Quantum Chemistry

Page No:
Date: / /

(17) 1) Expectation value for a series of measurements corresponding to the operator $\hat{O}$ is given by

$$\langle a \rangle = \frac{\int_{Volume} \psi^*(r)\, \hat{O}\, \psi(r)\, dr}{\int_{Volume} \psi^*(r)\, \psi(r)\, dr}$$

2) The wavefunction of a system changes with time according to the time-dependent Schrödinger equation

$$\hat{H}\psi(r,t) = i\hbar \frac{\partial \psi(r,t)}{\partial t}$$, where $\hat{H}$ is the Hamiltonian operator for the system.

3) $\psi^*\psi = |\psi|^2$

4) Normalization Condition: $\int_{allspace} \psi^*\psi\, d\tau = 1$

In spherical polar co-ordinates:

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} \psi^*(r,\theta,\phi)\, \psi(r,\theta,\phi)\, r^2 \cancel{dr} \sin\theta\, d\theta\, d\phi = 1$$

5) If ψ is not normalized:

$$\psi \rightarrow N\psi \Rightarrow N^2 \int_{all\,space} \psi^*\psi\, d\tau = 1 \Rightarrow N = \frac{1}{\left(\int_{all\,space} \psi^*\psi\, d\tau\right)}$$

) $\hat{x} = x \times$ [Position operator]

$\hat{p}_x = -i\hbar \dfrac{d}{dx}$ [Linear momentum operator]

$\hat{K} = -\dfrac{\hbar^2}{2m} \dfrac{d^2}{dx^2}$ [Kinetic energy operator]

$\hat{V} = \dfrac{1}{2} k x^2 \times$ [Potential energy (harmonic) opera

Linear Operator $\Rightarrow$ $\hat{A}\,[c_1 f_1(x) + c_2 f_2(x)]$

$= c_1 \hat{A} f_1(x) + c_2 \hat{A} f_2(x)$

Hermitian operators :

$\hat{A} f(x) = a f(x)$.

has to be real

4) A Hermitian operator must satisfy :

$$\int_{\text{all space}} \psi^* \hat{A} \psi \, d\tau = \int_{\text{all space}} \psi (\hat{A}\psi)^* \, d\tau$$

5) Eigenfunctions of a Hermitian operator form an orthonormal set i.e. satisfy the following orthonormality condition

$$\int_{\text{all space}} \psi_m^* \psi_n \, d\tau = \delta_{mn}$$

6) $$\langle a \rangle = \frac{\int_{volume} \psi^*(r) \hat{A} \psi(r) dr}{\int_{volume} \psi^*(r) \psi(r) dr}$$

7) If $\{\phi_n\}$ are the set of eigenfunctions of th operator $\hat{A}$ with corresponding eigenvalues a a_n, then we can write ψ as a linea superposition of the eigenfunctions of $\hat{A}$.

$$\psi = \sum_n c_n \phi_n \; ; \quad c_n \text{ are constants}$$

→ As ϕ_n are orthonormal, ψ has to be normali

$$\Rightarrow \sum_n |c_n|^2 = 1$$

→ Average value of observable A $= \sum |c_n|$

8) $\psi = \sum_n c_n \phi_n$ The value of c_n can be calc as follows : $\Rightarrow \int \phi_m^* \psi \, d\tau = \int_{\text{all space}} \phi_m^* \sum_n c_n \phi_n \, d\tau = c_n$

do not commute :

$$[\hat{x}, \hat{p}_x] = i\hbar \neq 0.$$

$$\Delta x \Delta p_x \geq \frac{\hbar}{2} \quad ; \quad \Delta t \Delta E \geq \frac{\hbar}{2}$$

$$E = h\nu$$

Time independent Schrödinger equation :

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

For three - dimensional case :

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(x,y,z) + \hat{V}(x,y,z)\psi(x,y,z) = E\psi($$

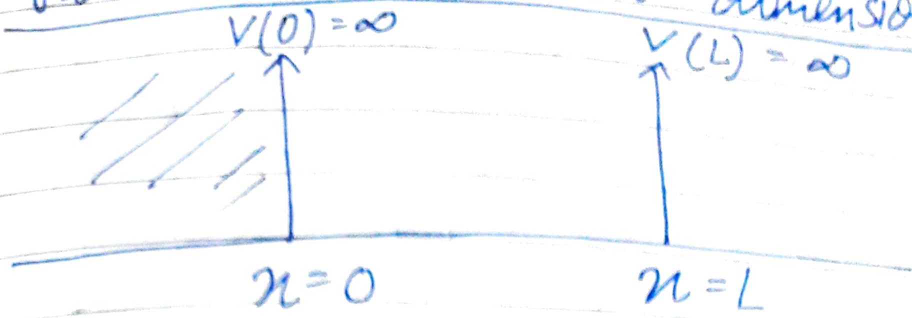
where $\nabla^2 = \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$

For time dependent case :

$$\psi(x,t) = \psi(x) e^{-iEt/\hbar} = \psi(x) e^{-i\omega t}$$

$$\psi_n(x,t) = \psi_n(x) e^{-iE_n t/\hbar}$$

L10 Particle in a one-dimensional box



1) $$\psi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right) \quad \text{for } 0 \le x \le L$$

$$= 0 \quad \text{otherwise}$$

2) Energy $E = \dfrac{n^2 h^2}{8mL^2}$; $n = 1, 2, \ldots$

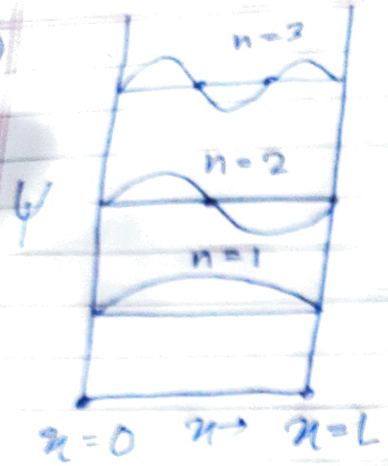
$$k = \frac{\sqrt{2mE}}{\hbar} = \frac{n\pi}{L} \; ; \; n = 1, 2 \ldots$$

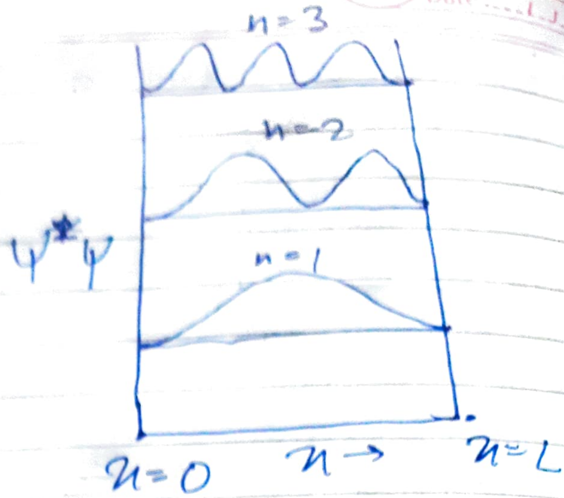
3) Zero-point energy is the lowest energy that the particle may possess $= \dfrac{h^2}{8mL^2}$.

4) Probability density $\psi_n^2(x) = \dfrac{2}{L} \sin^2\left(\dfrac{n\pi x}{L}\right)$

The non-uniformity is pronounced when n is small.

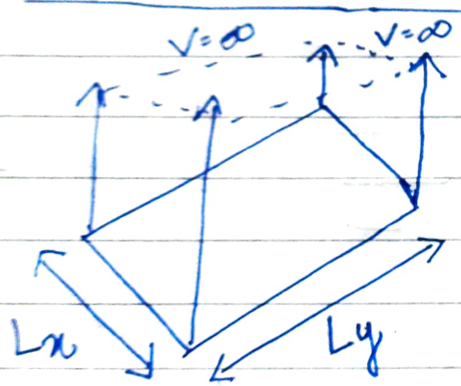
5)





L2

Particle in Two Dimensional Box :



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

$$0 \leq x \leq L_x$$
$$0 \leq y \leq L_y$$

$$\hat{H} = \hat{H}_x + \hat{H}_y$$

2) Using separation of variables:

$$\psi(x,y) = X(x)\,Y(y) = XY$$

$$\frac{\partial^2 \psi}{\partial x^2} = X''Y \quad \& \quad \frac{\partial^2 \psi}{\partial y^2} = XY''$$

So $$X''Y + XY'' = -\frac{2mE}{\hbar^2} XY$$

$$\Rightarrow \frac{X''}{X} + \frac{Y''}{Y} = -\frac{2mE}{\hbar^2}.$$

$$\frac{X''}{X} = -k_x^2, \quad \frac{Y''}{Y} = -k_y^2.$$

$$X = \sqrt{\frac{2}{L_x}} \sin\left(\frac{n_x \pi}{L_x} x\right)$$

$$Y = \sqrt{\frac{2}{L_y}} \sin\left(\frac{n_y \pi}{L_y} y\right).$$

$$\therefore \psi_{n_x, n_y}(x,y) = \frac{2}{\sqrt{L_x L_y}} \sin\left(\frac{n_x \pi}{L_x} x\right) \sin\left(\frac{n_y \pi}{L_y} y\right)$$

$$E_{n_x, n_y} = \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right).$$

Page No: ....
Date: ../../..

7) If the particle is confined in square box,
$L_x = L_y = L$

Then,
$\psi_{1,1} \rightarrow \psi_{2,2}$ etc. are non-degenerate.

$\psi_{1,2}$, $\psi_{2,1}$, $\psi_{1,3}$, $\psi_{3,1}$ etc. have 2 degrees degeneracies.

8) If it is a rectangle, then $\psi_{1,2}$ & ψ_{21} (and others) are not degenerate.

9) Similarly for 3-dimensional box,

$$\psi_{n_x, n_y, n_z}(x, y, z) = \frac{2\sqrt{2}}{\sqrt{L_x L_y L_z}} \sin\left(\frac{n_x \pi}{L_x} x\right) \sin\left(\frac{n_y \pi}{L_y} y\right) \sin\left(\frac{n_z \pi}{L_z} z\right).$$

$0 \le x \le L_x$, $0 \le y \le L_y$, $0 \le z \le L_z$

10) $$E_{n_x, n_y, n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$$

11) If the box is a cube,
$\psi_{1,1,1} \rightarrow$ Non-degenerate
$\psi_{1,2,1}$, $\psi_{2,1,1}$, $\psi_{1,1,2} \rightarrow$ 3-fold degeneracy.