Phys 231 2021

Lecture 34

Tues: HW by 5pm

Weds: Read 7.5, 7.6

Wavefunctions in spherical co-ordinates

A wavefunction in spherical co-ordinates can be used to determine probabilities of position measurement outcomes via

$$\boxed{\text{Prob}\left[r_0 \leq r \leq r_1 \text{ AND } \theta_0 \leq \theta \leq \theta_1 \text{ AND } \phi_0 \leq \phi \leq \phi_1\right] = \int_{r_0}^{r_1}\int_{\theta_0}^{\theta_1}\int_{\phi_0}^{\phi_1} |\psi(r,\theta,\phi)|^2 \, r^2 \sin\theta \, dr \, d\theta \, d\phi}$$

Example: The wavefunction

$$\psi(r,\theta,\phi) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a} e^{2i\phi}$$

is normalized. Determine the probability with which a position measurement outcome gives $r > a$ regardless of θ and ϕ

Answer:
$$\text{Prob}(r > a) = \int_a^\infty \underbrace{\int_0^\pi}_{\text{all } \theta} \underbrace{\int_0^{2\pi}}_{\text{all } \phi} \frac{1}{\pi a^3} e^{-2r/a} r^2 \sin\theta \, dr \, d\theta \, d\phi$$

$$= \frac{1}{\pi a^3} \int_a^\infty r^2 e^{-2r/a} dr \underbrace{\int_0^\pi \sin\theta \, d\theta}_{2} \underbrace{\int_0^{2\pi} d\phi}_{2\pi}$$

$$\Rightarrow \quad \text{Prob}(r>a) = \frac{1}{\cancel{\pi} a^3} \int_a^{\infty} e^{-2r/a} \, r^2 dr \quad 4\cancel{\pi}$$

$$= \frac{\cancel{4}}{\cancel{a^3}} \left[\frac{5\cancel{a^3} e^{-2}}{\cancel{4}} \right] = 5e^{-2} = 0.68 \qquad \boxtimes$$

Schrödinger equation in spherical co-ordinates

The TISE for the hydrogen atom is:

$$\frac{-\hbar^2}{2M_e} \left[\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right] - \frac{1}{4\pi\epsilon_0} \frac{e^2}{r} \psi = E\psi$$

mass of electron

We need to convert the derivatives into spherical co-ordinates. Note that

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \neq \frac{\partial^2 \psi}{\partial r^2} + \frac{\partial^2 \psi}{\partial \theta^2} + \frac{\partial^2 \psi}{\partial \phi^2}$$

To see this:

$$\frac{\partial \psi}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial \psi}{\partial r} + \frac{\partial \theta}{\partial x}\frac{\partial \psi}{\partial \theta} + \frac{\partial \phi}{\partial x}\frac{\partial \psi}{\partial \phi}$$

Then $r = \sqrt{x^2+y^2+z^2} \Rightarrow \frac{\partial r}{\partial x} = \frac{x}{r} = \sin\theta\cos\phi$

$$\theta = \tan^{-1}\left(\frac{z}{\sqrt{x^2+y^2}}\right) \Rightarrow \frac{\partial \theta}{\partial x} = \frac{\cos\theta\sin\phi}{r}$$

gives:

$$\frac{\partial \psi}{\partial x} = \sin\theta\cos\phi \frac{\partial \psi}{\partial r} + \frac{\cos\theta\sin\phi}{r}\frac{\partial \psi}{\partial \theta} + \dots$$

This gets more complicated when we take second derivatives.

A derivation eventually gives:

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

Then the TISE for the hydrogen atom in spherical co-ordinates is

$$\boxed{\begin{aligned} &-\frac{\hbar^2}{2m_e}\frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2 \frac{\partial \Psi}{\partial r}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial \Psi}{\partial \theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 \Psi}{\partial \phi^2}\right] \\ &- \frac{1}{4\pi\epsilon_0}\frac{e^2}{r}\Psi(r,\theta,\phi) = E\Psi(r,\theta,\phi) \end{aligned}}$$

Separation of variables for the hydrogen atom

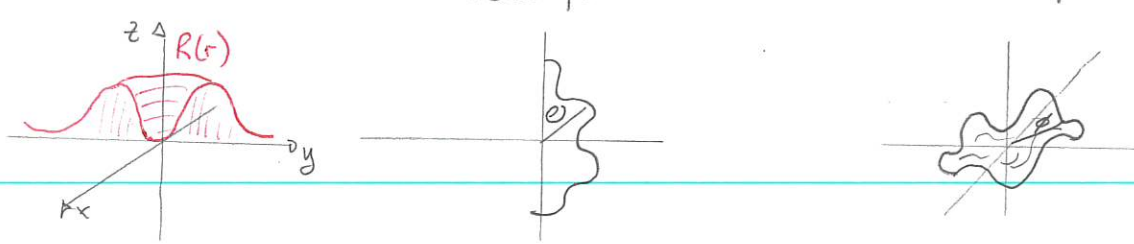
We solve the TISE by separating variables. Try

$$\Psi(r,\theta,\phi) = \underbrace{R(r)}\ \underbrace{\Theta(\theta)}\ \underbrace{\Phi(\phi)}$$

radial part

Polar part

azimuthal part



The mathematical steps for doing this are described on pg 247 The results are:

Azimuthal part: $$\frac{d^2\Phi}{d\phi^2} = -D\Phi$$

where D is a constant

Polar part

$$\sin\theta \frac{d}{d\theta}\left(\sin\theta \frac{d\Theta}{d\theta}\right) - C(\sin^2\theta)\Theta = D\,\Theta$$

where C is a constant.

Radial part

$$-\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2m_e r^2}{\hbar^2}E\,R(r) + \frac{2m_e r^2}{\hbar^2}\underbrace{U(r)}_{-\frac{1}{4\pi\epsilon_0}\frac{e^2}{r}}R(r) = C\,R(r)$$

The general strategy is:

Solve azimuthal part
$\rightsquigarrow$ gives Φ
$\rightsquigarrow$ constrains D

$\rightarrow$

Solve polar part using D
$\rightsquigarrow$ gives Θ
$\rightsquigarrow$ constrains C

$\rightarrow$

Solve radial part using D, C
$\rightsquigarrow$ gives $R(r)$
$\rightsquigarrow$ gives energy E

can be done for any spherically symmetric ~~part~~ potential

potential enters here and determines energy

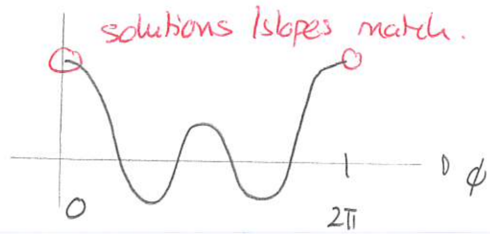
Azimuthal part:

The azimuthal equation give $\Phi(\phi)$ via:

$$\frac{d^2\Phi}{d\phi^2} = -D\,\Phi$$

and is constrain by the fact that Φ must be continuous. So at $\phi = 0$ and 2π the wavefunction must give the same results. Thus

* $\Phi(2\pi) = \Phi(0)$
* $\left.\frac{d\Phi}{d\phi}\right|_{2\pi} = \left.\frac{d\Phi}{d\phi}\right|_{0}$



There are two possibilities. First, if $D<0$ we get

$$\Phi(\phi) = A e^{\sqrt{-D}\,\phi} + B e^{-\sqrt{-D}\,\phi}$$

Then $\Phi(0) = \Phi(2\pi) \Rightarrow A + B = A e^{\sqrt{-D}\,2\pi} + B e^{-\sqrt{-D}\,2\pi}$

$\Phi'(0) = \Phi'(2\pi) \Rightarrow A - B = A e^{\sqrt{-D}\,2\pi} - B e^{-\sqrt{-D}\,2\pi}$

adding gives $\quad A = A e^{-\sqrt{D}\,2\pi} \Rightarrow D = 0$

$\quad B = B e^{-\sqrt{-D}\,2\pi} \Rightarrow D = 0$

Second consider $D > 0$. Then possible solutions are:

$$\Phi = e^{\pm i\sqrt{D}\,\phi}$$

Quiz 1 10% →

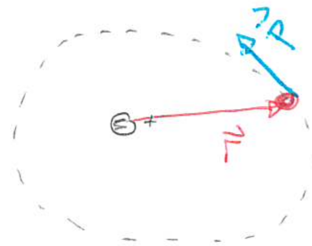
We see that we need $\sqrt{D}$ = integer $= m_\ell = 0, \pm1, \pm2, \ldots$ Then

$$\boxed{\Phi(\phi) = e^{i m_\ell \phi}}$$

where $m_\ell = 0, \pm1, \pm2, \ldots$ and $D = m_\ell^2$

We can interpret these solutions in terms of angular momentum. In classical physics the angular momentum of a particle is

$$\vec{L} = \vec{r} \times \vec{p}$$



and this has component form

$$\vec{L} = L_x \hat{x} + L_y \hat{y} + L_z \hat{z}$$

In quantum theory there must be any angular momentum operator associated with each component:

$\hat{L}_x \rightsquigarrow$ angular momentum x component

$\hat{L}_y \rightsquigarrow$ " " y "

$\hat{L}_z \rightsquigarrow$ " " z "

We can show the following.

In spherical co-ordinates the z-component angular momentum is

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}$$

and the expectation value of L_z for the states used here is

$$\langle L_z \rangle = \int \Psi^* \hat{L}_z \Psi \, dV \quad \Rightarrow \quad \langle L_z \rangle = m_\ell \hbar$$

and the uncertainty in L_z is $\sigma_z = 0$

Thus a solution with

$$\Phi(\phi) = e^{i m_\ell \phi}$$

corresponds to a z-component of angular momentum exactly equal to $m_\ell \hbar$

$$\Rightarrow L_z = 0, \pm\hbar, \pm 2\hbar, \pm 3\hbar, \ldots$$

Derivation First

$$\vec{L} = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} = (yp_z - zp_y)\hat{x} + (zp_x - xp_z)\hat{y} + (xp_y - yp_x)\hat{z}$$

$$\Rightarrow \quad L_z = xp_y - yp_x \quad \text{classically.}$$

The quantum operator is

$$\hat{L}_z = \hat{x}\hat{p}_y - \hat{y}\hat{p}_x$$

$$= x\left(-i\hbar\frac{\partial}{\partial y}\right) - y\left(-i\hbar\frac{\partial}{\partial x}\right) = -i\hbar\left[x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right]$$

Then in spherical co-ords:

$$\frac{\partial}{\partial x} = \frac{\partial r}{\partial x}\frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x}\frac{\partial}{\partial \theta} + \frac{\partial \phi}{\partial x}\frac{\partial}{\partial \phi}$$

$$\frac{\partial r}{\partial x} = \cos\phi \sin\theta$$

$$\theta = \tan^{-1}\left(\frac{z}{\sqrt{x^2+y^2}}\right) \Rightarrow \frac{\partial \theta}{\partial x} = \frac{1}{1 + z^2/(x^2+y^2)} \frac{z}{(x^2+y^2)^{3/2}}\left(\frac{-1}{2}\right)2x$$

$$= -\frac{1}{r^2}\frac{\cancel{r}\cos\theta \, \cancel{r}\cos\phi\cancel{\sin\theta}}{\cancel{r}\cancel{\sin\theta}}$$

$$= -\frac{1}{r}\cos\theta\cos\phi$$

$$\phi = \tan^{-1}\left(\frac{y}{x}\right) \Rightarrow \frac{\partial \phi}{\partial x} = \frac{1}{1 + y^2/x^2}\left(\frac{-y}{x^2}\right) = \frac{-y}{x^2+y^2} = \frac{-r\sin\theta\sin\phi}{r^2\sin^2\theta}$$

$$= \frac{-\sin\phi}{r\sin\theta}$$

Thus:

$$\frac{\partial}{\partial x} = \cos\phi \sin\theta \frac{\partial}{\partial r} - \frac{1}{r}\cos\theta\cos\phi\frac{\partial}{\partial\theta} - \frac{\sin\phi}{r\sin\theta}\frac{\partial}{\partial\phi}$$

Similarly

$$\frac{\partial}{\partial y} = \sin\phi\sin\theta\frac{\partial}{\partial r} - \frac{1}{r}\cos\theta\sin\phi\frac{\partial}{\partial\theta} + \frac{1}{r}\frac{\cos\phi}{\sin\theta}\frac{\partial}{\partial\phi}$$

So

$$\hat{L}_z = -i\hbar\left\{ r\cos\phi\sin\theta\left[\sin\phi\sin\theta\frac{\partial}{\partial r} - \frac{1}{r}\cos\theta\sin\phi\frac{\partial}{\partial\theta} + \frac{1}{r}\frac{\cos\phi}{\sin\theta}\frac{\partial}{\partial\phi}\right]\right.$$

$$\left. - r\sin\phi\sin\theta\left[\cos\phi\sin\theta\frac{\partial}{\partial r} - \frac{1}{r}\cos\theta\cos\phi\frac{\partial}{\partial\theta} - \frac{1}{r}\frac{\sin\phi}{\sin\theta}\frac{\partial}{\partial\phi}\right]\right\}$$

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi}$$

The expectation value is

$$\langle L_z\rangle = \int_0^\infty\int_0^\pi\int_0^{2\pi} \psi^*(r,\theta,\phi)\, L_z\, \psi(r,\theta,\phi)\, r^2\sin\theta\, dr\, d\theta\, d\phi$$

$$= \int_0^\infty\int_0^\pi\int_0^{2\pi} \psi^*(-i\hbar)\frac{\partial\psi}{\partial\phi}\, r^2\sin\theta\, dr\, d\theta\, d\phi$$

Then $\frac{\partial\psi}{\partial\phi} = i m_\ell \psi$ gives:

$$\langle L_z\rangle = m_\ell\hbar \underbrace{\int_0^\infty\int_0^\pi\int_0^{2\pi}\psi^*\psi\, r^2\sin\theta\, dr\, d\theta\, d\phi}_{1} = m_\ell\hbar$$

Then we can show $\langle L_z^2\rangle = m_\ell^2\hbar^2 \Rightarrow \sigma_{L_z} = \sqrt{\langle L_z^2\rangle - \langle L_z\rangle^2} = 0$