Lecture 36: 04/22/09

- Quantum Mechanics in 3-D
- Central Potentials $V = V(r)$
  - Spherical coordinates (r, θ, ϕ)

Recap:

VI Quantum Mechanics in 3-D:

S.E.: $i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \Psi + V(x,y,z)\, \Psi(x,y,z,t)$

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

stationary states: $\Psi_n(x,y,z,t) = \psi(x,y,z)\, e^{-iE_n/\hbar\, t}$

are solution of the time-indep. S.E.: $-\frac{\hbar^2}{2m} \nabla^2 \psi_n + V(x,y,z)\,\psi_n = E_n \psi_n(x,y,z)$

→ will consider two cases

I : separable potentials: $V(x,y,z)$
$= V_1(x) + V_2(y) + V_3(z)$

II : central potential: $V = V(\text{radius})$

distance from origin

VI$_2$ Separable Potentials

special case: $V(x,y,z) = V_1(x) + V_2(y) + V_3(z)$

$\Rightarrow$ any solution of time-indep. S.E. has form

$$\Psi(x,y,z) = \Psi_1(x)\,\Psi_2(y)\,\Psi_3(z)$$

$\Rightarrow$ try this:

$$-\frac{\hbar^2}{2m}\left[\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right]\Psi_1(x)\Psi_2(y)\Psi_3(z) + \left\{V_1(x) + V_2(y) + V_3(z)\right\}$$

$$\cdot\ \Psi_1(x)\,\Psi_2(y)\,\Psi_3(z) = E\ \Psi_1(x)\,\Psi_2(y)\,\Psi_3(z)$$

$$= -\frac{\hbar^2}{2m}\left[\Psi_2(y)\Psi_3(z)\frac{\partial^2\Psi_1(x)}{\partial x^2} + \Psi_1(x)\Psi_3(z)\frac{\partial^2\Psi_2(y)}{\partial y^2} + \Psi_1(x)\Psi_2(y)\frac{\partial^2\Psi_3(z)}{\partial z^2}\right.$$

$$+\ \Psi_2(y)\Psi_3(z)V_1(x)\Psi_1(x) + \Psi_1(x)\Psi_3(z)V_2(y)\Psi_2(y)$$

$$+\ \Psi_1(x)\Psi_2(y)V_3(z)\Psi_3(z)$$

$\Rightarrow$ devide by $\Psi_1(x)\cdot\Psi_2(y)\cdot\Psi_3(z) = \Psi(x,y,z)$

$$\Rightarrow \frac{1}{\psi_1(x)}\left[-\frac{\hbar^2}{2m}\frac{\partial^2\psi_1(x)}{\partial x^2} + V_1(x)\psi_1(x)\right] + \frac{1}{\psi_2(y)}\left[-\frac{\hbar^2}{2m}\frac{\partial^2\psi_2(y)}{\partial y^2} + V_2(y)\cdot\psi_2(y)\right]$$

$$+ \frac{1}{\psi_3(z)}\left[-\frac{\hbar^2}{2m}\frac{\partial^2\psi_3(z)}{\partial z^2} + V_3(z)\psi_3(z)\right] = E \quad \text{for all } x, y, z$$

$\Rightarrow$ have $f_1(x) + f_2(y) + f_3(z) = E = \text{const}$

$\Rightarrow$ $f_1(x) = E_1$, $f_2(y) = E_2$, $f_3(z) = E_3$

with $\boxed{E = E_1 + E_2 + E_3}$

$$\left.\begin{array}{l}\Rightarrow -\frac{\hbar^2}{2m}\frac{\partial^2\psi_1(x)}{\partial x^2} + V_1(x)\psi_1(x) = E_1\psi_1(x)\end{array}\right\} \text{1-D time-indep. S.E.}$$

$\Rightarrow$ similar for $\psi_2(y)$ and $\psi_3(z)$

$\Rightarrow$ can solve separately for $\psi_1(x)$, $\psi_2(y)$ and $\psi_3(z)$ by solving 1-D S.E.'s!

• Example: Rectangular box:

$$V(x,y,z) = \begin{cases} 0 & \text{for } 0 \le x \le L_1,\ 0 \le y \le L_2,\ 0 \le z \le L_3 \\ \infty & \text{otherwise} \end{cases}$$

⇒ separable potential

⇒ stationary states have form

$$\psi(x,y,z) = \underbrace{\psi_1(x)}_{\text{solution of 1-D time indep. S.E. for } \infty \text{ square well}} \cdot \psi_2(y) \cdot \psi_3(z)$$

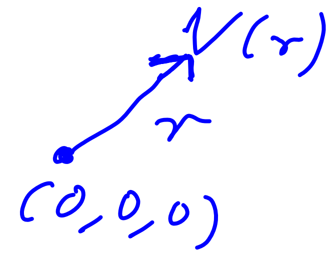
$$= \underbrace{\sqrt{\frac{2}{L_1}} \sin\left(\frac{n\pi x}{L_1}\right)}_{\psi_1(x)} \underbrace{\sqrt{\frac{2}{L_2}} \sin\left(\frac{m\pi y}{L_2}\right)}_{\psi_2(y)} \underbrace{\sqrt{\frac{2}{L_3}} \sin\left(\frac{j\pi z}{L_3}\right)}_{\psi_3(z)}$$

with energy:

$$E = E_1 + E_2 + E_3 = \frac{h^2}{8m}\left\{\frac{n^2}{L_1^2} + \frac{m^2}{L_2^2} + \frac{j^2}{L_3^2}\right\}$$ ⇒ 3 quantum numbers (n, m, j)

Note: in 3-D, can have degenerate energy levels! (orthogonal eigenfunctions of $\hat{H}$ with same eigenvalue E)

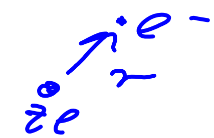
VI$_3$ Central Potentials



$$V(x,y,z) = V(\text{radius}) = V(r)$$

$$r = \text{distance from origin} = \sqrt{x^2+y^2+z^2}$$

Prime example: Coulomb potential



$$V(r) = -\frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r}$$

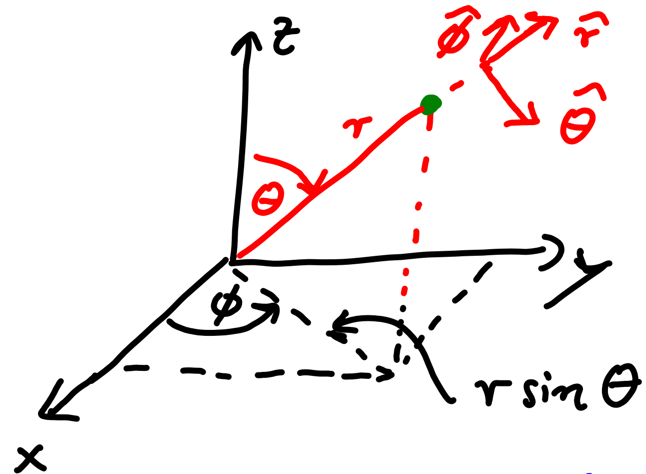
⇒ Hydrogen-like atoms

⇒ will find full solution

Note: in classical physics: energy and angular momentum about origin are conserved

⇒ reflected also in QM...

→ use spherical coordinates:

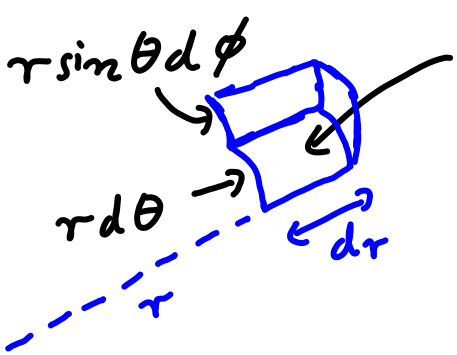


- radius r $(r \geq 0)$
- polar angle θ $(0 \leq \theta \leq \pi)$
- azimuthal angle ϕ $(0 \leq \phi \leq 2\pi)$

$$x = r \sin\theta \cos\phi$$
$$y = r \sin\theta \sin\phi$$
$$z = r \cos\theta$$

$$r = \sqrt{x^2 + y^2 + z^2}$$

⇒ volume element:



$$dV = r^2 \sin\theta \, d\phi \, d\theta \, dr$$

Example: volume of sphere:

$$\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \int_0^{R} dr \; r^2 \sin\theta = \frac{4}{3}\pi R^3$$

$\Rightarrow$ normalization condition for Ψ:

$$1 = \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \int_0^{\infty} dr \; r^2 \sin\theta \, |\Psi(r,\theta,\phi)|^2$$

$\Rightarrow$ Schrödinger equation in spherical coordinates:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi = E\Psi(r,\theta,\phi)$$

need to express Laplacian

$$\nabla^2 = \underbrace{\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}}_{\text{in cartesian coordinates}}$$ in terms of r, θ, ϕ!

Answer: (see F & T, appendix chapter 11)

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

⇒ to solve S.E. for $V = V(r)$ potential, try solution of form:

$$\psi(r,\theta,\phi) = \underbrace{R(r)}_{\text{separate } r\text{-dependence}} \cdot \underbrace{F(\theta,\phi)}_{\text{will separate } \theta \text{ and } \phi \text{ dependence later...}}$$

(separation of variables)

⇒ Can seperate S.E. into 3 more simple equations

$\Rightarrow$ insert into time-indep. S.E. :

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

$\Rightarrow$ devide by $-\frac{\hbar^2}{2mr^2}RF$

$$\Rightarrow\left\{\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{2mr^2}{\hbar^2}[V(r)-E]\right\}$$ ← depends on r only!

$$+\frac{1}{F}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial F}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2 F}{\partial\phi^2}\right\}=0$$ ← depends on θ,ϕ only, and <u>not</u> r

$\Rightarrow f_1(r)+f_2(\theta,\phi)=0$ for <u>all</u> r,θ,ϕ

$\Rightarrow f_1(r)=\beta=\text{const}\qquad f_2(\theta,\phi)=-\beta$

$\Rightarrow$ can separate this into two equations:

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

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

"separation constant"
will find physical
meaning later...

Note:

(i) Energy of the particle is determined by ②

(ii) Equation ① does not depend on central potential $V(r)$

$\Rightarrow$ can solve the angular part of Ψ once for all $V(r)$

$\Rightarrow$ solutions $F(\theta,\phi)$ will apply to any central potential $V(r)$ ← nice!

(iii) Can rewrite equation ②:

$\Rightarrow$ define $u(r) \equiv r R(r) \Leftrightarrow R(r) = \frac{u(r)}{r}$

$$\Rightarrow \frac{d}{dr}\left(r^2 \frac{dR}{dr}\right) = \frac{d}{dr}\left(r^2 \frac{d}{dr}\left(\frac{u(r)}{r}\right)\right)$$

$$= \frac{d}{dr}\left(r^2\left(\frac{1}{r}\frac{du}{dr} - \frac{u}{r^2}\right)\right) = \frac{d}{dr}\left(r\frac{du}{dr} - u\right)$$

$$= \frac{du}{dr} + r\frac{d^2u}{dr^2} - \frac{du}{dr} = \underline{r\frac{d^2u(r)}{dr^2}}$$

$\Rightarrow$ for equation ②:

$$\frac{r}{u(r)}\, r\, \frac{d^2u(r)}{dr^2} - \frac{2mr^2}{\hbar^2}\left[V(r) - E\right] = \beta$$

$\Rightarrow$ final version of 2:

$$\underbrace{-\frac{\hbar^2}{2m}\frac{d^2u(r)}{dr^2}}_{\substack{\text{term associated}\\ \text{with linear motion}\\ \text{in } r\text{-direction}\\ (\text{"kinetic energy"})}} + \Big\{\overbrace{\underbrace{\frac{\hbar^2\beta}{2mr^2}}_{?} + \underbrace{V(r)}_{\substack{\text{potential}\\ \text{energy}}}}^{}\Big\}u(r) = \underbrace{E}_{\substack{\text{total}\\ \text{energy}}}u(r)$$

$$\frac{\hbar^2\beta}{2mr^2} + V(r) = V_{eff}$$

$\Rightarrow$ similar to 1-D S.E., but extra term $\frac{\hbar^2\beta}{2mr^2}$

$$\hbar^2\beta \overset{?}{=} L^2$$