Part C

F02 Group 18

(a) Time-independent Schrödinger equation is:

$$\underbrace{-\frac{\hbar^2}{2m}\nabla^2\psi}_{\text{Kinetic energy}} + \underbrace{V\psi}_{\text{potential energy}} = \underbrace{E\psi}_{\text{Total energy}}$$

where $\hbar = \frac{h}{2\pi}$, h is the Planck's constant

ψ is the wave function

$$\underbrace{\nabla^2}_{\text{Laplaican operator}} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$$

So, the time-independent Schrödinger equation in spherical coordinates:

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

Assume: $\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$

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

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

dividing by $R(r)Y(\theta,\phi)$, multiplying r^2 at both sides

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

Using a separation constant $l(l+1)$, we have:

Radial Equation:

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

and Angular Equation:

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

Solving of Angular Equation.

(b)

Since $Y(\theta,\phi)=f(\theta)g(\phi)$, we have:

$$\frac{1}{f(\theta)\cancel{g(\phi)}\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)f(\theta)\cancel{g(\phi)}+\frac{1}{\cancel{f(\theta)}g(\phi)\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\cancel{f(\theta)}g(\phi)=-l(l+1)$$

$$\Rightarrow\quad\frac{1}{f(\theta)\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)f(\theta)+\frac{1}{g(\phi)\sin^2\theta}\frac{\partial^2}{\partial\phi^2}g(\phi)=-l(l+1)$$

dividing by $\sin^2\theta$ from both ends

$$\Rightarrow\quad\frac{\sin\theta}{f(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)f(\theta)+l(l+1)\sin^2\theta+\frac{1}{g(\phi)}\frac{\partial^2}{\partial\phi^2}g(\phi)=0$$

using a separation constant of m^2

Polar Angle equation

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

Azimuthal Angle equation

$$\frac{1}{g(\phi)}\frac{d^2}{d\phi^2}g(\phi)=-m^2$$

for the azimuthal angle equation

$$\frac{d^2 g(\phi)}{d\phi^2} = -m^2 g(\phi) \Rightarrow g(\phi) = e^{\pm im\phi}$$

$$g_m(\phi) = e^{im\phi} \quad , \text{ for } m \in \mathbb{Z}$$

for the polar angle equation

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

$$\underline{\sin\theta \frac{d}{d\theta} (\sin\theta \frac{d}{d\theta}) f(\theta)} + l(l+1)\sin^2\theta f(\theta) - m^2 f(\theta) = 0 \qquad ①$$

$$\downarrow$$

$$\begin{aligned}
\sin\theta \frac{d}{d\theta} (\sin\theta \frac{d}{d\theta}) f(\theta) &= \sin\theta \frac{d}{d\theta} (\sin\theta \frac{df(\theta)}{d\theta}) \\
&= \sin\theta \left[(\sin\theta)' \frac{df(\theta)}{d\theta} + \sin\theta (\frac{df(\theta)}{d\theta})' \right] \\
&= \sin\theta (\cos\theta \frac{df(\theta)}{d\theta} + \sin\theta \frac{d^2 f(\theta)}{d\theta^2}) \\
&= \sin^2\theta \frac{d^2 f(\theta)}{d\theta^2} + \sin\theta\cos\theta \frac{df(\theta)}{d\theta} \qquad ②
\end{aligned}$$

Sub ② → ①:

$$\sin^2\theta \frac{d^2 f(\theta)}{d\theta} + \sin\theta\cos\theta \frac{df(\theta)}{d\theta} + l(l+1)\sin^2\theta f(\theta) - m^2 f(\theta) = 0 \qquad ③$$

let $x = \cos\theta$, therefore $x' = -\sin\theta$

$$\frac{df(\theta)}{d\theta} = \frac{df(x)}{dx} \frac{dx}{d\theta} = \frac{df(x)}{d(x)} (-\sin\theta) \qquad ④$$

$$\begin{aligned}
\frac{d^2 f(\theta)}{d\theta^2} &= \frac{d}{d\theta}(-\sin\theta \frac{df(x)}{dx}) = (-\sin\theta)' \frac{df(x)}{dx} + (-\sin\theta)(\frac{df(x)}{dx})' \\
&= \cos\theta \frac{df(x)}{dx} - \sin\theta \frac{d}{d\theta} \frac{df(x)}{dx} \\
&= -\cos\theta \frac{df(x)}{dx} - \sin\theta \frac{d}{dx} \frac{dx}{d\theta} \frac{df(x)}{dx} \\
&= -\cos\theta \frac{df(x)}{dx} - \sin\theta \frac{d}{dx}(-\sin\theta) \frac{df(x)}{dx} \\
&= \cos\theta \frac{df(x)}{dx} + \sin^2\theta \frac{d^2 f(x)}{dx^2} \qquad ⑤
\end{aligned}$$

sub ④, ⑤ → ③:

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

dividing $\sin^2\theta$ from both sides:

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

since $x=\cos\theta$, $\sin^2\theta=1-\cos^2\theta=1-x^2$

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

when $m=0$, $(1-x^2)f''(x)-2xf'(x)+l(l+1)f(x)=0$ (Legendre equation)

Since legendre polynomial: $P_l(x)=\frac{1}{2^l l!}\left(\frac{\partial}{\partial x}\right)^l(x^2-1)^l$

associated legendre polynomial: $P_l^m(x)=(1-x^2)^{\frac{|m|}{2}}\left(\frac{\partial}{\partial x}\right)^{|m|}P_l(x)$

Legendre polynomial for $l=0,1,2,3$:

$P_0(x)=1$; $P_1(x)=\frac{1}{2}\frac{\partial}{\partial x}(x^2-1)=\frac{2x}{2}=x$

$$P_2(x)=\frac{1}{4\times2}\frac{\partial^2}{\partial x^2}(x^2-1)^2$$

$$=\frac{1}{8}\frac{\partial}{\partial x}\left[2(x^2-1)(2x)\right]=\frac{1}{2}\frac{\partial}{\partial x}(x^3-x)$$

$$=\frac{1}{2}(3x^2-1)=\frac{3}{2}x^2-\frac{1}{2}$$

$$P_3(x) = \frac{1}{8\times 6} \frac{\partial^3}{\partial x^3}(x^2-1)^3$$

$$= \frac{1}{48}\frac{\partial^2}{\partial x^2}\left[3(x^2-1)^2(2x)\right] = \frac{1}{8}\frac{\partial^2}{\partial x^2}(x^5-2x^3+x)$$

$$= \frac{1}{8}\frac{\partial}{\partial x}(5x^4-6x^2+1)$$

$$= \frac{1}{8}(20x^3-12x) = \frac{5}{2}x^3 - \frac{3}{2}x$$

Associated Legendre Polynomials for $l = 0, 1, 2, 3$; $m = 0, \pm 1, \pm 2, \pm 3$

$$P_l^m(x) = (1-x^2)^{\frac{|m|}{2}}\left(\frac{\partial}{\partial x}\right)^{|m|} P_l(x)$$
$$= (-1)^m\sqrt{(1-x^2)^m}\,\frac{d^m}{dx^m}P_l(x)$$

$$P_0^0(x) = (1-x^2)^0\left(\frac{\partial}{\partial x}\right)^0 P_0(x) = 1$$

$$P_1^1(x) = P_1^{-1}(x) = -(1-x^2)^{\frac{1}{2}}\frac{\partial}{\partial x}P_1(x)$$
$$= -\sqrt{1-x^2}\,\frac{\partial}{\partial x}x$$
$$= -\sqrt{1-x^2}$$

$$P_1^0(x) = (1-x^2)^0\left(\frac{\partial}{\partial x}\right)^0 P_1(x)$$
$$= P_1(x) = x$$

$$P_2^2(x) = P_2^{-2}(x) = (1-x^2)^1\frac{\partial^2}{\partial x^2}P_2(x)$$
$$= (1-x^2)\frac{\partial^2}{\partial x^2}\left(\frac{3}{2}x^2-\frac{1}{2}\right)$$
$$= (1-x^2)\frac{\partial}{\partial x}(3x)$$
$$= 3-3x^2$$

$$P_2^1(x) = P_2^{-1}(x) = -(1-x^2)^{\frac{1}{2}} \frac{\partial}{\partial x} P_2(x)$$

$$= -\sqrt{1-x^2}\,\frac{\partial}{\partial x}\left(\frac{3}{2}x^2 - \frac{1}{2}\right)$$

$$= -3x\sqrt{1-x^2}$$

$$P_2^0(x) = (1-x^2)^0 \left(\frac{\partial}{\partial x}\right)^0 P_2(x)$$

$$= P_2(x) = \frac{3}{2}x^2 - \frac{1}{2}$$

$$P_3^3(x) = P_3^{-3}(x) = -(1-x^2)^{\frac{3}{2}} \frac{\partial^3}{\partial x^3} P_3(x)$$

$$= -(1-x^2)\sqrt{1-x^2}\,\frac{\partial^3}{\partial x^3}\left(\frac{5}{2}x^3 - \frac{3}{2}x\right)$$

$$= -(1-x^2)\sqrt{1-x^2}\,\frac{\partial^2}{\partial x^2}\left(\frac{15}{2}x^2 - \frac{3}{2}\right)$$

$$= -(1-x^2)\sqrt{1-x^2}\,\frac{\partial}{\partial x}(15x)$$

$$= (15x^2 - 15)\sqrt{1-x^2}$$

$$P_3^2(x) = P_3^{-2}(x) = (1-x^2)^1 \frac{\partial^2}{\partial x^2} P_3(x)$$

$$= (1-x^2)\frac{\partial^2}{\partial x^2}\left(\frac{5}{2}x^3 - \frac{3}{2}x\right)$$

$$= (1-x^2)\frac{\partial}{\partial x}\left(\frac{15}{2}x^2 - \frac{3}{2}\right)$$

$$= 15x(1-x^2)$$

$$= 15x - 15x^3$$

$$P_3^1(x) = P_3^{-1}(x) = (1-x^2)^{\frac{1}{2}} \frac{\partial}{\partial x} P_3(x)$$

$$= \sqrt{1-x^2}\,\frac{\partial}{\partial x}\left(\frac{5}{2}x^3 - \frac{3}{2}x\right)$$

$$= \left(\frac{3}{2} - \frac{15}{2}x^3\right)\sqrt{1-x^2}$$

$$P_3^0(x) = (1-x^2)^0 \left(\frac{\partial}{\partial x}\right)^0 P_3(x)$$

$$= P_3(x)$$

$$= \frac{5}{2}x^3 - \frac{3}{2}x$$

since Normalized Angular Solution

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

$$\text{where } \epsilon = \begin{cases} (-1)^m & \text{for } m>0 \\ 1 & \text{for } m\leq 0 \end{cases}$$

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

$$Y_1^1(\theta,\phi) = \sqrt{\frac{3}{4\pi}\frac{1}{2}}\, e^{i\phi} P_1^1(\cos\theta)$$
$$= \sqrt{\frac{3}{8\pi}}\, e^{i\phi}\sqrt{1-\cos^2\theta}$$
$$= \sqrt{\frac{3}{8\pi}}\, e^{i\phi}\sin\theta$$

$$Y_1^{-1} = -\sqrt{\frac{3}{8\pi}}\, e^{-i\phi}\sin\theta$$

$$Y_1^0 = \sqrt{\frac{3}{4\pi}\frac{1}{1}}\, e^0 P_1^0(\cos\theta)$$
$$= \sqrt{\frac{3}{4\pi}}\cos\theta$$

$$Y_2^2 = \left(\frac{5}{4\pi}\frac{1}{4!}\right)^{\frac{1}{2}} \exp(2i\phi)\, P_2^2(\cos\theta)$$
$$= \sqrt{\frac{5}{96\pi}}\exp(2i\phi)(3-3\cos^2\theta)$$
$$= 3\sqrt{\frac{5}{96\pi}}\exp(2i\phi)\sin^2\theta$$
$$= \sqrt{\frac{15}{32\pi}}\exp(2i\phi)\sin^2\theta$$

$$Y_2^{-2} = \sqrt{\frac{15}{32\pi}}\exp(-2i\phi)\sin^2\theta$$

$$Y_2^1 = -\left(\frac{5}{4\pi}\frac{1}{3!}\right)^{\frac{1}{2}} e^{i\phi} P_2^1(\cos\theta)$$
$$= -\left(\frac{5}{24\pi}\right)^{\frac{1}{2}} \exp(i\phi)\, 3\cos\theta\sqrt{1-\cos^2\theta}$$
$$= -\sqrt{\frac{15}{8\pi}} \exp(i\phi)\cos\theta\sin\theta$$

$$Y_2^{-1} = \sqrt{\frac{15}{8\pi}} \exp(-i\phi)\cos\theta\sin\theta$$

$$Y_2^0 = \left(\frac{5}{4\pi}\frac{2}{2}\right)^{\frac{1}{2}} e^0 P_2^0(\cos\theta)$$
$$= \sqrt{\frac{5}{4\pi}}\left(\frac{3}{2}\cos^2\theta - \frac{1}{2}\right)$$
$$= \sqrt{\frac{5}{16\pi}}\left(3\cos^2\theta - 1\right)$$

$$Y_3^3 = \left(\frac{7}{4\pi}\frac{1}{6!}\right)^{\frac{1}{2}} e^{3i\phi} P_3^3(\cos\theta)$$
$$= \left(\frac{7}{2880\pi}\right)^{\frac{1}{2}} e^{3i\phi}\left(15\cos^2\theta - 15\right)\sin\theta$$
$$= -\sqrt{\frac{35}{64\pi}} \exp(3i\phi)\sin^3\theta$$

$$Y_3^{-3} = \sqrt{\frac{35}{64\pi}} \exp(-3i\phi)\sin^3\theta$$

$$Y_3^2 = \left(\frac{7}{4\pi}\frac{1}{5!}\right)^{\frac{1}{2}} e^{2i\phi} P_3^2(\cos\theta)$$
$$= \left(\frac{7}{480\pi}\right)^{\frac{1}{2}} \exp(2i\phi)\left(15\cos\theta - 15\cos^3\theta\right)$$
$$= \sqrt{\frac{105}{32\pi}} \exp(2i\phi)\cos\theta\sin^2\theta$$

$$Y_3^{-2} = \sqrt{\frac{105}{32\pi}} \exp(-2i\phi)\cos\theta\sin^2\theta$$

$$Y_3^1 = \left(\frac{7}{4\pi}\frac{2}{4!}\right)^{\frac{1}{2}} \exp(i\phi) P_3^1(\cos\theta)$$
$$= \left(\frac{14}{96\pi}\right)^{\frac{1}{2}} \exp(i\phi)\left(\frac{3}{2} - \frac{15}{2}\cos^3\theta\right)\sin\theta$$
$$= -\sqrt{\frac{21}{64\pi}} \exp(i\phi)\left(5\cos^2\theta - 1\right)\sin\theta$$

$$Y_3^{-1} = \sqrt{\frac{21}{64\pi}} \exp(i\phi)\left(5\cos^2\theta - 1\right)\sin\theta$$

$$Y_3^0 = \left(\frac{7}{4\pi}\frac{3!}{3!}\right)^{\frac{1}{2}} e^0 P_3^0(\cos\theta)$$
$$= \sqrt{\frac{7}{4\pi}}\left(\frac{5}{2}\cos^3\theta - \frac{3}{2}\cos\theta\right)$$
$$= \sqrt{\frac{7}{16\pi}}\left(5\cos^3\theta - 3\cos\theta\right)$$