vec{S}$

We're free to pick the axis how we want so pick them where $\vec{B} = B_0\hat{z}$

$H = -\gamma B_0 S_z \Rightarrow i\hbar\frac{\partial}{\partial t}\begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix} = \begin{pmatrix} -\gamma B_0\hbar/2 & 0 \\ 0 & \gamma B_0\hbar/2 \end{pmatrix}\begin{pmatrix} \chi_1 \\ \chi_2 \end{pmatrix}$

$i\hbar\frac{d\chi_1}{dt} = -\gamma B_0\frac{\hbar}{2}\chi_1 \Rightarrow \chi_1(t) = e^{i\gamma B_0 t/2}\chi_1(0)$

$i\hbar\frac{d\chi_2}{dt} = \gamma B_0\hbar/2\,\chi_2 \Rightarrow \chi_2(t) = e^{-i\gamma B_0 t/2}\chi_2(0)$

The eigenergies are $-\frac{\gamma B_0\hbar}{2}$ and $\frac{\gamma B_0\hbar}{2}$

To understand what this is trying to tell us, lets examine the most general state

$\chi(t) = e^{i\xi}\begin{pmatrix} \cos(\alpha/2) \\ \sin(\frac{\alpha}{2})e^{i\beta} \end{pmatrix}$ $\quad$ Does the $e^{i\xi}$ change anything?

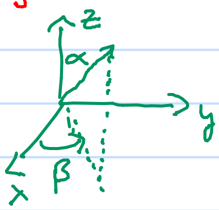
$$\langle \hat{S}_z \rangle = \chi^{\dagger} \underline{\underline{S_z}}\, \chi = \left(\cos(\tfrac{\alpha}{2}) \quad \sin(\tfrac{\alpha}{2})e^{-i\beta}\right)\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} \cos(\frac{\alpha}{2}) \\ \sin(\frac{\alpha}{2})e^{-i\beta} \end{pmatrix}$$

$$= \cos^2(\tfrac{\alpha}{2}) - \sin^2(\tfrac{\alpha}{2}) = \cos(\alpha)$$

$$\langle \hat{S}_x \rangle = \left(\cos(\tfrac{\alpha}{2}) \quad \sin(\tfrac{\alpha}{2})e^{-i\beta}\right)\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} \cos(\frac{\alpha}{2}) \\ \sin(\frac{\alpha}{2})e^{i\beta} \end{pmatrix}$$

$$= \cos(\tfrac{\alpha}{2})\sin(\tfrac{\alpha}{2})(e^{i\beta} + e^{-i\beta}) = \sin(\alpha)\cos(\beta)$$

$$\langle \hat{S}_y \rangle = \cos(\tfrac{\alpha}{2})\sin(\tfrac{\alpha}{2})(-i e^{i\beta} + i e^{-i\beta}) = \sin(\alpha)\sin(\beta)$$



Now add the time dependence

$$\chi(t) = e^{i\zeta}\begin{pmatrix} \cos(\frac{\alpha}{2})e^{i\gamma B_0 t/2} \\ \sin(\frac{\alpha}{2})e^{i\beta}e^{-i\gamma B_0 t/2} \end{pmatrix} = e^{i(\zeta + \gamma B_0 t/2)}\begin{pmatrix} \cos(\frac{\alpha}{2}) \\ \sin(\frac{\alpha}{2})e^{i(\beta - \gamma B_0 t)} \end{pmatrix}$$

$\langle S_z \rangle = \cos(\alpha)$ $\qquad$ $\langle S_x \rangle = \sin(\alpha)\cos(\beta - \gamma B_0 t)$ $\qquad$ $\langle S_y \rangle = \sin(\alpha)\sin(\beta - \gamma B_0 t)$

Why doesn't $\langle S_z \rangle$ change? Why doesn't tilt change?
What does this motion look like?

Look at the book discussion of Stern Gerlach experiment.

How to write the state when there are 2 or more particles with spin?
Two particles S_1, S_2 will have joint states

$|S_1 M_{s_1} S_2 M_{s_2}\rangle = |S_1 M_{s_1}\rangle |S_2 M_{s_2}\rangle$

These are rarely eigenstates of $\hat{H}$

One of the more common forms of interaction is proportional to $\vec{S}_1 \cdot \vec{S}_2$

This can be written as $\vec{S}_1 \cdot \vec{S}_2 = \frac{1}{2}\left[(\vec{S}_1 + \vec{S}_2)^2 - \vec{S}_1^{\,2} - \vec{S}_2^{\,2}\right]$

Instead of using eigenstates of $\vec{S}_1^{\,2}$, S_{1z}, $\vec{S}_2^{\,2}$, S_{2z} use the eigenstates of $\vec{S}_1^{\,2}$, $\vec{S}_2^{\,2}$, $\vec{S}^{\,2}$, S_z

$$\vec{S} \equiv \vec{S}_1 + \vec{S}_2 \qquad S_z = S_{1z} + S_{2z}$$

In classical mechanics, the $\vec{S}_1$ and $\vec{S}_2$ can be in any direction. The $\max|\vec{S}_1+\vec{S}_2| = |\vec{S}_1|+|\vec{S}_2|$ and the $\min|\vec{S}_1+\vec{S}_2| = \big|\,|\vec{S}_1|-|\vec{S}_2|\,\big|$

In Q.M. the allowed eigenvalues of $\vec{S}^{\,2}$ are $\hbar^2 s(s+1)$ with $s_1+s_2,\ s_1+s_2-1,\ \dots,\ |s_1-s_2|$

Example: Spin $\frac{5}{2}$ and spin $\frac{3}{2}$ Count states

Total number of $\frac{5}{2}$ states $2\,\frac{5}{2}+1 = 6$

" " " $\frac{3}{2}$ " $2\,\frac{3}{2}+1 = 4$

" " " states $= 6\cdot 4 = 24$

Total number of $\frac{5}{2}+\frac{3}{2}=4$ states $2\cdot 4+1 = 9$

" " " $\frac{5}{2}+\frac{3}{2}-1=3$ " $2\cdot 3+1 = 7$

" " " $\frac{5}{2}+\frac{3}{2}-2=2$ " $2\cdot 2+1 = 5$

" " " $\frac{5}{2}-\frac{3}{2}=1$ " $2\cdot 1+1 = 3$

sum = 24 states

Strategy for finding all of the eigenstates of $\vec{S}^{\,2}$ and S_z

① The state with $m_{s_1}=s_1$ and $m_{s_2}=s_2$ must be $s=s_1+s_2$, $m_s=s$

② Act on that state with $\hat{S}_-/(\hbar A^-_{s m_s})$. This must be $s=s_1+s_2$, $m_s=s-1$

③ Do $\hat{S}_-/(\hbar A^-_{s m_s-1})$ This must be $s=s_1+s_2$, $m_s=s-2$

etc until you've got $s=s_1+s_2$, $m_s=-s$

(?) The $s=s_1+s_2-1$, $m_s=s_1+s_2-1$ state must be the state orthogonal to the $s=s_1+s_2$, $m_s=s_1+s_2-1$ state

(?+1) Apply the $\hat{S}_-/(\hbar A^-_{s m_s})$ to this state to get $s=s_1+s_2-1$, $m_s=s_1+s_2-2$

etc

(??) The $s=s_1+s_2-2$, $m_s=s_1+s_2-2$ must be orthogonal to the states $s=s_1+s_2$, $m_s=s_1+s_2-2$ and $s=s_1+s_2-1$, $m_s=s_1+s_2-2$ states.

etc

Example: Spin 1 and spin $\frac{1}{2}$

$|\tfrac{3}{2},\tfrac{3}{2}\rangle = |1,1\rangle|\tfrac{1}{2},\tfrac{1}{2}\rangle$

$|\tfrac{3}{2},\tfrac{1}{2}\rangle = \frac{1}{\hbar}(S_{1-} + S_{2-})|1,1\rangle|\tfrac{1}{2},\tfrac{1}{2}\rangle \Big/ \sqrt{\left(\tfrac{15}{4} - \tfrac{3}{4}\right)} = \sqrt{\tfrac{2}{3}}|1,0\rangle|\tfrac{1}{2},\tfrac{1}{2}\rangle + \sqrt{\tfrac{1}{3}}|1,1\rangle|\tfrac{1}{2},-\tfrac{1}{2}\rangle$

$\vdots$

$|\tfrac{1}{2},\tfrac{1}{2}\rangle = -\sqrt{\tfrac{1}{3}}|1,0\rangle|\tfrac{1}{2},\tfrac{1}{2}\rangle + \sqrt{\tfrac{2}{3}}|1,1\rangle|\tfrac{1}{2},-\tfrac{1}{2}\rangle$

You can look up these coefficients

$$|s,m_s\rangle = \sum_{m_{1s}m_{2s}} |s_1 m_{1s}\rangle|s_2 m_{2s}\rangle \langle s_1 m_{1s} s_2 m_{2s}|s\, m_s\rangle \qquad m_{1s} + m_{2s} = m_s$$

The $\langle j_1 m_1\, j_2 m_2 | j\, m\rangle$ are Clebsch Gordon coefficients

Book notation $C^{s_1 s_2 s}_{m_1 m_2 m} = \langle s_1 m_1 s_2 m_2 | s\, m\rangle$

Show how to read the C.G. table

Example: $S_1 = 3/2 \quad S_2 = 1$

$|5/2, 5/2\rangle = |\tfrac{3}{2},\tfrac{3}{2}\rangle|1,1\rangle$

$|\tfrac{5}{2},\tfrac{3}{2}\rangle = \sqrt{\tfrac{2}{5}}|\tfrac{3}{2},\tfrac{3}{2}\rangle|1,0\rangle + \sqrt{\tfrac{3}{5}}|\tfrac{3}{2},\tfrac{1}{2}\rangle|1,1\rangle$

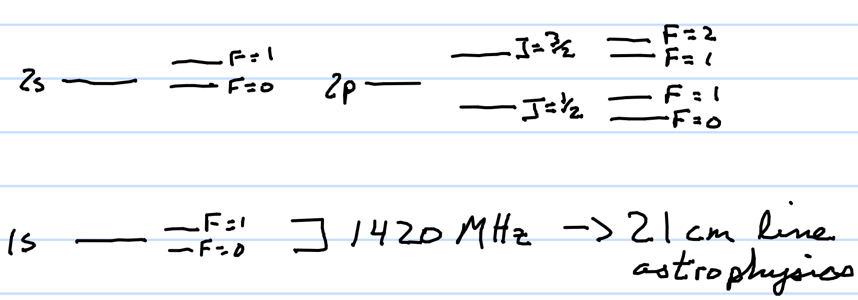
$|\tfrac{3}{2},\tfrac{3}{2}\rangle = \sqrt{\tfrac{3}{5}}|\tfrac{3}{2},\tfrac{3}{2}\rangle|1,0\rangle - \sqrt{\tfrac{2}{5}}|\tfrac{3}{2},\tfrac{1}{2}\rangle|1,1\rangle$

$|\tfrac{5}{2},\tfrac{1}{2}\rangle = \sqrt{\tfrac{1}{10}}|\tfrac{3}{2},\tfrac{3}{2}\rangle|1,-1\rangle + \sqrt{\tfrac{6}{10}}|\tfrac{3}{2},\tfrac{1}{2}\rangle|1,0\rangle + \sqrt{\tfrac{3}{10}}|\tfrac{3}{2},-\tfrac{1}{2}\rangle|1,1\rangle$

$|\tfrac{3}{2},\tfrac{1}{2}\rangle = \sqrt{\tfrac{6}{15}}|\tfrac{3}{2},\tfrac{3}{2}\rangle|1,-1\rangle + \sqrt{\tfrac{1}{15}}|\tfrac{3}{2},\tfrac{1}{2}\rangle|1,0\rangle - \sqrt{\tfrac{8}{15}}|\tfrac{3}{2},-\tfrac{1}{2}\rangle|1,1\rangle$

$|\tfrac{1}{2},\tfrac{1}{2}\rangle = \sqrt{\tfrac{3}{6}}|\tfrac{3}{2},\tfrac{3}{2}\rangle|1,-1\rangle - \sqrt{\tfrac{2}{6}}|\tfrac{3}{2},\tfrac{1}{2}\rangle|1,0\rangle + \sqrt{\tfrac{1}{6}}|\tfrac{3}{2},-\tfrac{1}{2}\rangle|1,1\rangle$

Schematic of fine structure and hyperfine structure in H



$\vec{J} = \vec{L} + \vec{S}_e$ Fine

$\vec{F} = \vec{J} + \vec{S}_p$ Hyperfine

Example : Energy splittings when $\hat{H} = \varepsilon_0 \vec{S}_1 \cdot \vec{S}_2 / \hbar^2$

$$\vec{S}_1 \cdot \vec{S}_2 = \frac{1}{2}\left(\vec{S}^2 - \vec{S}_1^2 - \vec{S}_2^2 \right)$$

$$E_s = \frac{\varepsilon_0}{2}\left[s(s+1) - s_1(s_1+1) - s_2(s_2+1) \right]$$

$s = |s_1 - s_2|, |s_1 - s_2| + 1, \ldots$
$\ldots, s_1 + s_2 - 1, s_1 + s_2$

For H ground state $s = 1$ and 0

$$E_1 - E_0 = (\varepsilon_0/2)\left[1 \cdot 2 - \tfrac{3}{4} - \tfrac{3}{4}\right] - (\varepsilon_0/2)\left[0 \cdot 1 - \tfrac{3}{4} - \tfrac{3}{4}\right] = \varepsilon_0 = h \cdot 1420\,\text{MHz}$$