PHYS-3301

Lecture 15

Oct. 15, 2024

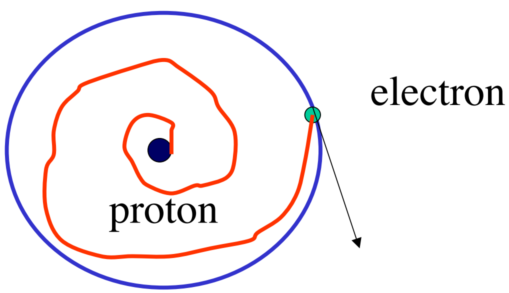
Chapter. 7
QM in 3-dims & Hydrogen Atom

Outline:

- The Schrödinger Eq. in 3-Dimensions
- The 3D Infinite Well
- Energy Quantization & Spectral Lines in Hydrogen
- The Schrödinger Eq. for a Central Force
- Angular Behavior in a Central Force
- The Hydrogen Atom
- Radial Probability
- Hydrogen-like Atoms

The most profound failure of classical physics (C.P.) is its inability to explain the simplest possible atom: hydrogen – an electron orbiting a proton. <u>According to the C.P., atom should be unstable since energy loss</u>

The Problem:



Energy loss due to Bremsstrahlung

(because of centripetal acceleration)

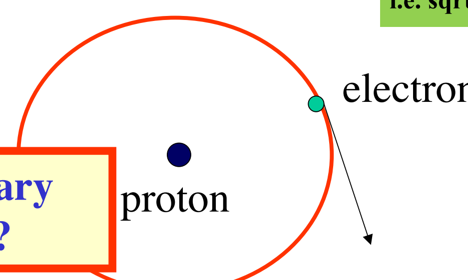
Toward the Hydrogen Atom

Electrostatic P.E. (or P.E. for the Hydrogen atom) is given by

$$U(r) = -\frac{1}{4\pi\epsilon_0}\frac{e^2}{r}$$

e = Fundamental charge

r = distance from the proton at the origin. i.e. sqrt($x^2+y^2+z^2$)



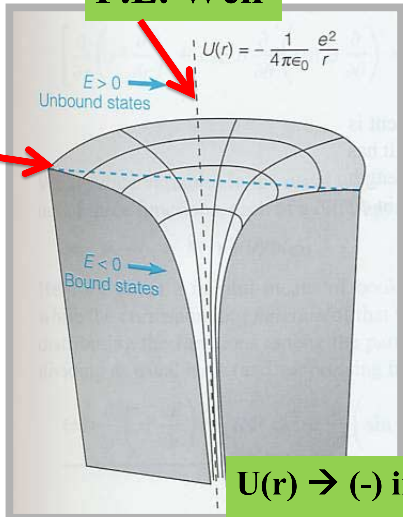
Stationary state?

YES!! – $m_p \sim 200\ m_e$; m_p is massive

Toward the Hydrogen Atom

P.E. Well

E = 0



U(r) → (-) infinity @ r = 0
U(r) → zero @ r = (+) infinity

Toward the Hydrogen Atom

Electron's P.E. depends only on r; u(**r**) = u(r)
i.e. Not (θ,ϕ)

$$U(r) = -\frac{1}{4\pi\epsilon_0}\frac{e^2}{r}$$

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

The force is necessarily along the radial direction and is known as a "central force".

Schrodinger Equation in 3 Dimensions

In 1-D

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x,t) + U(x)\Psi(x,t) = i\hbar\frac{\partial}{\partial t}\Psi(x,t)$$

$$\frac{p_x^2}{2m} \rightarrow \frac{\left(-i\hbar\frac{\partial}{\partial x}\right)^2}{2m} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$$

Section 5-8

KE operator

$$\frac{p_x^2+p_y^2+p_z^2}{2m} \rightarrow \frac{\left(-i\hbar\frac{\partial}{\partial x}\right)^2+\left(-i\hbar\frac{\partial}{\partial y}\right)^2+\left(-i\hbar\frac{\partial}{\partial z}\right)^2}{2m}$$

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

In 3-D

Schrodinger Equation in 3 Dimensions

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\Psi(x,y,z,t) + U(x,y,z)\Psi(x,y,z,t) = i\hbar\frac{\partial}{\partial t}\Psi(x,y,z,t)$$

Kinetic Energy term

Adopt the generic symbol (Del) from vector calculus

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

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(\mathbf{r},t) + U(\mathbf{r})\Psi(\mathbf{r},t) = i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t)$$

Bold face, r : Cartesian (x,y,z) or Spherical Polar (r,θ,ϕ)
Schrödinger eq → coordinate-independent form

Probability Density in 3 Dimensions

c.f. 1-D :: complex square of wave function = Prob. / unit length

$$\text{probability density} = \frac{\text{probability}}{\text{volume}} = |\Psi(\mathbf{r}, t)|^2$$

now, 3-D

Normalization

$$\int_{\text{all space}} |\Psi(\mathbf{r}, t)|^2 \, dV = 1$$

Total Prob. of finding a single particle somewhere in 3-D space ➔ 1.0 (100%)

Stationary States

First, let's separate position(s) from time

$$\Psi(\mathbf{r}, t) = \psi(\mathbf{r})\phi(t)$$

Spatial part — Temporal part

$$-\frac{\hbar^2}{2m}\nabla^2\Psi(\mathbf{r}, t) + U(\mathbf{r})\Psi(\mathbf{r}, t) = i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r}, t)$$

Separation of Variables

Divide both sides by ψ(r)ϕ(t)

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(\mathbf{r})}\nabla^2\psi(\mathbf{r}) + U(\mathbf{r}) = i\hbar\frac{1}{\phi(t)}\frac{\partial}{\partial t}\phi(t)$$

f(r) — *f(t)*

Variables are separate now

Key Assumption:

Factorization of the wave function

$$\Psi(x, t) = \psi(x)\phi(t)$$

Standard Math. Technique; "Separation of variables"

Wave function may be express as a product of …

Spatial Part — **Temporal Part**

Q: Why?, **A:** allows us to break a differential eq. with 2 independent variables (x,t) into simpler eqs. For position & time, separately!!

What happens with the Schrodinger equation?

$$\Psi(x, t) = \psi(x)\phi(t)$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + U(x)\psi(x) = E\psi(x)$$

… and factoring out terms constant w.r.t. the partial derivatives …

$$-\frac{\hbar^2}{2m}\phi(t)\frac{\partial^2\psi(x)}{\partial x^2} + U(x)\psi(x)\phi(t) = i\hbar\psi(x)\frac{\partial\phi(t)}{\partial t}$$

Divide both sides by ψ(x)ϕ(t)

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{\partial^2\psi(x)}{\partial x^2} + U(x) = i\hbar\frac{1}{\phi(t)}\frac{\partial\phi(t)}{\partial t}$$

Variables are separate now!!

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{\partial^2\psi(x)}{\partial x^2} + U(x) = i\hbar\frac{1}{\phi(t)}\frac{\partial\phi(t)}{\partial t}$$

t and x are independent

$$-\frac{\hbar^2}{2m}\frac{1}{\psi(x)}\frac{d^2\psi(x)}{dx^2} + U(x) = i\hbar\frac{1}{\phi(t)}\frac{d\phi(t)}{dt} = C$$

Consider only case in which P.E. is time-independent

Separation Constant

$$i\hbar\frac{1}{\phi(t)}\frac{d\phi(t)}{dt} = C \rightarrow \frac{d\phi(t)}{dt} = -\frac{iC}{\hbar}\phi(t)$$

The Temporal Part, $\phi(t)$

$$\phi(t) = Ae^{-i(C/\hbar)t}$$

$$E = \hbar\omega = C$$

Solution (see Appendix K)

$Ae^{i(kx-\omega t)} \sim Ae^{-i\omega t}$, $\omega = C/\hbar$

Stationary States

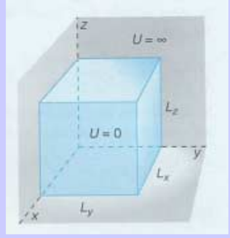
$$\phi(t) = e^{-i(E/\hbar)t}$$

temporal part

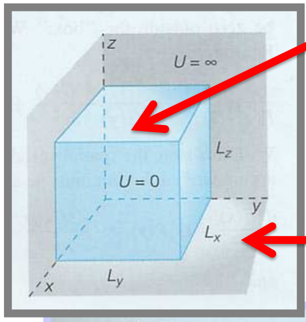
Separation of Variables

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

Time-independent Sch. equation



Stationary States in a 3-D Box



A particle bound in a box-shaped region by infinitely high potential well

$$U(\mathbf{r}) = \begin{cases} 0 & 0 < x < L_x,\ 0 < y < L_y,\ 0 < z < L_z \\ \infty & \text{otherwise} \end{cases}$$

The simplest 3-D bound system is infinite well!!

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

or

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

Stationary States in a 3-D Box

"Factorization"

Now, let's separate each position

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

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

or

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

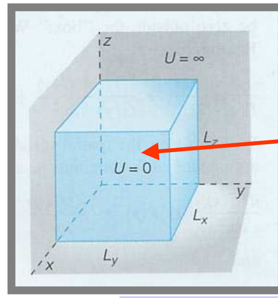
$$\psi(x, y, z) = F(x)G(y)H(z)$$

$$\frac{-\frac{\hbar^2}{2m}\left(GH\frac{\partial^2 F}{\partial x^2} + FH\frac{\partial^2 G}{\partial y^2} + FG\frac{\partial^2 H}{\partial z^2}\right) + U(x, y, z)(FGH)}{FGH} = \frac{E(FGH)}{FGH}$$

$$-\frac{\hbar^2}{2m}\left(\frac{1}{F}\frac{\partial^2 F}{\partial x^2} + \frac{1}{G}\frac{\partial^2 G}{\partial y^2} + \frac{1}{H}\frac{\partial^2 H}{\partial z^2}\right) + U(x, y, z) = E$$

$f(x)$ $f(y)$ $f(z)$ $f(x,y,z)$

… multiplying both side by -2m/h²



$$U(\mathbf{r}) = \begin{cases} 0 & 0 < x < L_x,\ 0 < y < L_y,\ 0 < z < L_z \\ \infty & \text{otherwise} \end{cases}$$

Separation is done!! Each term should be "Constant"; Cx, Cy, Cz

$$\frac{1}{F(x)}\frac{\partial^2 F(x)}{\partial x^2} + \frac{1}{G(y)}\frac{\partial^2 G(y)}{\partial y^2} + \frac{1}{H(z)}\frac{\partial^2 H(z)}{\partial z^2} = -\frac{2mE}{\hbar^2}$$

$$\frac{d^2F(x)}{dx^2} = C_x F(x), \quad \frac{d^2G(y)}{dy^2} = C_y G(y), \quad \frac{d^2H(z)}{dz^2} = C_z H(z),$$

and

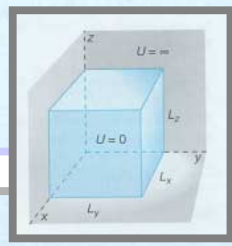
$$C_x + C_y + C_z = -\frac{2mE}{\hbar^2}$$

Things now look rather familiar

$$\frac{d^2F(x)}{dx^2} = C_x F(x), \quad \frac{d^2G(y)}{dy^2} = C_y G(y), \quad \frac{d^2H(z)}{dz^2} = C_z H(z),$$

and

$$C_x + C_y + C_z = -\frac{2mE}{\hbar^2}$$

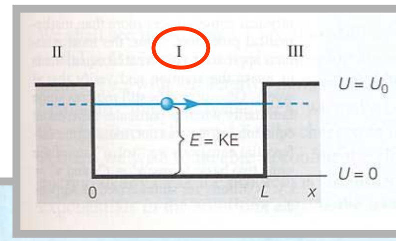


$C_x \rightarrow -k_x^2$

The mathematical solution to the "x-equation" is thus

$$\frac{d^2F(x)}{dx^2} = -k_x^2 F(x) \quad \Rightarrow \quad F(x) = A \sin k_x x + B \cos k_x x$$

$$F(0) = 0 \quad \rightarrow \quad A \sin k_x 0 + B \cos k_x 0 = 0 \quad \Rightarrow \quad B = 0$$



Region I ($0 < x < L$)

Since $U(x) = 0$ here, the time-independent Schrödinger equation (4-8) is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = E\psi(x) \quad \text{or} \quad \frac{d^2\psi(x)}{dx^2} = -\frac{2mE}{\hbar^2}\psi(x)$$

For convenience, let us make the following definition (which we very soon see is a wave number, thus the symbol):

$$k \equiv \sqrt{\frac{2mE}{\hbar^2}} \qquad (4\text{-}11)$$

Thus,

$$\frac{d^2\psi(x)}{dx^2} = -k^2\psi(x) \qquad \psi(x) = A \sin kx + B \cos kx$$

$F(L_x) = 0 \quad \rightarrow \quad A \sin k_x L_x = 0 \quad \Rightarrow \quad k_x L_x = n_x \pi$

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

$$F(x) = A \sin \frac{n_x \pi x}{L_x} \quad \text{and} \quad C_x = -k_x^2 = -\frac{n_x^2 \pi^2}{L_x^2}$$

$$G(y) = A \sin \frac{n_y \pi y}{L_y} \quad \text{and} \quad C_y = -k_y^2 = -\frac{n_y^2 \pi^2}{L_y^2}$$

$$H(z) = A \sin \frac{n_z \pi z}{L_z} \quad \text{and} \quad C_z = -k_z^2 = -\frac{n_z^2 \pi^2}{L_z^2}$$

n_x, n_y, n_z = Quantum Number

Stationary States in a 3-D Box

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

F(x), G(y), H(z)

$$\psi_{n_x,n_y,n_z}(x, y, z) = A \sin \frac{n_x \pi x}{L_x} \sin \frac{n_y \pi y}{L_y} \sin \frac{n_z \pi z}{L_z}$$

↓

$$\frac{1}{F(x)} \frac{\partial^2 F(x)}{\partial x^2} + \frac{1}{G(y)} \frac{\partial^2 G(y)}{\partial y^2} + \frac{1}{H(z)} \frac{\partial^2 H(z)}{\partial z^2} = -\frac{2mE}{\hbar^2}$$

$$-\frac{n_x^2 \pi^2}{L_x^2} - \frac{n_y^2 \pi^2}{L_y^2} - \frac{n_z^2 \pi^2}{L_z^2} = -\frac{2mE}{\hbar^2}$$

Stationary States in a 3-D Box

Solution

$$\psi_{n_x,n_y,n_z}(x, y, z) = A \sin \frac{n_x \pi x}{L_x} \sin \frac{n_y \pi y}{L_y} \sin \frac{n_z \pi z}{L_z}$$

$$E_{n_x,n_y,n_z} = \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right) \frac{\pi^2 \hbar^2}{2m}$$

$$example: L_x = 1, L_y = 2, L_z = 3$$

Just arbitrary units

$$E_{n_x,n_y,n_z} = \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right) \frac{\pi^2 \hbar^2}{2m}$$

The lowest energy (n_x=1, n_y=1, n_z=1)

$$E_{1,1,1} = \left(\frac{1^2}{1^2} + \frac{1^2}{2^2} + \frac{1^2}{3^2} \right) \frac{\pi^2 \hbar^2}{2m} = \frac{49 \pi^2 \hbar^2}{72m}$$

Corresponding wave function:

$$\psi_{1,1,1}(x, y, z) = A \sin \frac{1 \pi x}{1} \sin \frac{1 \pi y}{2} \sin \frac{1 \pi z}{3}$$

Stationary States in a 3-D Box

Suppose the box is as symmetric as possible (i.e. Cube)

$$L_x = L_y = L_z \equiv L$$

$$E_{n_x,n_y,n_z} = \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)\frac{\pi^2\hbar^2}{2m}$$

$$E_{n_x,n_y,n_z} = (n_x^2 + n_y^2 + n_z^2)\frac{\pi^2\hbar^2}{2mL^2}$$

$$\psi_{3,3,3} = A \sin\frac{3\pi x}{L} \sin\frac{3\pi y}{L} \sin\frac{3\pi z}{L} \qquad \psi_{5,1,1} = A \sin\frac{5\pi x}{L} \sin\frac{1\pi y}{L} \sin\frac{1\pi z}{L}$$

$$\psi_{1,5,1} = A \sin\frac{1\pi x}{L} \sin\frac{5\pi y}{L} \sin\frac{1\pi z}{L} \qquad \psi_{1,1,5} = A \sin\frac{1\pi x}{L} \sin\frac{1\pi y}{L} \sin\frac{5\pi z}{L}$$

Sets of Q.N. for many allowed energies in the 3-D well

n_x, n_y, n_z	E_{n_x, n_y, n_z} *
1, 1, 1	3
2, 1, 1	6
1, 2, 1	6
1, 1, 2	6
1, 2, 2	9
2, 1, 2	9
2, 2, 1	9
3, 1, 1	11
1, 3, 1	11
1, 1, 3	11
2, 2, 2	12
1, 2, 3	14
2, 1, 3	14
1, 3, 2	14
2, 3, 1	14
3, 1, 2	14
3, 2, 1	14

These correspond to unique sets of Q.N. e.g. (111), (222)

$$E_{n_x,n_y,n_z} = \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)\frac{\pi^2\hbar^2}{2m}$$

E27 results from 4 different sets of Q.N.

Same E, but each sets of Q.N. corresponds to different wave function!!

1, 4, 2	21
2, 4, 1	21
4, 1, 2	21
4, 2, 1	21
2, 3, 3	22
3, 2, 3	22
3, 3, 2	22
4, 2, 2	24
2, 4, 2	24
2, 2, 4	24
1, 3, 4	25
3, 1, 4	25
1, 4, 3	25
3, 4, 1	25
4, 1, 3	25
4, 3, 1	25
3, 3, 3	27
5, 1, 1	27
1, 5, 1	27
1, 1, 5	27

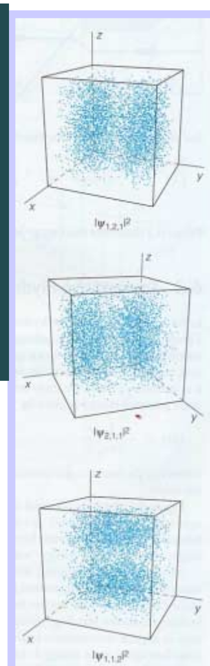
Such coincidence, <u>different wave function having the same E,</u> is called "degeneracy"

So, E27 is said to be 4-fold degenerate!!

& E3, E12 → Nondegenerate!!

Degeneracy in a cubic infinite well –

Equal E but different states



$|\Psi_{1,2,1}|^2$

$|\Psi_{2,1,1}|^2$

$|\Psi_{1,1,2}|^2$