Schrodinger equation in spherical coordinates

$$\hat{H} = \frac{\hat{p}^2}{2m} + U(r)$$ central potential, depends only on r

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

$$\hat{H}\psi(r,\theta,\varphi) = -\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial r^2} + \frac{2}{r}\frac{\partial\psi}{\partial r}\right) + \frac{\hat{L}^2\psi}{2mr^2} + U(r)\psi = E\psi$$

$$\hat{L}^2\psi(r,\theta,\varphi) = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\varphi^2}\right]$$

$$\hat{L}_z\psi(r,\theta,\varphi) = -i\hbar\frac{\partial\psi}{\partial\varphi}$$

For central potential the angular momentum is conserved, so $[\hat{H},\hat{L}^2]=0$ and $[\hat{H},\hat{L}_z]=0$
So we can use eigenstates of $\hat{L}^2$ & $\hat{L}_z$ to describe the ~~spatial~~ angular dependence of the wave functions

$$\hat{L}^2 Y_{lm}^{(\theta,\varphi)} = \hbar^2 l(l+1)\, Y_{lm}^{(\theta,\varphi)} \qquad \hat{L}_z Y_{lm} = \hbar m\, Y_{lm}$$

$$\psi_{nlm}(r,\theta,\varphi) = \frac{u_{nl}(r)}{r} Y_{lm}(\theta,\varphi)$$

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

quazi- 1D Schrodinger eqn

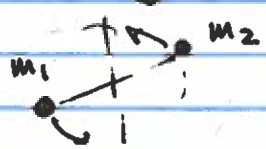
What can we solve with this eqn?

1. Nuclear structure
Strong force → strong confinement →
spherical infinite well model
Particles → protons, neutrons

2. Atomic structure
Coulumb force $U(r) = -\frac{ke^2}{r}$
Can describe ground / excited states of an electron in an atom

3. Molecular motion
- vibration → Harmonic potential
$U(r) \approx U(r_0) + \frac{1}{2}\mu\omega^2 (r-r_0)^2$

- rotation around center of mass
"Rigid" rotator



Rotational kinetic energy

Classical: $K = I\omega^2$ $\vec{L} = I\vec{\omega}$ $K = \frac{L^2}{2I}$

Quantum: $\hat{H} = \frac{\hat{L}^2}{2I}$ (no r-dependence!)

Eigenstates → $Y_{lm}(\theta,\varphi)$

$\hat{H}\, Y_{lm}(\theta,\varphi) = \frac{\hbar^2 l(l+1)}{2I} Y_{lm}(\theta,\varphi)$ $E_{lm} \equiv E_l = \frac{\hbar^2}{2I} l(l+1)$

Rotator energy spectrum

$E_3 = \frac{6\hbar^2}{I}$

$E_2 = \frac{3\hbar^2}{I}$

$E_1 = \frac{2\hbar^2}{2I} = \frac{\hbar^2}{I}$

$E_0 = 0$

In practice, it is hard to map the energy levels of an object, in most cases we can only measure the <u>difference</u> b/w the levels by detecting the energy of photons emitted when the particle "jumps" b/w the levels.

$E_3 = 6E_1$

$\Delta E_{32} = E_3 - E_2 = 3\hbar^2/I$

$E_2 = 3E_1$

$\Delta E_{21} = E_2 - E_1 = 2\hbar^2/I$

$E_1 = \hbar^2/I$

$\Delta E_{10} = E_1 - E_0 = \hbar^2/I$

$E_0 = 0$

$$\Delta E_{\ell,\ell-1} = E_\ell - E_{\ell-1} = \frac{\hbar^2}{2I}\underbrace{\left[\ell(\ell+1) - (\ell-1)\ell\right]}_{2\ell} = \frac{\hbar^2 \ell}{I}$$

Photon frequency $\hbar\omega_{\ell,\ell-1} = \Delta E_{\ell,\ell-1} = \frac{\hbar^2 \ell}{I}$

$$\omega_{\ell,\ell-1} = \frac{\hbar \ell}{I}$$

Photon wavelength $\lambda_{\ell,\ell-1} = \frac{2\pi c}{\omega_{\ell,\ell-1}} = \frac{2\pi I}{\hbar \ell}$

~~What if we~~ What about transitions with $\Delta\ell > 1$, should we account for them?
No, because of the selection rules

Photon has spin (angular momentum) 1, so we have to obey the conservation of the angular momentum $L_{fin} - L_{ini} = \pm 1$ $\hat{L}_{phot}$

Thus, we can only emit photons in transitions with $\Delta\ell = \pm 1$

A rotator in a magnetic field

$$\hat{\vec{\mu}} = \mu_B g_L \hat{\vec{L}} \qquad \vec{B} = (0,0,B) \qquad -\hat{\vec{\mu}}\vec{B} = \mu_B \cdot g_L B \cdot \hat{\vec{L}}$$
$$= \omega_B \hat{\vec{L}}$$

$$\hat{H} = \frac{\hat{L}^2}{2I} + \omega_B \hat{L}_z \qquad Y_{\ell m}(\theta,\varphi) \text{ — still eigenstates!}$$

$$\hat{H} Y_{\ell m} = \frac{1}{2I} \hat{L}^2 Y_{\ell m} + \omega_B \hat{L}_z Y_{\ell m} = \frac{\hbar^2}{2I} \ell(\ell+1) Y_{\ell m} + \hbar\omega_B m\, Y_{\ell m}$$

$$E_{\ell m} = \frac{\hbar^2}{2I} \ell(\ell+1) + \hbar\omega_B m$$

We usually observe the dependence of energy on m in the presence of magn. field, since it breaks rotational symmetry

Time evolution

$t=0 \qquad \psi_{\ell m}(\theta,\varphi,t^{0}) = Y_{\ell m}(\theta,\varphi)$

$t>0 \qquad \psi_{\ell m}(\theta,\varphi,t) = e^{-iE_{\ell m}t/\hbar}\, Y_{\ell m}(\theta,\varphi)$

$$Y_0^0(\theta,\phi)=\frac{1}{2}\,\frac{1}{\sqrt{\pi}}$$

$$Y_1^{-1}(\theta,\phi)=\frac{1}{2}\sqrt{\frac{3}{2\pi}}\,\sin\theta\, e^{-i\phi}$$

$$Y_1^0(\theta,\phi)=\frac{1}{2}\sqrt{\frac{3}{\pi}}\,\cos\theta$$

$$Y_1^1(\theta,\phi)=-\frac{1}{2}\sqrt{\frac{3}{2\pi}}\,\sin\theta\, e^{i\phi}$$

$$Y_2^{-2}(\theta,\phi)=\frac{1}{4}\sqrt{\frac{15}{2\pi}}\,\sin^2\theta\, e^{-2i\phi}$$

$$Y_2^{-1}(\theta,\phi)=\frac{1}{2}\sqrt{\frac{15}{2\pi}}\,\sin\theta\cos\theta\, e^{-i\phi}$$

$$Y_2^0(\theta,\phi)=\frac{1}{4}\sqrt{\frac{5}{\pi}}\,\left(3\cos^2\theta-1\right)$$

$$Y_2^1(\theta,\phi)=-\frac{1}{2}\sqrt{\frac{15}{2\pi}}\,\sin\theta\cos\theta\, e^{i\phi}$$

$$Y_2^2(\theta,\phi)=\frac{1}{4}\sqrt{\frac{15}{2\pi}}\,\sin^2\theta\, e^{2i\phi}$$

$$Y_3^{-3}(\theta,\phi)=\frac{1}{8}\sqrt{\frac{35}{\pi}}\,\sin^3\theta\, e^{-3i\phi}$$

$$Y_3^{-2}(\theta,\phi)=\frac{1}{4}\sqrt{\frac{105}{2\pi}}\,\sin^2\theta\cos\theta\, e^{-2i\phi}$$

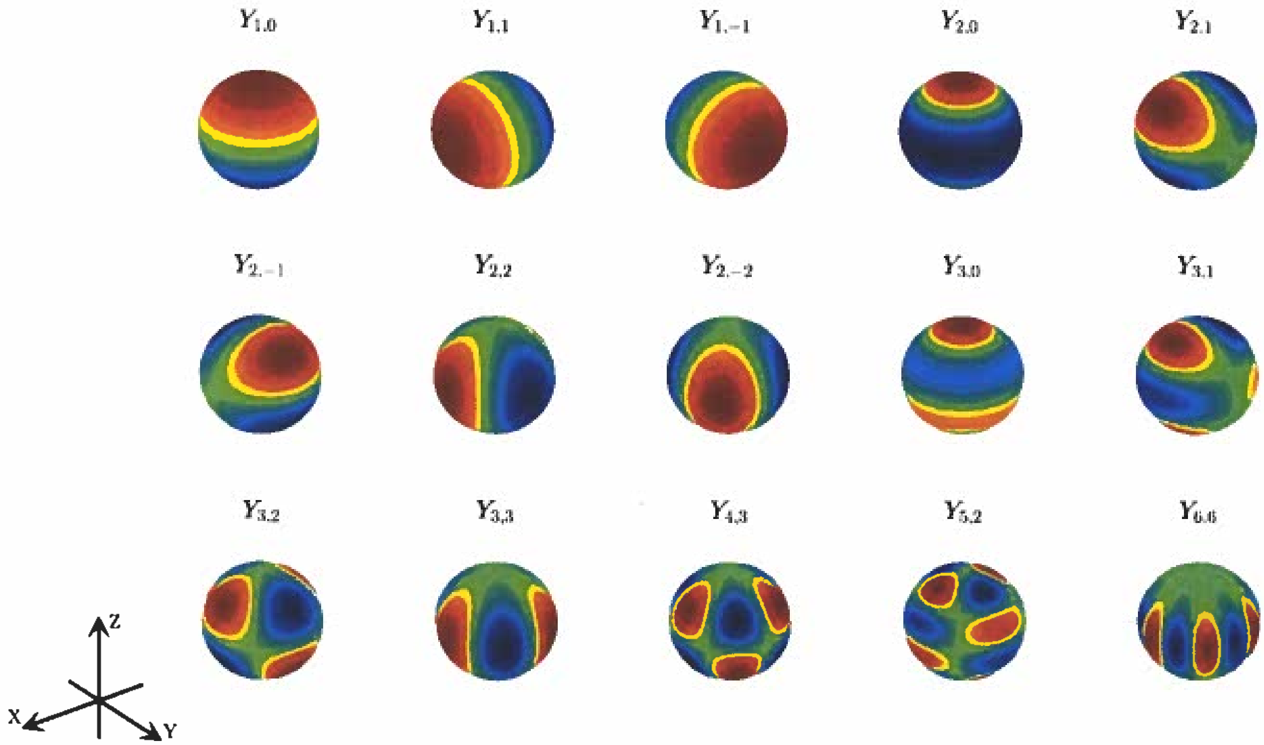
$$Y_3^{-1}(\theta,\phi)=\frac{1}{8}\sqrt{\frac{21}{\pi}}\,\sin\theta\left(5\cos^2\theta-1\right)e^{-i\phi}$$

$$Y_3^0(\theta,\phi)=\frac{1}{4}\sqrt{\frac{7}{\pi}}\,\left(5\cos^3\theta-3\cos\theta\right)$$

$$Y_3^1(\theta,\phi)=-\frac{1}{8}\sqrt{\frac{21}{\pi}}\,\sin\theta\left(5\cos^2\theta-1\right)e^{i\phi}$$

$$Y_3^2(\theta,\phi)=\frac{1}{4}\sqrt{\frac{105}{2\pi}}\,\sin^2\theta\cos\theta\, e^{2i\phi}$$

$$Y_3^3(\theta,\phi)=-\frac{1}{8}\sqrt{\frac{35}{\pi}}\,\sin^3\theta\, e^{3i\phi}.$$



Spherical functions

$$Y_l^m(\theta, \phi) \equiv \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}} P_l^m(\cos\theta) e^{im\phi}.$$

Associate Legandre polynomials

$$P_n^m(x) = \frac{(1-x^2)^{\frac{m}{2}}}{2^n n!} \frac{d^{n+m}}{dx^{n+m}} (x^2-1)^n.$$