Lecture #8 sections 3.7 – 3.9

I. Average Values: Expectation Values from wavefunctions and operators

II. Uncertainty Principle applied to PIB

III. 3-D Particle in A Box,

BE SURE TO ANSWER THE 3 Questions in this lecture displayed in a blue font!

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I. Average Values : Expectation Values from wavefunctions and operators

The average value of observable "m" in basis functions {ψ} is given by:

$$< m > = \int (a y^*) \mathrm{M} (\mathrm{a} y) \mathrm{d} t$$

$$< \mathrm{m} > = \mathrm{a}^2 \int y^* \mathrm{M} y \mathrm{d} t = \frac{\int y^* \mathrm{M} y \mathrm{d} t}{\int y^* y \mathrm{d} t}$$

Think of $\int y^* \mathrm{M} y \mathrm{d} t$ as $\int M \left(y^* y \mathrm{d} t \right) = \int observable \times probability$

For PIB of length "a": $y = \left(\frac{2}{a} \right)^{\frac{1}{2}} \sin \frac{npx}{a}$ n = 1, 2, 3…

Note: the integrals below found on pages 85-86 of your text (Physical Chemistry by McQuarrie) are also found in Tables of Integrals, Series, and Products by I.S. Gradshteyn & I.M. Ryzhik pages 185-186 formulae 2.636 numbers 3 and 4.

Average value of x is:

$$\langle x \rangle = \int_{x=0}^{a} \left[\left(\frac{2}{a} \right)^{\frac{1}{2}} \sin \frac{npx}{a} \right]^* x \left[\left(\frac{2}{a} \right)^{\frac{1}{2}} \sin \frac{npx}{a} \right] dx$$

$$= \frac{2}{a} \int_{x=0}^{a} x \sin^2 \frac{npx}{a} dx = \frac{2}{a} \frac{a^2}{4} = \frac{a}{2}$$

Average value of x^2 is:

$$\langle x^2 \rangle = \int_{x=0}^{a} \left[\left(\frac{2}{a} \right)^{\frac{1}{2}} \sin \frac{npx}{a} \right]^* x^2 \left[\left(\frac{2}{a} \right)^{\frac{1}{2}} \sin \frac{npx}{a} \right] dx$$

$$= \frac{2}{a} \int_{x=0}^{a} x^2 \sin^2 \frac{npx}{a} dx = \left(\frac{a}{2pn} \right)^2 \left(\frac{4p^2 n^2}{3} - 2 \right) = \frac{a^2}{3} - \frac{a^2}{2n^2 p^2}$$

Variance $\sigma_x^2 = <x^2> - <x>^2$ $\left[\frac{a^2}{3} - \frac{a^2}{2n^2 p^2} \right] - \frac{a^2}{4} = \frac{a^2}{12} - \frac{a^2}{2n^2 p^2} = \left(\frac{a}{2pn} \right)^2 \left(\frac{p^2 n^2}{3} - 2 \right)$

So the standard deviation $\sigma_x = \sqrt{\sigma_x^2} = \left(\frac{a}{2pn}\right)\left(\frac{p^2n^2}{3} - 2\right)^{\frac{1}{2}}$

$$\langle momentum \rangle_{PIB} = \langle P_x \rangle = \left\langle -i\hbar\frac{\partial}{\partial x}\right\rangle = \int_0^a \left(\frac{2}{a}\right)^{\frac{1}{2}} \sin\frac{npx}{a}\left(-i\hbar\frac{\partial}{\partial x}\right)\left(\frac{2}{a}\right)^{\frac{1}{2}} \sin\frac{npx}{a}\,dx$$

$$= \left(\frac{2}{a}\right)(-i\hbar)\int_0^a \sin\frac{npx}{a}\frac{np}{a}\cos\frac{npx}{a}\,dx = -i\hbar\frac{2np}{a^2}\left[\int_0^a \sin\frac{npx}{a}\cos\frac{npx}{a}\,dx\right] = 0$$

Note: The [integral (sin npx/a)(cos npx/a)dx] =0 as noted in the back cover of your text (McQuarrie).

$$\langle P_x^{\ 2} \rangle = \left\langle -i\hbar\frac{\partial}{\partial x}\right\rangle = \int_0^a \left(\frac{2}{a}\right)^{\frac{1}{2}} \sin\frac{npx}{a}\left(-i\hbar\frac{\partial}{\partial x}\right)\left(-i\hbar\frac{\partial}{\partial x}\right)\left(\frac{2}{a}\right)^{\frac{1}{2}} \sin\frac{npx}{a}\,dx$$

$$= \left(\frac{2}{a}\right)\left(-\hbar^2\right)\int_0^a \sin\frac{npx}{a}\frac{np}{a}\left(\frac{\partial}{\partial x}\right)\cos\frac{npx}{a}\,dx = \left(\frac{2}{a}\right)\left(\hbar^2\right)\left(\frac{np}{a}\right)^2\left[\int_0^a \sin\frac{npx}{a}\sin\frac{npx}{a}dx\right]$$

$$= \left(\frac{2}{a}\right)\left(\hbar^2\right)\left(\frac{np}{a}\right)^2\left(\frac{a}{2}\right) = \left(\frac{np\hbar}{a}\right)^2$$

Note: Momentum = a vector = mass × velocity**,** since average velocity is zero (random directions) average momentum should be zero, but average momentum squared should be nonzero (i.e. RMS velocity).

II. Uncertainty Principle applied to PIB

Proving that $s_p s_x \geq \frac{\hbar}{2}$ for PIB.

$$s_p = \sqrt{s_p^{\ 2}} = \sqrt{\langle P^2 \rangle - \langle P \rangle^2} = \sqrt{\left(\frac{np\hbar}{a}\right)^2 - 0} = \frac{np\hbar}{a} \qquad s_x = \left(\frac{a}{2pn}\right)\left(\frac{p^2n^2}{3} - 2\right)^{\frac{1}{2}}$$

$$s_p s_x = \frac{np\hbar}{a}\left(\frac{a}{2pn}\right)\left(\frac{p^2n^2}{3} - 2\right)^{\frac{1}{2}} = \frac{\hbar}{2}\left(\frac{p^2n^2}{3} - 2\right)^{\frac{1}{2}} \geq \frac{\hbar}{2}\left(\frac{p^2(n=1)^2}{3} - 2\right)^{\frac{1}{2}} = \frac{\hbar}{2}\times 1.136$$

$$Thus \quad s_p s_x \geq \frac{\hbar}{2}$$

Note: a ↓ (localized) $\rightarrow \sigma_p \uparrow$ For a free particle a $\rightarrow \infty$, $\sigma_p \rightarrow 0$ & $\sigma_x \rightarrow \infty$

III. 3-D PIB

PLAN: Solve the 3-D PIB Schrodinger equation to determine the normalized eigenfunctions and eigenvalues (energy level expressions parametrically dependent on quantum numbers n_x, n_y, n_z)

3-D PIB S.E.: $-\frac{\hbar^2}{2m}\nabla^2\psi = E\psi \qquad where\ \nabla^2 = \frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$ (1)

$0 \le x \le a,\qquad 0 \le y \le b,\qquad 0 \le z \le c$

boundary conditions: ψ(0,y,z) = ψ (a,y,z) = 0 for all y,z
ψ (x,0,z) = ψ (x,b,z) = 0 x,z
ψ (x,y,0) = ψ (x,y,c) = 0 x,y

ψ(x,y,z) = X(x) Y(y) Z(z) (2)

Inserting Eq. 2 into 1 and multiplying by 1/ψ yields:

$$-\frac{\hbar^2}{2m}\frac{1}{X}\frac{d^2X}{dx^2}-\frac{\hbar^2}{2m}\frac{1}{Y}\frac{d^2Y}{dy^2}-\frac{\hbar^2}{2m}\frac{1}{X}\frac{d^2X}{dz^2}=E \qquad (3)$$

3 terms on LHS may vary independently (i.e. $-\frac{\hbar^2}{2m}\frac{1}{X}\frac{d^2X}{dx^2}=E_x$) thus

$E_x + E_y + E_z = E$ (4)

Applying the boundary conditions to equation 2:
X(0)=X(a)=Y(0)=Y(b)=Z(0)=Z(c) = 0

Thus we may solve the 3-D S.E. (Eq. 3) by solving three 1-D equations and imposing the boundary conditions to yield)

(1) YOU MUST BE ABLE TO DO THIS! – We can do this in discussion session.

$$X(x) = A_x \sin\frac{n\pi x}{a} \qquad n_x = 1, 2, 3...$$

$$Y(y) = A_y \sin\frac{n\pi y}{b} \qquad n_y = 1, 2, 3... \qquad (5)$$

$$Z(z) = A_z \sin\frac{n\pi z}{c} \qquad n_z = 1, 2, 3..$$

$$\Psi = \boldsymbol{X(x)Y(y)Z(z)} = \boldsymbol{A_x A_y A_z \sin\frac{n\pi x}{a}\ \sin\frac{n\pi y}{b}\ \sin\frac{n\pi z}{c}} \qquad (6)$$

Thus ***Normalization over all axes i.e. triple*** **integral**

$$\Psi = \left(\frac{8}{\boldsymbol{abc}}\right)^{\frac{1}{2}} \boldsymbol{\sin\frac{n\pi x}{a}\ \sin\frac{n\pi y}{b}\ \sin\frac{n\pi z}{c}} \qquad \textbf{(7)}$$

(2) You must be able to show how to get equation #7 from equation #6 (triple integral normalization)

To obtain the energy eigenvalues simply insert equation 7 (eigenfunctions) into the schrodinger equation (Eq. 1). **(3) You must be able to obtain eigenvalues (Eq. 8) from equations 1 & 7.**

$$E_{n_x n_y n_z} = \frac{h^2}{8m}\left(\frac{n_x^{\ 2}}{a^2} + \frac{n_y^{\ 2}}{b^2} + \frac{n_z^{\ 2}}{c^2}\right) \qquad (8)$$

Note: if a=b≠c, we may have doubly degenerate states: (a,b,c) = {(1,2,1), (2,1,1)} {(2,4,1),(4,2,1)}…

If a=b=c, we may have triply degenerate states: (a,b,c) = {(2,11),(1,2,1),(1,1,2)} {(3,3,1),(3,1,3),(1,3,3)}..

Or even 6-fold degenerate states: {(2,3,1),(3,2,1),(2,1,3)(3,1,2),(1,2,3),(1,3,2)}…

Note: none of the n values may be zero since that's trivial solution: n_x = 1,2,3.. n_y = 1,2,3.. n_z = 1,2,3…

Degenerate states have the same ENERGY!