NO.

DATE / /

Quantum Mechanics in Three Dimensions

The Schrodinger Equation

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi = \underbrace{\left[\frac{p^2}{2m} + V(x)\right]}_{\frac{1}{2m}(p_x^2+p_y^2+p_z^2)+V(\vec{r})}\Psi$$

$$i\hbar \frac{\partial \Psi(\vec{r},t)}{\partial t} = H\Psi(\vec{r},t) \qquad \Psi(\vec{r},t) = \psi(\vec{r})\phi(t),\ \phi(t) = e^{-\frac{iEt}{\hbar}}$$

$$\Rightarrow H\psi(\vec{r}) = E\psi(\vec{r})$$

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

Example : infinite potential box

$$V(x,y,z)\begin{cases} 0 & 0<x,y,z<a \\ \infty & \text{otherwise} \end{cases}$$

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

B.C.s $\psi(x,y,0) = \psi(x,y,a) = \psi(x,0,z) = \psi(x,a,z) = \psi(0,y,z) = \psi(a,y,z) = 0$

let $\psi(x,y,z) = X(x)Y(y)Z(z)$

$$\Rightarrow -\frac{\hbar^2}{2m}\frac{d^2X}{dx^2} = E_x X \qquad E_x + E_y + E_z = E$$

$$-\frac{\hbar^2}{2m}\frac{d^2Y}{dy^2} = E_y Y \qquad E_x = \frac{\hbar^2 k_x^2}{2m} \quad E_y = \frac{\hbar^2 k_y^2}{2m} \quad E_z = \frac{\hbar^2 k_z^2}{2m}$$

$$-\frac{\hbar^2}{2m}\frac{d^2Z}{dz^2} = E_z Z$$

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

$X(0) = 0$, $A = 0$

$X(a) \Rightarrow k_x a = n_x \pi$

$$\Rightarrow \psi(x,y,z) = \left(\frac{2}{a}\right)^{\frac{3}{2}} \sin\frac{n_x \pi x}{a} \sin\frac{n_y \pi y}{a} \sin\frac{n_z \pi z}{a}$$

$$E = \frac{\pi^2\hbar^2}{2ma^2}(n_x^2 + n_y^2 + n_z^2)$$

Spherical Coordinates

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

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

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

$$\psi(r,\theta,\phi) = R(r)\underbrace{Y(\theta,\phi)}_{=\Theta(\theta)\Phi(\phi)} \quad \text{spherical harmonic function}$$

NO.

DATE / /

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

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

$\div YR$
$\times -\frac{2mr^2}{\hbar^2}$

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

$$\frac{1}{Y}\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial Y}{\partial\theta}) + \frac{1}{Y\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2} = \text{const.} = -l(l+1)$$

$\times Y\sin^2\theta$

$\frac{d\Theta}{d\theta}\Phi$

The Angular Equation

$\sin\theta\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial\Theta\Phi}{\partial\theta}) + \frac{\partial^2\Theta\Phi}{\partial\phi^2}$
$= -l(l+1)\sin^2\theta\,\Theta\Phi$

$$\sin\theta\frac{\partial}{\partial\theta}(\sin\theta\frac{\partial Y}{\partial\theta}) + \frac{\partial^2 Y}{\partial\phi^2} = -l(l+1)\sin^2\theta Y$$

Laplace's eq.

$Y = \Theta(\theta)\Phi(\phi)$
$\div\Theta\Phi$

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

$$\Rightarrow \frac{\sin\theta}{\Theta}\frac{d}{d\theta}(\sin\theta\frac{d\Theta}{d\theta}) + l(l+1)\sin^2\theta = \text{const.} = m^2$$

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -\text{const} = -m^2,\quad \frac{d^2\Phi}{d\phi^2} = -m^2\Phi,\quad \Phi(\phi) = e^{im\phi},\quad \Phi(\phi+2\pi) = \Phi(\phi)$$

$$e^{im(\phi+2\pi)} = e^{im\phi},\quad e^{im\cdot 2\pi} = 1,\quad m = 0, \pm1, \pm2\cdots$$

$e^{i2\pi} = \cos 2\pi + i\sin 2\pi$
$e^{-i2\pi} = \cos 2\pi + i\sin(-2\pi)$

$$\sin\theta\frac{d}{d\theta}(\sin\theta\frac{d\Theta}{d\theta}) + [l(l+1)\sin^2\theta - m^2]\Theta = 0$$

let $\cos\theta = x$
$-\sin\theta\, d\theta = dx$ $\quad \frac{1}{d\theta} = -\frac{\sin\theta}{dx}$
$\sin^2\theta = 1-x^2$

$$\sin^2\theta\frac{d}{dx}(\sin^2\theta\frac{df}{dx}) + [l(l+1)\sin^2\theta - m^2]f(x) = 0$$

$\sin\theta \cdot \sin\theta\frac{d}{dx}(\sin^2\theta\frac{df}{dx})$

$$(1-x^2)\frac{d}{dx}\left[(1-x^2)\frac{df}{dx}\right] + [l(l+1)(1-x^2)-m^2]f(x) = 0$$

(i) let $m=0$

$$\Rightarrow (1-x^2)\frac{d}{dx}\left[(1-x^2)\frac{df}{dx}\right] + l(l+1)(1-x^2)f = 0$$

$$(1-x^2)^2\frac{d^2f}{dx^2} - 2x(1-x^2)\frac{df}{dx} + l(l+1)(1-x^2)f = 0,\quad (1-x^2)\frac{d^2f}{dx^2} - 2x\frac{df}{dx} + l(l+1)f = 0$$

Legendre equation

let $f(x) = \sum_{n=0}^{\infty} a_n x^n \quad f'(x) = \sum_{n=0}^{\infty} n a_n x^{n-1} \quad f''(x) = \sum_{n=0}^{\infty} n(n-1)a_n x^{n-2}$

$$\Rightarrow a_{n+2} = -\frac{(l-n)(l+n+1)}{(n+1)(n+2)}a_n$$

for $n \gg 1$, $a_{n+2} \simeq a_n$ $\quad f(x) \simeq 1 + x^2 + x^4 + \cdots \to \infty$ if $x = \pm1 \Rightarrow \psi$ is not normalizable

① a_0 series is finite & $a_1 = 0$
② a_1 series is finite & $a_0 = 0$

$\Rightarrow l$ is a positive integer, $0, 1, 2, 3\cdots$?

$a_2 = \frac{-0\times1}{1\times2}a_0$
$a_3 = \frac{-(-1)}{3\times2}a_1$

for $l=0$ (①) $a_2 = 0$, $f(x) = a_0 = P_0(x) = 1$ (we set)

$l=1$ (②) $a_0 = 0 = a_2 = a_4\cdots$ $\quad P_1(x) = a_1(x) = x$
$a_3 = 0$

$l=2$ $\quad a_1 = a_3 = a_5 = \cdots = 0$ $\quad P_2(x) = a_0 + a_2x^2 = a_0(1-3x^2)$
$a_2 = -3a_0 \quad a_4 = 0$ $\quad = \frac{1}{2}(1-3x^2)$

NO.

DATE / /

(ii) for $m \neq 0$

Rodrigues formula $P_l(x) = \frac{1}{2^l l!}\left(\frac{d}{dx}\right)^l (x^2-1)^l$

let $f(x) = (1-x^2)^{\left|\frac{m}{2}\right|} u(x)$

$\Rightarrow (1-x^2)u'' - 2(m+1)xu' + [l(l+1) - m(m+1)]u = 0 \quad \downarrow \frac{d}{dx}$

$\Rightarrow (1-x^2)(u')'' - 2(m+2)x(u')' + [l(l+1) - (m+1)(m+2)]u' = 0$ —①

Legendre polynomial

$P_l(x)$ is a solution for $m=0$

associated Legendre function

$P_l^m(x)$ is a solution for $m=m$ if $P_l^m(x) = (1-x^2)^{\left|\frac{m}{2}\right|}\left(\frac{d}{dx}\right)^{|m|} P_l(x)(-1)^m$

$\Rightarrow l \geq |m|$

$$Y_l^m(\theta,\phi) = c\, P_l^m(\theta) e^{im\phi} = \sqrt{\frac{(2l+1)}{4\pi}\frac{(l-m)!}{(l+m)!}}\; e^{im\phi} \underbrace{(-1)^m (1-x^2)^{\frac{m}{2}} \left(\frac{d}{d\cos\theta}\right)^m \overbrace{\left[\frac{1}{2^l l!}\left(\frac{d}{d\cos\theta}\right)^l (x^2-1)^l\right]}^{P_l(\cos\theta)}}_{P_l^m(\cos\theta)}$$

$$\int_0^{2\pi}\int_0^{\pi} Y_l^{m*}(\theta,\phi)\, Y_l^m(\theta,\phi) \underbrace{\sin\theta\, d\theta\, d\phi}_{d\Omega} = 1$$

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

for $m \neq m'$

$$\int_0^{2\pi} e^{-im'\phi} e^{im\phi}\, d\phi = \frac{1}{i(m-m')} e^{i(m-m')\phi}\Big|_0^{2\pi} = 0$$

for $m=m'$ but $l \neq l'$

$$\int_0^{\pi} P_{l'}^m(\theta) P_l^m(\theta) \sin\theta\, d\theta$$

$$① \Rightarrow \underbrace{(1-x^2)P_l^m(x)'' - 2xP_l^m(x)'}_{\frac{d}{dx}[(1-x^2)P_l^m(x)']} - \left[l(l+1) - \frac{m^2}{1-x^2}\right]P_l^m = 0 \quad \times P_{l'}^m$$

$$-)\ (1-x^2)P_{l'}^m(x)'' - 2xP_{l'}^m(x)' - \left[l'(l'+1) - \frac{m^2}{1-x^2}\right]P_{l'}^m = 0 \quad \times P_l^m$$

$$P_{l'}^m\left[\frac{d}{dx}(1-x^2)P_l^{m'}\right] - P_l^m\left[\frac{d}{dx}(1-x^2)P_{l'}^{m'}\right] + [l(l+1) - l'(l'+1)]P_l^m P_{l'}^m = 0$$

$$\frac{d}{dx}\left[(1-x^2)(P_l^{m'}P_{l'}^m - P_{l'}^{m'}P_l^m)\right] + [l(l+1) - l'(l'+1)]P_l^m P_{l'}^m = 0$$

$$\underbrace{(1-x^2)\, P_l^{m'}P_{l'}^m - P_{l'}^{m'}P_l^m\Big|_{-1}^{+1}}_{0} = \underbrace{[l'(l'+1) - l(l+1)]}_{0}\int_{-1}^{1} P_l^m P_{l'}^m\, dx$$

$\Rightarrow \langle l$

$Y_0^0 = \sqrt{\frac{1}{4\pi}}\, P_0^0(\cos\theta)$

$\cos 0 = 1$

$P_0(1) = \frac{1}{1} \quad P_l^l(x) = |x|x$