3-D Quantum mechanics

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi \qquad \hat{H} = \frac{1}{2}m\vec{v}^2 + V(\vec{r}) = \frac{1}{2m}(\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2) + V(\vec{r})$$

$$\hat{p}_i = -i\hbar \frac{\partial}{\partial x_i}$$

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

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

where $\int |\Psi|^2 d^3\vec{r} = 1$ $\quad \Psi \to \Psi(x,y,z,t)$ or $\Psi(r,\theta,\phi,t)$

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

and $\hat{H}\psi = E\psi$ or $-\frac{\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi$

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

Canonical commutation relations

$$[r_i, p_j] = i\hbar\delta_{ij} \quad , \quad [r_i, r_j] = [p_i, p_j] = 0$$

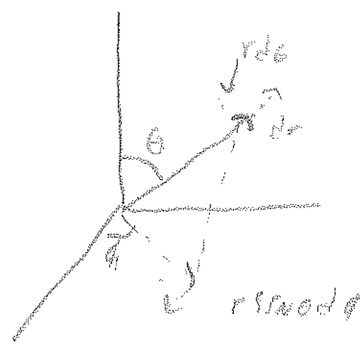
SOV $\rightarrow$ Typically $V(\vec{r}) = V(|r|)$ $|r| \rightarrow$ distance

Hydrogen $V(|r|) = \frac{1}{4\pi\epsilon_0 r} q_1 q_2$ $q_1 = \overset{p}{|e|}$ $q_2 = -\overset{e}{|e|}$

now $d\vec{r}$ in cartesian $= dx\,\hat{e}_x + dy\,\hat{e}_y + dz\,\hat{e}_z$

For r, θ, ϕ $d\vec{r} = dr\,\hat{e}_r + r\,d\theta\,\hat{e}_\theta + r\sin\theta\,d\phi\,e_\phi$

$= h_1\,dx_1\,\hat{e}_1 + h_2\,dx_2\,\hat{e}_2 + h_3\,dx_3\,\hat{e}_3$



$\nabla^2 = \nabla\cdot\nabla(\ )$ $h_1 = 1$ $h_2 = r$ $h_3 = r\sin\theta$

$$= \frac{1}{h_1 h_2 h_3}\left(\frac{\partial}{\partial x_1}\frac{h_2 h_3}{h_1}\frac{\partial}{\partial x_1} + \frac{\partial}{\partial x_2}\frac{h_1 h_3}{h_2}\frac{\partial}{\partial x_2} + \frac{\partial}{\partial x_3}\frac{h_1 h_2}{h_3}\frac{\partial}{\partial x_3}\right)$$

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

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

$$\hat{H}\psi = E\psi \rightarrow -\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial \psi}{\partial r} + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta} \sin\theta \frac{\partial \psi}{\partial \theta} + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 \psi}{\partial \phi^2}\right] + V(r)\psi = E\psi$$

Look for $\psi(r,\theta,\phi) = R(r)\,Y(\theta,\phi)$

$$-\frac{\hbar^2}{2m}\left[\frac{Y}{r^2}\frac{d}{dr} r^2 \frac{dR}{dr} + \frac{R}{r^2 \sin\theta}\frac{\partial}{\partial \theta} \sin\theta \frac{\partial Y}{\partial \theta} + \frac{R}{r^2 \sin^2\theta}\frac{\partial^2 Y}{\partial \phi^2}\right] + RY\,V(r) = RYE$$

Divide by RY, multiply by $-\frac{2mr^2}{\hbar^2}$

$$\left[\frac{1}{R}\frac{d}{dr} r^2 \frac{dR}{dr} - \frac{2mr^2}{\hbar^2}\left(V(r) - E\right)\right] + \frac{1}{Y}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial \theta} \sin\theta \frac{\partial Y}{\partial \theta} + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial \phi^2}\right] = 0$$

$F(r) \overset{?}{=} \ell(\ell+1)$ $\qquad$ $F(\theta,\phi) = -\ell(\ell+1)$

Separated

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

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

Why later

Example → IS cube $V=0$ $x, y, z \in [0, a]$

$\psi_n(r)$? $$-\frac{\hbar^2}{2m}\left[\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right]=E\psi$$

$$\psi = X_{(x)}\,Y_{(y)}\,Z_{(z)}$$

$$-\frac{\hbar^2}{2m}\left[YZ\frac{\partial^2 X}{\partial x^2}+XZ\frac{\partial^2 Y}{\partial y^2}+XY\frac{\partial^2 Z}{\partial z^2}\right]=XYZE$$

$$-\frac{\hbar^2}{2m}\left[\frac{1}{X}\frac{\partial^2 X}{\partial x^2}+\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}+\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}\right]=E$$

Or $$\frac{1}{X}\frac{\partial^2 X}{\partial x^2}+\frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}+\frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}=-\frac{2m}{\hbar^2}E=-\frac{2m}{\hbar^2}(E_x+E_y+E_z)=-\frac{2mE_x}{\hbar^2}-\frac{2mE_y}{\hbar^2}-\frac{2mE_z}{\hbar^2}$$

Or $$\frac{1}{X}\frac{\partial^2 X}{\partial x^2}=-\frac{2mE_x}{\hbar^2},\quad \frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}=-\frac{2mE_y}{\hbar^2},\quad \frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}=-\frac{2mE_z}{\hbar^2}$$

1D → $\frac{p^2}{2m}=E \to \frac{\hbar^2 k^2}{2m}=E$ So $k^2=\frac{2mE}{\hbar^2}$

$$\frac{1}{X}\frac{\partial^2 X}{\partial x^2}=-k_x^2,\quad \frac{1}{Y}\frac{\partial^2 Y}{\partial y^2}=-k_y^2,\quad \frac{1}{Z}\frac{\partial^2 Z}{\partial z^2}=-k_z^2$$

↓

$$\frac{\partial^2 X}{\partial x^2}=-k_x^2 X \to \frac{\partial^2 X}{\partial x^2}+k_x^2 X=0$$

$X(x) = A\cos(k_x x) + B\sin(k_x x)$

$X(0) = 0 \rightarrow A = 0 \quad B\sin(k_x a) = 0 \quad k_x a = n_x\pi \quad k_x = \frac{n_x \pi}{a}$

$X(x) = B\sin\left(\frac{n_x \pi x}{a}\right) \quad k_x = \frac{n_x \pi}{a} \quad E_x = \frac{1}{2m}\left(\frac{n_x \pi \hbar}{a}\right)^2$

iterate $x \rightarrow y \rightarrow z$

$\Psi(x,y,z) = XYZ = B_x \sin\left(\frac{n_x \pi x}{a}\right) B_y \sin\left(\frac{n_y \pi y}{a}\right) B_z \left(\frac{n_z \pi}{a} z\right)$

$$\underline{E = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 \pi^2}{2ma^2}\left[n_x^2 + n_y^2 + n_z^2\right]}$$

$\int |\Psi|^2 d^3r = \int |\Psi|^2 dx\,dy\,dz = \int_0^a X^2 dx \int_0^a Y^2 dy \int Z^2 dz$

$B_x = B_y = B_z = \sqrt{\frac{2}{a}} \quad \underline{\Psi(x,y,z) = \left(\sqrt{\frac{2}{a}}\right)^3 \sin\left(\frac{n_x \pi}{a} x\right)\sin\left(\frac{n_y \pi}{a} y\right)\sin\left(\frac{n_z \pi}{a} z\right)}$

What if not a but L_x, L_y, L_z?

E? Ψ?

Ok, back to r, θ, ϕ What is the same?

$V = V(r)$ only not $V(\theta, \phi)$

We only need to solve the angular equation ONCE!!

Then $R(r)$ depends on $V(r)$

Angular Equation $\rightarrow$ call $Y(\theta,\phi) = \Theta(\theta)\,\Phi(\phi)$

$$\rightarrow \frac{1}{\Theta}\left[\sin(\theta)\frac{d}{d\theta}\sin(\theta)\frac{d\Theta}{d\theta}\right] + l(l+1)\sin^2(\theta) + \frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = 0$$

↑ call this $-m^2$

$$\frac{1}{\Theta}\left(\sin(\theta)\frac{d}{d\theta}\sin(\theta)\frac{d\Theta}{d\theta} + l(l+1)\sin^2\theta\right) = m^2$$

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m^2 \rightarrow \frac{d^2\Phi}{d\phi^2} + m^2\Phi = 0$$

$\Phi(\phi) = e^{\pm im\phi}$ or $e^{im\phi}$ where m positive or negative

and $e^{im\phi} = e^{im(\phi+2\pi)}$

The Θ equation is $\sin\theta \dfrac{d}{d\theta} \sin\theta \dfrac{d\Theta}{d\theta} + \left[\ell(\ell+1)\sin^2\theta - m^2 \right] \Theta = 0$

is harder

Solution $= A\, P_\ell^m(\cos\theta)$

$P_\ell^m \rightarrow$ associated Legendre function

$= P_\ell^m(x) = (1-x^2)^{|m|/2} \left(\dfrac{d}{dx}\right)^{|m|} P_\ell(x) \qquad x = \cos(\theta)$

$P_\ell(x) \rightarrow$ Legendre Polynomial $= \dfrac{1}{2^\ell \ell!} \left(\dfrac{d}{dx}\right)^\ell (x^2-1)^\ell \rightarrow$ Rodrigues Formula

$P_0(x) = 1 \qquad P_1(x) = \dfrac{1}{2^1 1!} \dfrac{d}{dx}(x^2-1)^1 = \dfrac{1}{2} \cdot 2x = x$

$P_2(x) = \dfrac{1}{2^2 2!} \left(\dfrac{d}{dx}\right)^2 (x^2-1)^2 = \dfrac{1}{8} \dfrac{d^2}{dx^2}(x^4 - 2x^2 + 1) = \dfrac{1}{8}\dfrac{d}{dx}(4x^3 - 4x)$

$= \dfrac{1}{8}(12x^2 - 4) = \dfrac{3}{2}x^2 - \dfrac{1}{2} = \dfrac{1}{2}(3x^2 - 1)$

$P_2(x) = \frac{1}{2}(3x^2-1)$ $\quad P_2^1 = (1-x^2)^{1/2} \frac{d}{dx}\left(\frac{1}{2}(3x^2-1)\right)$

$= \sqrt{1-x^2} \cdot 3x$ but $\underline{x = \cos(\theta)}$

$= \sqrt{1-\cos^2\theta} \cdot 3\cos\theta = 3\sin\theta\cos\theta$

$P_2^2 = (1-x^2)^{2/2}\left(\frac{d}{dx}\right)^2\left(\frac{1}{2}(3x^2-1)\right) = \frac{1-x^2}{2}\frac{d}{dx}(6x) = \frac{(1-x^2)}{2} \cdot 6 = 3(1-x^2) = 3\sin^2\theta$

Now $P_\ell(x) = \frac{1}{2^\ell \ell!}\left(\frac{d}{dx}\right)^\ell (x^2-1)^\ell$ $\quad \underline{\ell = 0, 1, 2, \ldots}$

$P_\ell^m(x) = (1-x^2)^{|m|/2}\left(\frac{d}{dx}\right)^{|m|} P_\ell(x)$ $\quad$ if $|m| > \ell$ $\; P_\ell^m(x) = 0$

So $|m| \leq \ell$ or No Solution

if $\ell = 0$ $m = 0$ $\quad$ if $\ell = 1$ $m = -1, 0, 1$ $\quad \ell = 2$ $\; -2, -1, 0, 1, 2$

in general m has $2\ell+1$ values.

Spherical Harmonics $\quad Y(\theta, \phi) = \Phi(\theta) = A P_\ell^m(\theta) e^{im\phi}$

Now $\Psi(r,\theta,\phi) = R(r)\,Y(\theta,\phi)$ $\quad d^3r = r^2 \sin\theta\, dr\, d\theta\, d\phi$

$$\int |\Psi|^2 d^3r = \int |R|^2 r^2 dr \int |Y|^2 \sin\theta\, d\theta\, d\phi = 1$$

or $\int |R|^2 r^2 dr = 1$ and $\int |Y|^2 \sin\theta\, d\theta\, d\phi = 1$

Generic Normalization Beyond the Scope

$$Y_\ell^m(\theta,\phi) = \begin{bmatrix} (-1)^m & / & 1 \\ m \geq 0 & / & m \leq 0 \end{bmatrix} \sqrt{\frac{(2\ell+1)}{4\pi}\frac{(\ell-|m|)!}{(\ell+|m|)!}}\; e^{im\phi}\, P_\ell^m(\cos\theta)$$

and $$\int_0^{2\pi}\int_0^{\pi} Y_{\ell'}^{m'*} Y_\ell^m \sin\theta\, d\theta\, d\phi = \delta_{\ell\ell'}\,\delta_{mm'}$$

$$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta \qquad Y_1^1 = -\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta \, e^{i\phi}$$

$$\langle Y_1^0 | Y_1^1 \rangle = -\frac{3}{\pi} \cdot \frac{1}{\sqrt{32}} \int_0^{2\pi} e^{i\phi} d\phi \int_0^{\pi} \cos\theta \sin^2\theta \, d\theta$$

$$\int_0^{2\pi} e^{i\phi} d\phi = \frac{1}{i} e^{i\phi} \Big|_0^{2\pi} = \frac{1}{i}\left[\underset{1}{\underset{\uparrow}{e^{2\pi i}}} - \underset{1}{\underset{\uparrow}{e^0}}\right] \rightarrow 0$$

$$\langle Y_1^1 | Y_1^1 \rangle = \frac{3}{8\pi} \int_0^{2\pi} e^{i\phi} e^{-i\phi} d\phi \int_0^{\pi} \sin^3\theta \, d\theta$$

$$= \frac{3}{8\pi} \cdot 2\pi \int_0^{\pi} \sin\theta(1-\cos^2\theta) \, d\theta$$

$$= \frac{3}{4}\left[\int_0^{\pi} \sin\theta \, d\theta - \int_0^{\pi} \sin\theta \cos^2\theta \, d\theta\right] \qquad u = \cos\theta \quad du = -\sin\theta \, d\theta$$

$$\theta = 0 \quad u = 1 \quad \theta = \pi \quad u = -1$$

$$= \frac{3}{4}\left[\cos\theta \Big|_{\pi}^{0} + \int_1^{-1} u^2 \, du\right]$$

$$= \frac{3}{4}\left[2 + \frac{u^3}{3}\Big|_1^{-1}\right] \qquad -\frac{1}{3} - \frac{1}{3} = -\frac{2}{3}$$

$$= \frac{3}{4}\left[2 - \frac{2}{3}\right]$$

$$= \frac{3}{4}\left[\frac{4}{3}\right] = \underline{1}$$

The Radial Equation

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

Let $u(r) = r\,R(r)$

Then $u(r)r^{-1} = R(r)$

$$\frac{dR}{dr} = \frac{d\,(u(r)r^{-1})}{dr} = \frac{u'(r)}{r} - \frac{u(r)}{r^2}$$

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

$$r\,u''(r) - \frac{2mr}{\hbar^2}\left[V - E\right]u(r) = \ell(\ell+1)\frac{u(r)}{r}$$

$$u''(r) - \frac{2m}{\hbar^2}\left[V - E\right]u(r) = \ell(\ell+1)\frac{u(r)}{r^2}$$

$$-\frac{\hbar^2}{2m}u''(r) + \left[V - E\right]u(r) = -\frac{\hbar^2}{2m}\ell(\ell+1)\frac{u(r)}{r^2}$$

or
$$\underline{-\frac{\hbar^2}{2m}u''(r) + \underbrace{\left[V + \frac{\hbar^2}{2mr^2}\ell(\ell+1)\right]}_{V_{eff}}u(r) = E\,u(r)}$$

Ex.) $V(r) = \begin{cases} 0 & r < a \\ \infty & r > a \end{cases}$

$$u'' = \left(\frac{\ell(\ell+1)}{r^2} - k^2 \right) u \qquad k = \frac{\sqrt{2mE}}{\hbar}$$

$\ell = 0 \quad u'' + k^2 u = 0$

$$u = A\cos(kr) + B\sin(kr) \qquad R = \frac{u(r)}{r}$$

$$R(r) = \frac{A\cos(kr)}{r} + \frac{B\sin(kr)}{r}$$

$$\lim_{r \to 0} R(r) = \frac{1}{0} + \frac{0}{0}? \to \frac{kB\cos(kr)}{1} = \frac{Bk}{1} \text{ finite}$$

$\uparrow$ ∞ $A=0$

$$R(r) = \frac{B\sin(kr)}{r} \quad \text{now } \sin(ka) = 0 \quad \text{so } ka = n\pi \quad E = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

Now, $\psi_{n00} = \frac{1}{\sqrt{2\pi a}} \frac{\sin(n\pi r/a)}{r}$

$\ell \neq 0$ harder answer $u(r) = A r j_\ell(kr) + B r n_\ell(kr)$

Spherical Bessel function

Spherical Neumann function

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

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

Neumann $\rightarrow$ $\eta_0(x) = -\frac{1}{x}$, $\eta_1(x) = -\frac{\cos(x)}{x^2} - \frac{\sin(x)}{x}$, ...

$\eta_\ell(x) \longrightarrow \infty$ as $x \to 0$

So $u(r) = A\,r\,j_\ell(kr)$

need $j_\ell(ka) = 0$ so energies are zeros of $j_\ell(x) \to$ need

To do numerically

$k = \frac{1}{a} \beta_{n\ell}$ ℓ zeros $\quad E_{n\ell} = \frac{\hbar^2}{2ma^2}\beta$

$\psi_{n\ell m} = A_{n\ell}\, j_\ell(\beta_{n\ell} r/a)\, Y_\ell^m(\theta, \phi)$