3-D Infinite Potential Well

Use conservation of energy

$$E = KE + V = \frac{p^2}{2m} + V$$

& expand p^2 given operator definition $\hat{p}_i = -i\hbar\,\partial/\partial x_i$, we get

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

-or-

$$\boxed{\frac{-\hbar^2}{2m}\nabla^2\psi + V\psi = E\psi}$$

Interpretation of ψ:

$$\psi^*\psi = \frac{\text{Probability}}{\text{Volume}} \quad (\text{"probability density"})$$

Normalization in 3-D:

$$\int \psi^*\psi \, dv = 1$$

To arrive at a solution, take approach of 'separation of variables', i.e.

$$\psi(x,y,z) = F(x)G(y)H(z)$$

We will use this technique a bit later for the Hydrogen atom potential. For 3-D infinite potential well, Cartesian coordinates are sensible

$$\psi(\vec{r}) = A_x \sin(k_x x) A_y \sin(k_2 y) A_z \sin(k_3 z)$$

$$= \boxed{A \sin(k_1 x) \sin(k_2 y) \sin(k_3 z)}$$

General notation for 3-D vector

As in 1-D case, $\psi = 0$ at $x = 0$ and $x_i = L_i$

$$\therefore \boxed{k_i L_i = n_i \pi}$$

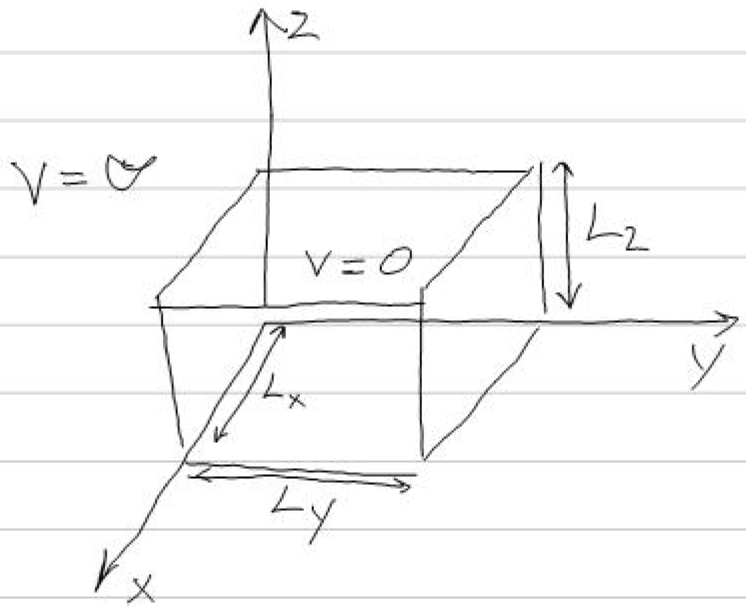
($n_i = 1, 2, 3 \ldots$ for x, y, z independently)

3-D means 3 quantum numbers.

3-8 Infinite Potential Well:

$$V = 0 \quad \begin{cases} 0 < x < L_x & \& \\ 0 < y < L_y & \& \\ 0 < z < L_z \end{cases}$$

$$V = \infty \quad \text{everywhere else}$$



Energy levels turn out to be

$$\boxed{E_n = \frac{\pi^2 \hbar^2}{2m}\left(\frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2}\right)}$$

Would define quantum state by n_i:

	n_1	n_2	n_3	
A	1	1	1	→ lowest energy level
B	1	1	2	
C	1	2	1	
D	2	1	1	

<u>If $L_1 = L_2 = L_3$</u>, then

$$\underline{E_n = \frac{\pi^2 \hbar^2}{2mL^2}\left(n_1^2 + n_2^2 + n_3^2\right)}$$

cases B, C + D above termed 'degenerate'

→ different quantum states give same Energy

Hydrogen Atom

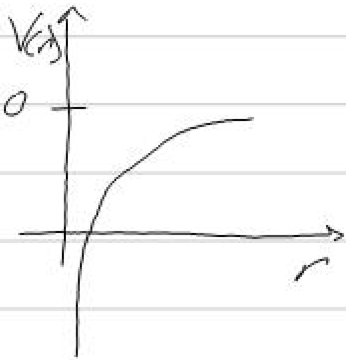
In 3-D, the Coulomb potential is

$\ominus e^-$

$\oplus p^+$ $\underline{H}$

$$\underline{V(r) = \frac{-e^2}{4\pi\epsilon_0 r}}$$

Spherically symmetric potential

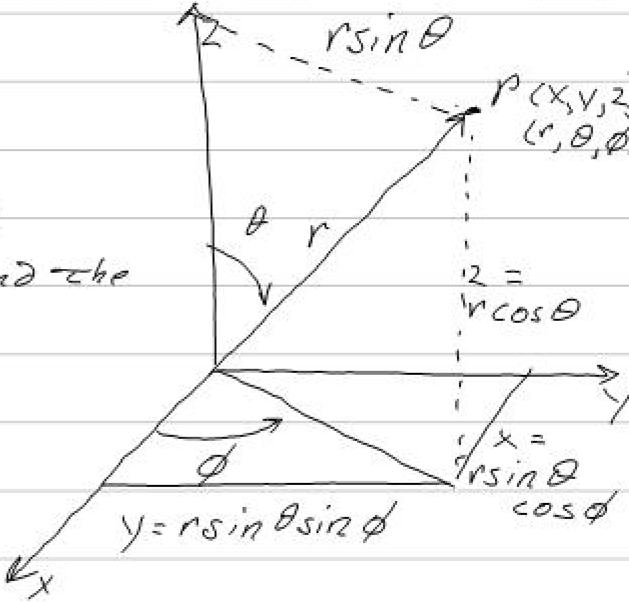


Will be very painful to solve Schröd. Eq. in Cartesian coordinates

$\Rightarrow$ <u>convert to spherical coordinates</u>

Spherical Coordinates 101

We talk about 'polar' (θ) and 'azimuthal' (ϕ) angles. → around the axis



Some useful conversions:

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

$$\theta = \cos^{-1} z/r = \cos^{-1} \frac{z}{\sqrt{x^2+y^2+z^2}}$$

$$\phi = \tan^{-1} y/x$$

Schrödinger Eq. in polar Coordinates ⑦

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

$$+ \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 \psi}{\partial \phi^2} + \frac{2m}{\hbar^2}(E - V(r))\psi = 0$$

Multiplying both sides by r^2 and substituting $\psi(\vec{r}) = R(r)\Theta(\theta)\Phi(\phi)$ to perform separation of variables,

$$\Theta\Phi \frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) + \frac{R\Phi}{\sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial \Theta}{\partial \theta}\right)$$

$$+ \frac{R\Theta}{\sin^2\theta}\frac{\partial^2 \Phi}{\partial \phi^2} = \frac{-2mr^2}{\hbar^2}(E - V(r))R\Phi\Theta$$

Divide by $R\Theta\Phi$ and rearrange:

$$\frac{1}{\Theta\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Theta}{\partial\theta}\right) + \frac{1}{\sin^2\theta\,\Phi}\frac{\partial^2\Phi}{\partial\phi^2}$$

$$= -\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{2mr^2}{\hbar^2}(E - V(r))$$

Since both sides depend on different variables, they must each equal a constant

$$\boxed{-\frac{1}{R}\frac{\partial}{\partial r}\left(r^2\frac{\partial R}{\partial r}\right) - \frac{2mr^2}{\hbar^2}(E - V(r)) = C}$$

Radial Equation

Separating Angular Variables

We know

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

Multiply both sides by $\sin^2\theta$ and rearrange:

$$\frac{\sin\theta}{\Theta} \frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial\Theta}{\partial\theta}\right) - C\sin^2\theta = -\frac{1}{\Phi} \frac{\partial^2\Phi}{\partial\phi^2}$$

Again, both sides must equal a constant

$$\boxed{\frac{\sin\theta}{\Theta} \frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial\Theta}{\partial\theta}\right) - c\sin^2\theta = D}$$

Polar Equation

$$\boxed{-\frac{1}{\Phi} \frac{\partial^2\Phi}{\partial\phi^2} = D}$$

Azimuthal Equation

Azimuthal Equation

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

If $D<0$: exponential solution
- not physical since ϕ is an angular variable & Φ must come back to itself

If $D>0$: sinusoidal solution
- has proper behavior for Φ ~~if~~ to repeat every 2π when

$$\sqrt{D} = \boxed{m_\ell = 0, \pm 1, \pm 2, \pm 3, \ldots}$$

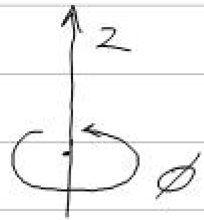
-and-

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

m_ℓ is a quantum # associated with azimuthal degree of freedom

$$\boxed{\frac{d^2\Phi(\phi)}{d\phi^2} = -m_\ell^2\,\Phi(\phi)}$$

what is physical property quantized?



ψ_{e^-} is a standing wave

- m_l indicates # λ's fit in circumference when consider real part of wave function (i.e. $2\pi r = m_l \lambda$)
- λ can be related to angular momentum

$$\underline{\underline{L_z}} = mvr = \left(\frac{m_l h}{2\pi r}\right) r = \underline{\underline{m_l \hbar}}$$

So m_l is associated with the angular momentum in z-direction.

m_l termed "magnetic" quantum number.

Polar Equation

$$\frac{\sin\theta}{\Theta}\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right) - C\sin^2\theta = 0$$

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

Solution is complicated but again considering boundary conditions

$$C = \begin{matrix}\text{negative}\\\text{integer}\end{matrix} = 0, -2, -6, -12, \ldots$$

Express this as

$$\underline{C = -l(l+1)} \text{ where } \boxed{l = 0, 1, 2, \ldots}$$

Quantum # 'l' associated with polar angle (θ) dimension. It's quantization corresponds to standing wave conditions in θ.

It turns out m_l and l are connected

$$\boxed{m_l = 0, \pm 1, \pm 2, \ldots \pm l}$$

What does l quantize?

Go back to the Angular Eq.

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

Substituting for C + multiplying by $\Theta\Phi$,

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

We can think of an angular momentum operator, $\hat{L}$ such that

$$\boxed{\hat{L}^2 = \frac{-\hbar^2}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\right) - \frac{\hbar^2}{\sin^2\theta}\frac{d^2}{d\phi^2}}$$

The angular differential Eq. would then be

$$\hat{L}^2\, Y_{l,m_l}(\theta,\phi) = \underbrace{l(l+1)\hbar^2}_{L^2}\, Y_{l,m_l}(\theta,\phi)$$

where $Y_{l,m_l}(\theta,\phi) = \Theta\Phi$ and are called "spherical harmonics". We get

$$\boxed{|L| = \sqrt{l(l+1)}\,\hbar} \qquad l = 0, 1, 2, \ldots$$

So l quantizes the total angular momentum, L.

Space Quantization

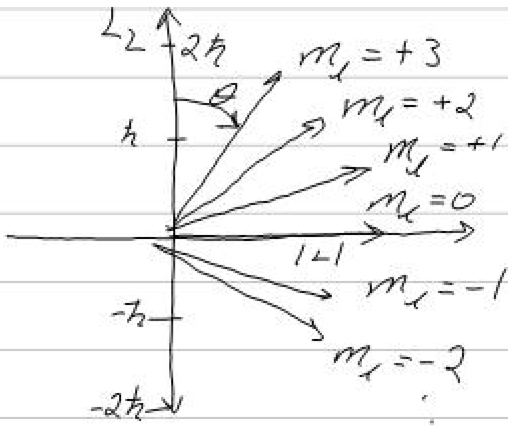
Since $|m_l| \le l$ and

$L_z = m_l \hbar$ and $|L| = l(l+1)\hbar$

L_z is always $< |L|$.

Also, $L_z/|L|$ takes on discrete ratios for a given l.

Example



If $l=3$, what is smallest polar angle?

θ minimized by maximizing L_z

$\therefore m_l = +3$

$$\cos\theta = L_z/|L| = 3\hbar/\sqrt{3(3+1)}\,\hbar = 3/\sqrt{12}$$

$$\boxed{\theta = \cos^{-1}\left(\sqrt{3}/2\right) = 30^\circ}$$

The Radial Equation

Substituting for C & rearranging,

$$\underbrace{\frac{-\hbar^2}{2m}\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)R(r)}_{KE_{rad}} + \underbrace{\frac{\hbar^2 l(l+1)}{2mr^2}R(r)}_{KE_{rotation}}$$

$$+ \underbrace{U(r)R(r)}_{\text{Pot. } E} = \underbrace{E\,R(r)}_{\text{total } E}$$

By supposition, considering other terms

- KE corresponding to motion toward or away from nucleus

If use Coulomb potential

$$U(r) = -e^2/4\pi\epsilon_0 r$$

only get physical results when

Bohr E levels!!

$$\boxed{E = \frac{-me^4}{2(4\pi\epsilon_0)^2\hbar^2}\frac{1}{n^2}} \quad n = 1, 2, 3, \ldots$$

principal quantum #

and l is constrained as

$$\boxed{l = 0, 1, 2, \ldots n-1}$$

Solutions to Radial Eq.

When $l=0$, no angular momentum
- 2nd term (KE_{rot}) $\to 0$

wave function

Spherically symmetric wave func.

$$R(r) = Ae^{-r/a_0} \longrightarrow a_0 = \frac{4\pi\epsilon_0 \hbar^2}{me^2}$$

Bohr radius!

Ground state energy

$$E = \frac{-\hbar^2}{2ma_0^2} = -E_0 = -13.6\,eV$$

Ground state E of Bohr atom!

Fact that n comes from radial Eq. indicating some relation between 'size' of shell e^- harbors & E_n
- lower n, smaller orbits, more tightly bound e^-

Quantum #s

$$\boxed{\begin{array}{l} n>0 \\ l<n \\ |m_l| \le l \end{array}} \quad \begin{array}{l} \to E_n \\ \to |L| \\ \to L_z \end{array}$$

Example: what are quantum #s for $n=4$ state?

n	l	m_l
4	0	0
4	1	-1, 0, +1
4	2	-2, -1, 0, +1, +2
4	3	-3, -2, -1, 0, +1, +2, +3

Terminology

$l=0$	1	2	3	4	5
s	p	d	f	g	h

Spectro-scopic Notation $\begin{cases} n=2,\ l=1: & \text{"2p state"} \\ n=4,\ l=2: & \text{"4d state"} \end{cases}$