

QUANTUM CHEMISTRY

Hand written notes

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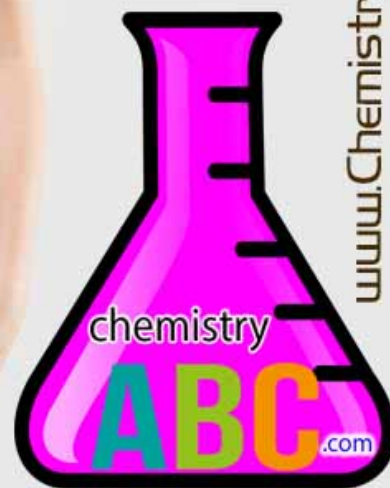
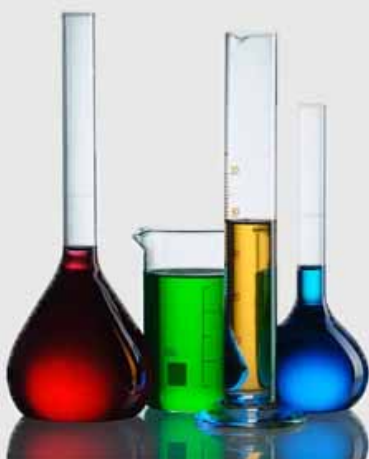
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PHILOSOPHY OF QUANTUM MECHANICS

The behavioral study of matter when it is in motion. Behavioral study means to determine the value of different observables such as position, momentum, kinetic energy, potential energy, total energy etc. If the study of matter is at macroscopic scale then it comes under the study of classical mechanics. Otherwise if it is at microscopic scale then it comes under the study of quantum mechanics.

Quantum mechanics is the study of describing, explaining and **predicting** behavior of matter at atomic and molecular level quantum mechanics. It is the theory that describes **the dynamics of matter at microscopic scale**. Theory is based on several statement called postulates. These postulates are assumed not proven. It may seem difficult to understand the entire model of electron atom and molecule is based on assumptions but the reason is simple because the statements based on these assumptions lead to **prediction** about atoms and molecules that agree with observation. With agreement between theory and experiment is so abundant, the unproven postulates are accepted and no longer questioned. The statement and equations based on these postulates agree with experiment and so constitute an appropriate model for the description of subatomic matter, especially electrons.

When we study the behaviour of matter at microscopic level or when Materials is reduced to the nanoscale can suddenly show very different properties compared to what they show on a macroscale. For instance, opaque substances become transparent (copper); inert materials become catalysts (platinum); stable materials turn combustible (aluminum); solids turn into liquids at room temperature (gold); insulators become conductors (silicon)

The Main idea is—

According to De Broglie every moving particle have wave nature. If mass is large, than it is difficult to associate wave nature in heavier particle. But if mass is small than it is very easy to observe wave properties if electron has the wave properties then there must be a wave function to describe the electron wave just as wave of light, sound and strings are described. This wave equation was purposed by Schrödinger and the role of this Schrodinger equation is analogous to that of Newton law in classical mechanics. The solution of wave equation is wave function. So behavior of electron may be described by wave function and it contains within it all possible information that can be known about the system. Wave function are not arbitrary mathematically wave functions but must satisfy certain simple conditions like as they must be continuous.

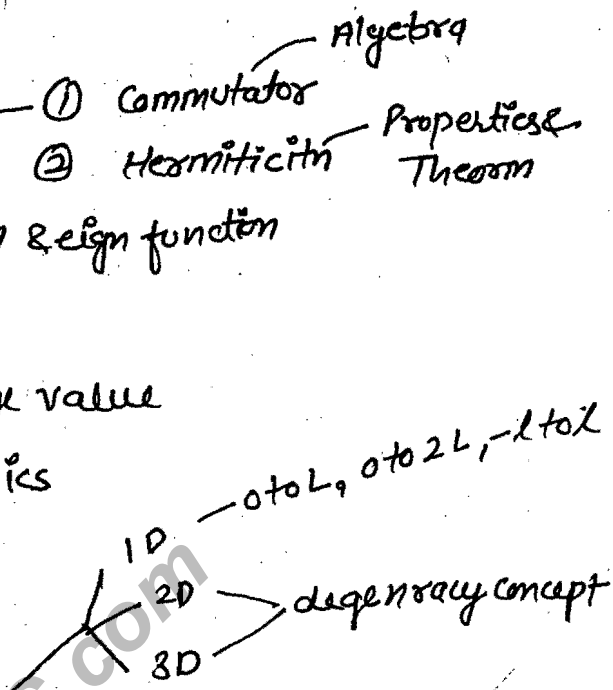
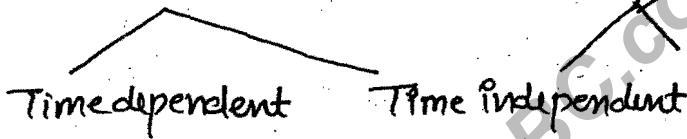
QUANTUM MECHANICS	CLASSICAL MECHANICS
Quantum mechanics is the theory that describe dynamics of matter at microscopic scale	Classical mechanics is the study of matter at macroscopic scale
It is invisible world	It is visible world.
Theory is based on assumptions called postulates. These postulates are unproven but accepted and no longer questioned. Eg. De Broglie and Schrodinger equation	Classical theory is well packaged theory Eg. Newton's mechanics Maxwell's electrodynamics Einstein's relativity
Observables can be determined by using interplay of wave function determined by wave equation and the operator defined for every observable is core area of studying quantum mechanics.	There are formulae to determine the value of observable in case of classical mechanics for every type of motion.



Quantum Mechanics

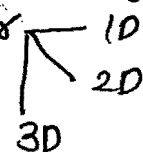
Unit-I

- ① Mathematics involved in quantum chemistry
- ② Operators & function
 - ↳ operator algebra
 - ① Commutator
 - ② Hermiticity
 - ↳ eigen value eqn & eigen function
- ③ Normalization & probability
- ④ Expectation value OR average value
- ⑤ Postulates of Quantum mechanics
- ⑥ Schrodinger eqn



⑦ Application of Schrodinger eqn

- ① Particle in-box
- ② Hydrogenic atom → Identification of wave function of Atoms
- ③ Simple Harmonic oscillator
- ④ Rigid rotor



- ⑧ Spin-angular momentum & orbital angular momentum
- ⑨ Potential barrier problem

↳ Concept of Tunneling

Unit-2

Approximation Method in Q.M (www.chemistryABC.com)

Perturbation method - 1st order perturbation

(Concept of Dirac delta function)

2nd order perturbation & its application

Variational principle & its application.

Unit-3

Atomic structure & spectroscopy -

Term Symbol $\left\{ \begin{array}{l} \text{Atomic} \\ \text{molecular} \end{array} \right.$

- selection rule corresponding to transition
- many e^- system
- Pauli Antisymmetry principle (Concept of spin)

Unit-4

Chemical Bonding in diatomic molecule

Quantum mech. treatment of MOT & VBT

Comparison of MOT & VBT

Huckel MO Theory & its applications to

Conjugated system & annulenes.

Mathematics Involved in Q.M. -

① Differentiation - (-ve)

$$\textcircled{1} \frac{d}{dx} x^n = nx^{n-1}$$

$$\textcircled{2} \frac{d}{dx} c = 0$$

$$\textcircled{3} \frac{d}{dx} cx^n = c \cdot \frac{d}{dx} x^n = cnx^{n-1}$$

$$\textcircled{4} \frac{d}{dx} f(x) \neq 0$$

$$\textcircled{5} \frac{d}{dx} \overset{\text{I}}{u(x)} \overset{\text{II}}{v(x)} = \overset{\text{I}}{u(x)} \frac{d}{dx} \overset{\text{II}}{v(x)} + \overset{\text{II}}{v(x)} \frac{d}{dx} \overset{\text{I}}{u(x)}$$

$$\textcircled{6} \frac{d}{dx} \overset{\text{-ve}}{\sin x} = \overset{\text{-ve}}{\cos x} \quad \begin{array}{l} -\text{ve} \times -\text{ve} = +\text{ve} \\ \begin{array}{|c|c|} \hline S & C \\ \hline 19 & 3 \end{array} \end{array}$$

$$\textcircled{7} \frac{d}{dx} \overset{\text{+ve}}{\cos x} = \overset{\text{-ve}}{-\sin x} \quad \begin{array}{l} -\text{ve} + \text{+ve} = -\text{ve} \\ \begin{array}{|c|c|} \hline C & S \\ \hline 3 & 19 \end{array} \end{array}$$

$$\textcircled{8} \frac{d}{dx} e^x = e^x$$

$$\begin{aligned} \textcircled{9} \frac{d}{dx} e^{ax} &= e^{ax} \frac{d}{dx} ax \\ &= e^{ax} a \cdot \frac{d}{dx} x \\ &= ae^{ax} \end{aligned}$$

$$\begin{aligned} \textcircled{10} \frac{d}{dx} e^{-ax^2} &= e^{-ax^2} \frac{d}{dx} (-ax^2) \\ &= e^{-ax^2} (-a) \frac{d}{dx} x^2 \\ &= -2ax e^{-ax^2} \end{aligned}$$

$$\textcircled{11} \frac{d}{dx} \sin ax = a \cos ax$$

$$\textcircled{12} \frac{d}{dx} \cos ax = -a \sin ax$$

Integration -

$$\textcircled{1} \quad \int x^n dx = \left[\frac{x^{n+1}}{n+1} \right]$$

$$\textcircled{2} \quad \int u(x)v(x) dx = \left[u(x) \int v(x) dx - \int \left[\frac{d}{dx} u(x) \int v(x) dx \right] dx \right]$$

$$\textcircled{3} \quad \int \sin x dx = -\cos x$$

$$\textcircled{4} \quad \int \cos x dx = \sin x$$

$$\textcircled{5} \quad \int \sin ax = -\frac{\cos ax}{a}$$

$$\textcircled{6} \quad \int \cos ax = \frac{\sin ax}{a}$$

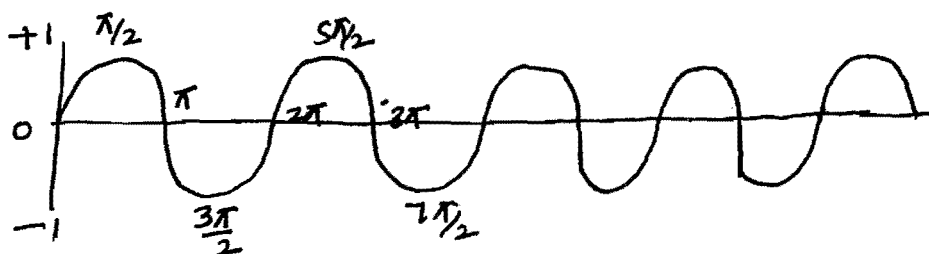
Trigonometry -

$$\textcircled{1} \quad \sin^2 \theta = \frac{1 - \cos 2\theta}{2}$$

$$\textcircled{2} \quad \cos^2 \theta = \frac{1 + \cos 2\theta}{2}$$

$$\textcircled{3} \quad \sin \theta \cos \theta = \frac{\sin 2\theta}{2}$$

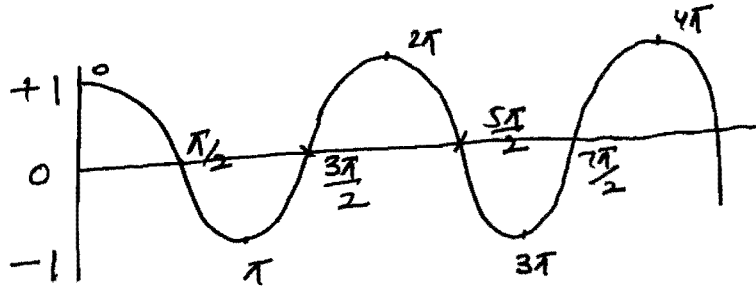
	0	30°	45°	60°	90°
Sin	0	1/2	1/√2	√3/2	1
cos	1	√3/2	1/2	1/√2	0



$$\sin\left(\frac{3\pi}{2}, \frac{7\pi}{2}, \dots\right) = -1$$

$$\sin(\pi, 2\pi, \dots, n\pi) = 0$$

$$\sin\left(\frac{\pi}{2}, \frac{5\pi}{2}, \frac{9\pi}{2}, \dots\right) = 1$$



$$\cos(0, 2\pi, 4\pi, \dots, n\pi) = 1$$

$$\cos n\pi = +1$$

n - even integer

$$\cos\left(\frac{\pi}{2}, \frac{3\pi}{2}, \frac{5\pi}{2}, \frac{7\pi}{2}, \dots\right) = 0$$

$$\cos n\pi = -1$$

n - odd integer

$$\cos(\pi, 3\pi, 5\pi, \dots) = -1$$

$$(4) \quad \sin(A+B) = \sin A \cos B + \cos A \sin B$$

$$(5) \quad \cos(A+B) = \cos A \cos B - \sin A \sin B$$

$$(6) \quad \int \sin^2 bx \, dx = \int \frac{1 - \cos 2bx}{2} \, dx = \frac{1}{2} [x] - \frac{1}{2} \left[\frac{\sin 2bx}{2b} \right]$$

$$= \frac{1}{2} [x] - \frac{1}{4b} [\sin 2bx]$$

$$(7) \quad \int \cos^2 bx \, dx = \int \frac{1 + \cos 2bx}{2} \, dx = \frac{1}{2} [x] + \frac{1}{4b} [\sin 2bx]$$

$$(8) \quad \int_{-l}^l \sin\left(\frac{n\pi}{l}x\right) \, dx \quad \frac{n\pi}{l} = b \Rightarrow l$$

$$\sin A \sin B = \frac{1}{2} [\cos(A-B) - \cos(A+B)]$$

Operator and function -

function is a rule that relates two or more variable

$$z = x^2 y$$

$$z = z(x, y)$$

z is a function of x & y

Operator is an entity that operates on a function and generate a new function or a constt. entity

To determine the value of operator or square of operator we need a function

(operator without a function is useless)

→ operator generally denoted by '∇'

eg- ① $\frac{d}{dx} x^2 = 2x$

↓ operator ↓ function → New function

② $\frac{d}{dx} x = 1$

↓ operator ↓ function ↓ Constt.

Basic characteristics of operator -

① operator are directional in nature i.e. have specific direction.

eg- $\frac{d}{dx} x^3 = 3x^2$

$$x^3 \frac{d}{dx} \neq 3x^2$$

(operator generally operates from the left side of the function (from the reverse side))

② nth power of operator means operator is operated n times.

$$\hat{A}^2 f(x) = \hat{A} \hat{A} f(x)$$

$$\left(\frac{d}{dx} + \hat{x}\right)^2 f(x) = \left(\frac{d}{dx} + \hat{x}\right) \left(\frac{d}{dx} + \hat{x}\right) f(x)$$

$$\left(\frac{d^2}{dx^2} + x^2 + 2\frac{d}{dx}x\right) \text{ (X)}$$

③ To every observable in classical mechanics there corresponds an operator in Q.M.

Observable	operator	operation
Position x y z	\hat{x} \hat{y} \hat{z}	multiplication
Momentum p_x p_y p_z	$\hat{p}_x = -i\hbar \frac{d}{dx}$ $\hat{p}_y = -i\hbar \frac{d}{dy}$ $\hat{p}_z = -i\hbar \frac{d}{dz}$	differentiation w.r.t. x and multiply by $-i\hbar$ OR $\frac{\hbar}{i}$ OR $\frac{h}{2\pi i}$
K.E. k_x k_y k_z	$k_x = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$ $k_y = -\frac{\hbar^2}{2m} \frac{d^2}{dy^2}$ $k_z = -\frac{\hbar^2}{2m} \frac{d^2}{dz^2}$	Double differentiation and multiply by $-\frac{\hbar^2}{2m}$
P.E. V_x V_y V_z	$\hat{V}_x = V_x$ $\hat{V}_y = V_y$ $\hat{V}_z = V_z$	multiplication

$$\hat{x} x^2 = x^3$$

$$\hat{x} f(x) = x f(x)$$

$$\hat{x} y f(x) = \hat{x} y f(x) = x y f(x)$$

$$\hat{p}_x = -i\hbar \frac{d}{dx}$$

$$= -\frac{i\hbar}{i} \frac{d}{dx}$$

$$= \frac{\hbar}{i} \frac{d}{dx}$$

$$= \frac{h}{2\pi i} \frac{d}{dx}$$

$$\hbar = \frac{h}{2\pi}$$

$$i^2 = -1$$

$$\hat{p}_x x^3 = -i\hbar \frac{d}{dx} x^3 = -i\hbar 3x^2 = -3i\hbar x^2$$

GATE-1995

Qus. - find \hat{A}^2 if $\hat{A} = x + \frac{d}{dx}$ operating on an arbitrary function $f(x)$

Solⁿ -

$$\hat{A}^2 f(x) = \hat{A} \hat{A} f(x)$$

$$= \left(x + \frac{d}{dx} \right) \left(x + \frac{d}{dx} \right) f(x)$$

$$= \left(x + \frac{d}{dx} \right) \left(x f(x) + \frac{d}{dx} f(x) \right)$$

$$= \left(x + \frac{d}{dx} \right) \left(x f(x) + \frac{df(x)}{dx} \right)$$

$$= x^2 f(x) + x \frac{df(x)}{dx} + f(x) + x \frac{df(x)}{dx} + \frac{d^2 f(x)}{dx^2}$$

$$\hat{A}^2 f(x) = x^2 f(x) + 2x \frac{df(x)}{dx} + f(x) + \frac{d^2 f(x)}{dx^2}$$

$$\left(x + \frac{d}{dx} \right)^2 = x^2 + 2x \frac{d}{dx} + \frac{d^2}{dx^2} + 1$$

Kinetic energy operator -

$$p_x = -i\hbar \frac{d}{dx}$$

$$p_y = -i\hbar \frac{d}{dy}$$

$$p_z = -i\hbar \frac{d}{dz}$$

$$K.E. = \frac{1}{2} m v^2$$

$$= \frac{p^2}{2m} \quad (\because p = mv)$$

$$K_x = \frac{p_x^2}{2m}$$

$$K_y = \frac{p_y^2}{2m}$$

$$K_z = \frac{p_z^2}{2m}$$

$$K_x = \frac{p_x^2}{2m} = \frac{\left(-i\hbar \frac{\partial}{\partial x}\right)^2}{2m} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \quad (\because i^2 = -1)$$

★ Potential energy operator -

P.E. is position dependent

∴ It will show multiplication operation

$$\hat{V}_x = V_x$$

$$\hat{V}_y = V_y$$

$$\hat{V}_z = V_z$$

★ Total Energy - (K.E. + P.E.)

$$\hat{H} = K.E. + P.E.$$

$$\hat{H}_x = K_x + V(x) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + V(x)$$

$$\hat{H}_y = K_y + V(y) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} + V(y)$$

$$\hat{H}_z = K_z + V(z) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} + V(z)$$

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

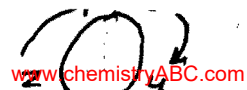
$$= -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + V(x) + V(y) + V(z)$$

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

↓
Hamiltonian operator

↓
Laplacian operator

* Representation of angular momentum operators -



$$\vec{L} = \vec{L}_x + \vec{L}_y + \vec{L}_z$$

$$\hat{L}_x = y p_z - z p_y = y \left(-i\hbar \frac{\partial}{\partial y} - z \left(-i\hbar \right) \frac{\partial}{\partial y} \right)$$

$$\hat{L}_y = z p_x - x p_z = -i\hbar \left[y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right]$$

$$\hat{L}_z = x p_y - y p_x$$

$$\vec{L} = -i\hbar \left[x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right]$$

$$\vec{L} = \vec{r} \times \vec{p}$$

$$\downarrow \quad \downarrow$$

$$(x, y, z) \quad (p_x, p_y, p_z)$$

$$\vec{L} = \vec{r} \times \vec{p}$$

$$= (x\hat{i} + y\hat{j} + z\hat{k}) \times (p_x\hat{i} + p_y\hat{j} + p_z\hat{k})$$

$$\begin{vmatrix} \hat{i} & \hat{j} & \hat{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix}$$

$$= \hat{i} [y p_z - z p_y] + \hat{j} [x p_z - z p_x] + \hat{k} [x p_y - y p_x]$$

$$\hat{i} (y p_z - z p_y) + \hat{j} (z p_x - x p_z) + \hat{k} (x p_y - y p_x)$$

$$L = L_x \hat{i} + L_y \hat{j} + L_z \hat{k}$$

Property of operators -

(4) Operators must be linear in Q.M.

$$(4) \hat{A}(f+g) = \hat{A}f + \hat{A}g$$

$$\frac{d}{dx} (4x^3) = \frac{d}{dx} (3x^3 + x^3) = \frac{d}{dx} 3x^3 + \frac{d}{dx} x^3$$

↓

$$12x^2$$

$$= 9x^2 + 3x^2$$

$$= 12x^2$$

④ ④) SQR - operator in non-linear differential operator is linear

$$\text{SQR}(7) = \text{SQR}(3+4)$$

$$49 \neq 25$$

(ii) $\hat{A} C f = C \hat{A} f \Rightarrow$ operator should not apply on Const.

$$\frac{d}{dx} 3x^2 = 3 \frac{d}{dx} x^2 = 3 \cdot 2x = 6x$$

$$\text{SQRT}(25x^2) = \pm 5x \quad \text{--- Non-linear}$$

⑤ * Commutator -

Commutator is a mathematical operation in which we interchange the position of operator, if after changing the position the value remains same then operator is called commute

If two operators commute then the observable corresponding to the operator may be determined simultaneously, if don't commute can't be determined. If two operators commute they violate ~~laeiq~~ heisenberg uncertainty principle.

$$[A, B] = \hat{A}\hat{B} - \hat{B}\hat{A}$$

$$\text{If } [A, B] = 0$$

OR

$$AB - BA = 0$$

OR

$$AB = BA$$

Then A & B are said to be commute.

If A & B commute, the observable for which operator is given may be determined simultaneously.

$$\text{If } [A, B] \neq 0$$

A & B are not commute

\Rightarrow follows Heisenberg uncertainty principle.

Qus - find the value of commutator

$$\left(x, \frac{d}{dx}\right)$$

Soln -

$$\hat{x} \frac{d}{dx} f(x) - \frac{d}{dx} x f(x)$$

we choose a wave function (arbitrary) $\psi(x)$ to determine value of commutator

$$\begin{aligned} \left(\hat{x}, \frac{d}{dx}\right) \psi(x) &= \hat{x} \frac{d}{dx} \psi(x) - \frac{d}{dx} \hat{x} \psi(x) \\ &= x \frac{d\psi(x)}{dx} - \frac{d}{dx} x \psi(x) \\ &= x \frac{d\psi(x)}{dx} - x \frac{d\psi(x)}{dx} - \psi(x) \end{aligned}$$

$$\left(x, \frac{d}{dx}\right) \psi(x) = -\psi(x)$$

$$\boxed{\left(x, \frac{d}{dx}\right) = -1}$$

operators don't commute

GATE-2008

The operation of commutator $\left(x, \frac{d}{dx}\right)$ on function $f(x)$ is

$$\left(\hat{x}, \frac{d}{dx}\right) = -f(x)$$

☆

$$\left(x, \frac{d}{dx}\right) = -1$$

$$\left(x^2, \frac{d}{dx}\right) = -2x$$

$$\left(x^3, \frac{d}{dx}\right) = -3x^2$$

⋮
⋮
⋮

$$\left(x^n, \frac{d}{dx}\right) = -nx^{n-1}$$

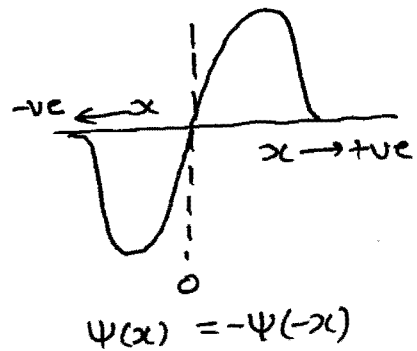
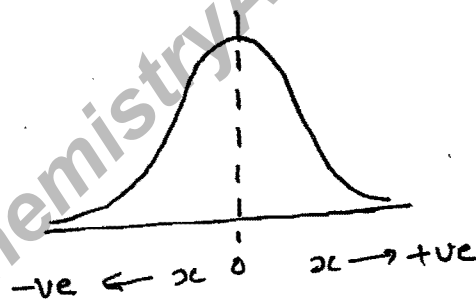
Imp.

Properties of commutator -

① Antisymmetric -

$$\psi(x) = \psi(-x) \quad \text{Symmetric}$$

$$\psi(x) = -\psi(-x) \quad \text{Antisymmetric}$$



In case of commutator -

$$[A, B] = -[B, A]$$

$$[A, B] = [AB - BA] = -[BA - AB]$$

$$= -[B, A]$$

$$\left[x^n, \frac{d}{dx} \right] = -nx^{n-1}$$

$$\left[\frac{d}{dx}, x^n \right] = nx^{n-1}$$

$$\Rightarrow \left[x^n, \frac{d}{dx} \right] = - \left[\frac{d}{dx}, x^n \right] = -nx^{n-1}$$

Commutator diff. नहीं होता परन्तु 1st derivative and position की कोई power, commutator के दौरान वही Result दिखाती है जो differentiation के दौरान दिखाती है।

$$[p_x, x^n]$$

$$\left[-i\hbar \frac{d}{dx}, x^n \right]$$

$$-i\hbar nx^{n-1}$$

$$[x^n, p_x] = i\hbar nx^{n-1} = -[p_x, x^n]$$

eg - $[x^3, p_x] = i\hbar 3x^2$

$$[p_x, x^3] = -i\hbar 3x^2$$

② Linearity -

$$[A, B+C] = [A, B] + [A, C]$$

$$[A+B, C+D] = [A, C] + [A, D] + [B, C] + [B, D]$$

$$[K(x), x]$$

$$[K(x) + U(x), x] = [K(x), x] + [U(x), x]$$

③ Distributivity -

$$[A, BC] = [A, B]C + B[A, C]$$

$$[A, B, C] = A[B, C] + [A, C]B$$

Qus- find the value of $[x, p_x^2]$

Soln $[x, p_x p_x] = p_x [p_x, x] + [p_x, x] p_x$

OR

$$[x, p_x] p_x + p_x [x, p_x]$$

$$= i\hbar p_x + p_x i\hbar$$

$$= 2i\hbar p_x$$

Qus- find the value of $[x, p_x^3]$

Soln

$$= 3i\hbar p_x^2$$

Similarly

$$[x, p_x^n] = n i\hbar p_x^{n-1}$$
$$= i\hbar n p_x^{n-1}$$

$$[x^n, p_x] = +i\hbar n x^{n-1}$$

$$[x, p_x^n] = +i\hbar n p_x^{n-1}$$

$$[p_x, x^n] = -i\hbar n x^{n-1}$$

$$[p_x^n, x] = -i\hbar n p_x^{n-1}$$

$$-i\hbar = \frac{\hbar}{i} = \frac{h}{2\pi i}$$

④ Operators commute with itself and with its power www.chemistryABC.com

$$[\hat{A}, \hat{A}] = 0$$

$$[\hat{A}, \hat{A}^2] = 0$$

$$\left[\frac{d}{dx}, \frac{d}{dx} \right] = 0$$

$$\left[\frac{d}{dx}, \frac{d^2}{dx^2} \right] = 0$$

$$\left[\frac{d}{dx}, 2 \frac{d}{dx} \right] = 0$$

DPP-1

⑤

$$[T_x, P_x]$$

$$\left[\frac{p_x^2}{2m}, p_x \right]$$

$$\frac{1}{2m} [p_x^2, p_x] = 0$$

[from property, ④]

④

(x, H_x)

DPP 1 Quantum chemistry

1. The value of A^2 [if $A = x - (d/dx)$] is

- a) $x^2 + (d^2/dx^2) - 2x(d/dx)$ (b) $(d^2/dx^2) - 2x(d/dx) + x^2 - 1$
 (c) $-(d^2/dx^2) - 2x(d/dx) + x^2 - 1$ (d) $x^2 + (d^2/dx^2) - 2x(d/dx) + 1$

2. The value of commutator (x^3, p_x) is equal to

GATE 2010

- (a) $-\frac{3h}{2\pi i}x^2$ (b) $-\frac{3ih}{2\pi}x^2$ (c) $\frac{hx}{2\pi i}$ (d) $\frac{h}{2\pi i}x^2$

3. Which of the following pairs of operator commute GATE 2006

- (a) x and (d/dx) (b) (d/dx) and $(d^2/dx^2) + 2(d/dx)$ (c) $x^2(d/dx)$ and (d^2/dx^2) (d) x^3 and (d/dx)

4. The value of commutator (x, H_x) is

- (a) $(h^2/4\pi^2m)(d^2/dx^2)$ (b) $(h^2/8\pi^2m)(d^2/dx^2)$ (c) $(h^2/4\pi^2m)(d^2/dx^2)$ (d) $-(h^2/8\pi^2m)(d^2/dx^2)$

5. The commutator of kinetic energy operator T_x and the momentum operator p_x for the one-dimensional case is CSIR JUNE 2014

- (a) $(ih/2\pi)$ (b) $(ih/2\pi)(d/dx)$ (c) 0 (d) $(ih/2\pi)x$

6. The value of commutator (x^2, p_x^2) is equal to

- (a) $(ih/2\pi)(xp_x + p_x x)$ (b) $(ih/\pi)(xp_x + p_x x)$ (c) 0 (d) $2ih/\pi$

7. Consider the statement

i) if A is linear operator then the value of $[A f(x)]^2 = A^2 f(x)$? F

ii) The value of commutator $[x, (x, p_x^2)]$ is equal to 0. F

iii) The multiplication of two linear operator is linear. T

iv) Square root is not linear but square is a linear operator F

The correct statements above are (a) i and iii (b) ii and iv (c) i, ii, iii (d) iii only (e) I only

8. Consider the statement

i) The commutator of d/dx with x is a unit operator T

ii) Differentiation and integration operator are linear because for being a linear operator $A\{C_1 f_1(x) + C_2 f_2(x)\} = C_1 A f_1(x) + C_2 A f_2(x)$ is the condition T

iii) Linear operator always commute with any number. T

The correct statement above are (a) I and ii (b) ii and iii (c) i, ii, iii (d) none

9. The value of $[x, p_y]$, $[p_x, p_y]$ respectively are (arbitrary function state function)

- (a) $0, 0$ (b) $0, \text{not zero}$ (c) $\text{not zero}, 0$ (d) $\text{not zero}, \text{not zero}$

10. The SQRT and SQR operator

Commutate (b) $\left(\frac{d}{dx}, \frac{d^2}{dx^2}\right) + \left(\frac{d}{dx}\right)$

$$\sqrt{x^4} = \sqrt{x^2 x^2}$$

$$\pm x^2 \neq x^2$$

Commute with each other do not commute with each other can not determine

11. Given 2 hermitian operator A and B we construct the following four operator AB, ABA, $i[A, B]$, $A^2 B$ Choose the correct option from below CSIRJRFNET

- a) All these 4 operators are Hermitian
- b) Only 3 of these are Hermitian
- Only 2 of these operators are Hermitian
- d) Only 1 of these operators is Hermitian

12) Identify which of the following operator is not Hermitian CSIRJRFNET

- a) $(h/2\pi i)(d/dx)$ $i(d^2/dx^2)$ (c) d^2/dx^2 (d) x^2

13) The value of commutator $[L_x, p_y]$ is

- (a) $(ih/2\pi)$ (b) $(ih/2\pi)x$ $(ih/2\pi)p_z$ (d) 0

14) The hermitian conjugate of d/dx is CSIRJRFNET

- $-d/dx$ (b) d/dx (c) x (d) 0

15) The degree of freedom which value depends on the volume of container is (MSQ)

- Translational (b) Rotational (c) vibrational (d) electronic

16) Consider the statement

i Hermitian operator always commute to each other. **F**

ii Hermitian operator have real eigenvalue always. **T**

iii Eigenfunction corresponding to hermitian operator are orthogonal. **F**

The correct statement above are (a) i, ii (b) ii, iii (c) I, iii ii only (e) iii only (f) none

17 Consider the statements

(i) If A is hermitian B is hermitian than $[AB+BA]$ is hermitian but $[AB-BA]$ is antihermitian. **T**

(ii) If A is hermitian B is hermitian $i[A+B]$ is antihermitian and $i[A-B]$ is hermitian. **F**

(iii) The multiplication of two commuting hermitian is hermitian. **T**

Which of the above statements is true (a) i (b) ii (c) i and ii i and iii (d) i, ii, iii

18) Uncertainty in the velocity of an electron if uncertainty in its position is 100 pm ism/sec **$5.25 \times 10^6 \text{ m/s}$**

19. When we operate the operator (d^2/dx^2) on $\cos ax + \sin ax$ than eign value is **$-a^2$**

20. when operator $/dx$ is operated on $100e^{5x}$ then eign value is **5**

⑤ Linear operator always commute with constant entity.

$$\begin{aligned} [\hat{A}, c] &= 0 = \hat{A}c\psi - c\hat{A}\psi \\ &= c\hat{A}\psi - c\hat{A}\psi \\ &= 0 \end{aligned}$$

eg.

$$\begin{aligned} [x_1, (x_1 p_x)] \\ \downarrow \\ [x_1, i\hbar] &\Rightarrow [x_1, i\hbar] = 0 \\ \downarrow \\ \text{constt} \end{aligned}$$

$$[x_1, (x_1^2 p_x)]$$

$$[x_1, i\hbar x]$$

$$i\hbar [x_1, x] = 0 \quad [\text{Prop. (4)}]$$

⑥ If both operator have the multiplication as the operation then they commute because multiplication itself commutative

$$[x, y]\psi(x, y) = xy\psi(x, y) - yx\psi(x, y)$$

$$\text{But } xy = yx$$

$$\therefore [x, y]\psi(x, y) = 0$$

eg.

$$[x, v(x)] = 0$$

Both have multiplication as operation.

$\times \rightarrow$ Anti-Commutate -

(Zetuu)

$$[A, B]_{+} = AB + BA = 0$$

\Rightarrow anticommutate

$$AB + BA \neq 0$$

\Rightarrow Not anticommutate

\rightarrow It is given by Arnold has

Qus- The operator $[x, (x, p_x^2)]$ is identical with-

(a) $[p_x, (x, p)]$

(b) $[x, p, (x, p)]$

(c) $-[p, (x^2, p)]$

(d) $[x, (x^2, p)]$

Solⁿ-

$$[x, (x, p_x^2)]$$

$$= [x, i\hbar 2px]$$

$$= 2i\hbar [x, px]$$

$$= 2i\hbar (i\hbar) = -2\hbar^2$$

(a) $[px, i\hbar] \rightarrow$ constt. $= 0$

(b) $[x, p, i\hbar] = 0$

(c) $-[p, (x^2, p)] = [p, 2i\hbar x]$

(d) $[x, +2i\hbar x] = 2i\hbar [x, x] = 0$

(1) $\dagger = \text{Transpose} \rightarrow *$

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$$(p_x)^\dagger = \left(-i\hbar \frac{d}{dx}\right)^\dagger$$

$$= (-i\hbar)^* \left(\frac{d}{dx}\right)^\dagger$$

$$= i\hbar \left(-\frac{d}{dx}\right)$$

$$= -i\hbar \frac{d}{dx}$$

\Rightarrow Hermitian

$$(K_{xc})^\dagger = \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2}\right)^*$$

$$= \left(-\frac{\hbar^2}{2m}\right)^* \left(\frac{d}{dx} \frac{d}{dx}\right)^\dagger$$

$$= -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$$

\Rightarrow Hermitian

$$\int \psi^* \hat{A} \psi d\tau = \int \psi \hat{A}^\dagger \psi d\tau$$

OR

$$\int f^* \hat{A} g d\tau = \int g \hat{A}^\dagger f d\tau$$

$$x \neq y \neq 0$$

$$x \neq p \neq 0$$

$$(x, px) = +i\hbar$$

$$= 2i\hbar [px, x]$$

$$= -2i\hbar [-i\hbar]$$

$$= -2\hbar^2$$

- ⑥ Operators used in Q.M. must be Hermitian.
 → Hermitian operator always gives real value or results
 → An operator \hat{A} said to be hermitian only when -

$$\int \psi^* \hat{A} \psi d\tau = \int \psi \hat{A}^* \psi^* d\tau$$

-OR-

$$\int g^* \hat{A} f d\tau = \int f \hat{A}^* g^* d\tau$$

* → complex conjugate

$$i \rightarrow -i$$

$$\psi = A + iB$$

$$\psi^* = A - iB$$

→ Show that operator \hat{p}_x is Hermitian

Solⁿ -

\hat{A} is Hermitian

$$\int \psi^* \hat{A} \psi d\tau = \int \psi \hat{A}^* \psi^* d\tau$$

If we have to show \hat{p}_x is hermitian

$$\int_{-\infty}^{+\infty} \psi^* \hat{p}_x \psi dx = \int_{-\infty}^{+\infty} \psi \hat{p}_x^* \psi^* dx$$

L.H.S -

$$\int \psi^* \left(-i\hbar \frac{\partial}{\partial x} \right) \psi dx$$

$$= -i\hbar \int_{-\infty}^{\infty} \psi^* \frac{d\psi}{dx} dx$$

$$= -i\hbar \left[(\psi^* \psi) \Big|_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty} \frac{d\psi^*}{dx} \psi dx \right]$$

$$= -i\hbar \left[(\psi^* \psi) \Big|_{-\infty}^{+\infty} - \int_{-\infty}^{\infty} \frac{d\psi^*}{dx} \psi dx \right]$$

$$= -i\hbar \left[0 - \int_{-\infty}^{\infty} \frac{d\psi^*}{dx} \psi dx \right] \quad \left[\text{function vanish at infinite} \right]$$

$$= i\hbar \int \frac{d\psi^*}{dx} \psi dx$$

R.H.S.

$$\int \psi \left(-i\hbar \frac{d}{dx}\right)^* \psi^* dx$$
$$= i\hbar \int \psi \frac{d\psi^*}{dx} dx$$

L.H.S = R.H.S

$\Rightarrow p_x$ is Hermitian

$$\left(\psi \psi^*\right)_{-\infty}^{\infty} = 0$$

$$(\psi)_{\infty} - (\psi)_{-\infty} \neq 0$$

function vanishes
at infinite

- OR - (In case of objective)

Hermitian adjoint - (Hermitian conjugate)

It is a mathematical operation that involve operation transpose and complex conjugate in it.

It is denoted by '†' (dagger)

By using Hermitian adjoint we can check Hermiticity of an operator.

$$\int g^* \hat{A} f d\tau = \int f \hat{A}^* g^* d\tau$$

$$\downarrow \oplus$$
$$\int f \hat{A} g^* d\tau$$

$$\downarrow *$$
$$\int f \hat{A}^* g^* d\tau$$

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Properties of Hermitian adjoint -

* Basic property

- ① $(A^T)^T = A$
- ② $(AB)^T = B^T A^T$
- ③ $(\alpha A)^T = \alpha^* A^T$
- ④ $(A+B)^T = A^T + B^T$
- ⑤ $(A^T)^n = (A^n)^T$
- ⑥ $\left(\frac{d}{dx}\right)^T = -\frac{d}{dx}$
- ⑦ $x^T = x$
- ⑧ $(A^T)^{-n} = (A^{-n})^T$

* Specific property

- (i) A is Hermitian only when
 $A^T = A$
- (ii) A is Anti-Hermitian only when
 $A^T = -A$

→ Show that \hat{p}_x is Hermitian

Soln-

$$\begin{aligned}(\hat{p}_x)^T &= p_x \\ \left(-i\hbar \frac{d}{dx}\right)^T &= (-i\hbar)^* \left(\frac{d}{dx}\right)^T \\ &= i\hbar \left(-\frac{d}{dx}\right) \\ &= -i\hbar \frac{d}{dx} \\ &= p_x\end{aligned}$$

⇒ \hat{p}_x is Hermitian

→ Show that \hat{k}_x is Hermitian

$$\begin{aligned}(\hat{k}_x)^T &= \left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2}\right)^T = \left(-\frac{\hbar^2}{2m}\right)^* \left(\frac{d^2}{dx^2}\right)^T \\ &= -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} = \hat{k}_x\end{aligned}$$

$$\begin{aligned} \textcircled{12} \quad (a) \quad \left(\frac{\hbar}{2\pi i} \frac{d}{dx} \right)^\dagger &= \left(\frac{\hbar}{2\pi i} \right)^\dagger \left(\frac{d}{dx} \right)^\dagger \\ &= -\frac{\hbar}{2\pi i} - \left(\frac{d}{dx} \right) \\ &= \frac{\hbar}{2\pi i} \end{aligned}$$

$$\begin{aligned} (b) \quad \left(i \frac{d^2}{dx^2} \right)^\dagger &= (i)^\dagger \left(\frac{d}{dx} \frac{d}{dx} \right)^\dagger \\ &= -i \frac{d^2}{dx^2} \end{aligned}$$

⑪

$$\begin{aligned} (AB)^\dagger &= B^\dagger A^\dagger \\ &= BA \end{aligned}$$

$$\begin{aligned} A^\dagger &= A \\ B^\dagger &= B \end{aligned} \quad \text{given}$$

$$(AB)^\dagger \neq AB \quad \Rightarrow \quad AB \text{ not Hermitian}$$

★ generally multiplication of two hermitian operators is not hermitian

multiplication is hermitian only when operators commute means multiplication of two commutative hermitian operator is hermitian.

$$\begin{aligned} (ABA)^\dagger &= A^\dagger B^\dagger A^\dagger \\ &= ABA \end{aligned}$$

\Rightarrow Hermitian

$$\begin{aligned} [i[A, B]]^\dagger &= i^\dagger [AB - BA]^\dagger \\ &= -i [(AB)^\dagger - (BA)^\dagger] = -i [BA - AB] \\ &= i [AB - BA] \\ &= i [A, B] \quad \textcircled{H} \end{aligned}$$

$$[A^2B]^T = [AAB]^T = B^T A^T A^T$$

$$= BAA$$

$$= [BA^2]$$

Not Hermitian

(17) (i) $(AB+BA)^T = (BA+AB)$ Hermitian

$(AB-BA)^T = (BA-AB)$ Not Hermitian

(ii) $(A+B)^T = A^T + B^T = A+B$ } Hermitian
 $(A-B)^T = A^T - B^T = A-B$ }

★ The commutator of two hermitian operators is anti-Hermitian

$$A = A^T$$

$$B^T = B$$

$$[AB-BA] \rightarrow \text{Antihermitian.}$$

★ The addition and subtraction of two hermitian operators is hermitian i.e. $(A+B)$ & $(A-B)$

★ $[A, B] = \text{Anti-Hermitian}$

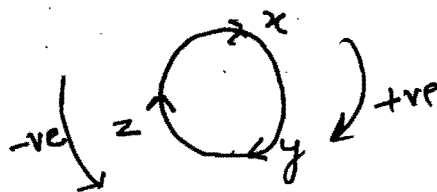
$i[A, B] = \text{Hermitian}$

$$\frac{d^2}{dx^2} = \text{Hermitian}$$

$$i \frac{d^2}{dx^2} = \text{Anti-Hermitian}$$



Commutators of Angular Momentum operators -



$$[L_x, x], [L_y, y], [L_z, z] = 0 \quad \& \quad [p_x, x], [p_y, y], [p_z, z] = -i\hbar$$

$$[L_y, y] = i\hbar z$$

$$[L_y, z] = i\hbar x$$

$$[L_z, x] = i\hbar y$$

$$[L_x, p_y] = i\hbar p_z$$

$$[L_y, p_z] = i\hbar p_x$$

$$[L_z, p_x] = i\hbar p_y$$

$$[L_x, L_y] = i\hbar L_z$$

$$[L_y, L_z] = i\hbar L_x$$

$$[L_z, L_x] = i\hbar L_y$$

One operator is angular momentum (L_x) and other is position (y) the resultant will be position (z)

One operator - mom (Ang) L_x

2nd, by momentum p_y
Result = momentum (p_z)

1st - Angular (L_x)
2nd - " (L_y)

Result = L_z (Angular)

$$[y, L_x] = -i\hbar z$$

$$[p_y, L_x] = -i\hbar p_z$$

$$[L_y, L_x] = -i\hbar L_z$$

Spin angular momentum -

$$(S_x, S_y) = i\hbar S_z$$

$$(S_y, S_z) = i\hbar S_x$$

$$(S_z, S_x) = i\hbar S_y$$

$$\begin{aligned}
 \star [L_x, x] \psi(x) &= L_x x \psi(x) - x L_x \psi(x) \\
 &= -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) x \psi(x) - x \left(-i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \psi(x) \right) \\
 &= 0
 \end{aligned}$$

$$\begin{aligned}
 \star [L_x, y] \psi(x, y) &= L_x y \psi(x, y) - y L_x \psi(x, y) \\
 &= -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) y \psi(x, y) - y \left[-i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \psi(x, y) \right] \\
 &= i\hbar z \frac{\partial}{\partial y} y \psi(x, y) - i\hbar z y \frac{\partial}{\partial y} \psi(x, y) \\
 &= i\hbar z \left[y \frac{\partial \psi(x, y)}{\partial y} + \psi(x, y) \frac{dy}{dy} \right] - i\hbar z y \frac{\partial \psi(x, y)}{\partial y} \\
 &= i\hbar z \left[y \frac{\partial \psi(x, y)}{\partial y} + \psi(x, y) \right] - i\hbar z y \frac{\partial \psi(x, y)}{\partial y} \\
 &= i\hbar z \left[\cancel{y \frac{\partial \psi(x, y)}{\partial y}} - y \frac{\partial \psi(x, y)}{\partial y} + \psi(x, y) \right]
 \end{aligned}$$

$$[L_x, y] \psi(x, y) = i\hbar z \psi(x, y)$$

$$\boxed{[L_x, y] = i\hbar z}$$

$$\star [L_x, p_y] = i\hbar p_z$$

$$\begin{aligned}
 [y p_z - z p_y, p_y] &= [y p_z, p_y] - [z p_y, p_y] \\
 &= [y, p_y] p_z + y [p_z, p_y] - [z, p_y] p_y \\
 &\quad - z [p_y, p_y]
 \end{aligned}$$

$$= 0 + i\hbar p_z + 0 - 0 - 0$$

$$\boxed{[L_x, p_y] = i\hbar p_z}$$

orbital angular momentum operators

$$L_+ = L_x + iL_y$$

$$L_- = L_x - iL_y$$

$$S_+ = S_x + iS_y \text{ - Spin raising operator}$$

$$S_- = S_x - iS_y \text{ } \left. \begin{array}{l} \downarrow \\ \text{Spin lowering} \\ \text{operator} \end{array} \right\}$$

NET

Qus. - The operator S_{\pm} is defined as $S_{\pm} = S_x \pm iS_y$

where S_x and S_y are component of spin angular momentum

$$[S_z, S_+] = ?$$

Soln

$$[S_z, S_x + iS_y]$$

$$= [S_z, S_x] + [S_z, iS_y]$$

$$= i\hbar S_y + i[S_z, S_y]$$

$$= i\hbar S_y + i(-i\hbar S_x)$$

$$= i\hbar S_y + \hbar S_x$$

$$= \hbar(S_x + iS_y)$$

$$\boxed{= \hbar S_+}$$

★

$$[S_+, S_-]$$

$$S_x + iS_y, S_x - iS_y$$

$$= \underbrace{[S_x, S_x]}_0 + [S_x, -iS_y] + \underbrace{[iS_y, S_y]}_0 + [iS_y, -iS_y]$$

$$\begin{aligned}
 &= -i[S_x, S_y] + i[S_y, S_x] \\
 &= -i[i\hbar S_z] + i[-i\hbar S_z] \\
 &= -i^2 \hbar S_z \\
 &= \hbar S_z
 \end{aligned}$$

★ Eigen value eqⁿ -

$$\hat{A}\psi = a\psi \rightarrow \text{eigen value}$$

↙ operators of eigen function (समान) ↘ eigen function

$$\frac{d}{dx} e^{ax} = a e^{ax} \rightarrow \text{eigen value}$$

↙ operator of eigen function ↘ eigen function

After the operation of an operator if function doesn't lose its identity, then it is known as eigen function, & the constt. value attached with function is called eigen value, the whole operation is called eigen value equation.

eg.

$$\frac{d^n}{dx^n} e^{ax} = a^n e^{ax} \rightarrow \text{eigen value}$$

↙ eigen function

It is one of the methods that is generally used to determine the value of observable by using operator of observable and function of motion.

example -

$$\begin{aligned} \frac{d^2}{dx^2} \sin ax &= \frac{d}{dx} \frac{d}{dx} \sin ax \\ &= \frac{d}{dx} a \cos ax \\ &= -a^2 \sin ax \end{aligned}$$

\downarrow
 operator of eigen function
 \downarrow
 eigen value

→ A function is not always an eigen function

eg-

$$\frac{d}{dx} \sin ax = a \cos ax \quad \text{not eigen function}$$

$$\frac{d^2}{dx^2} \sin ax = -a^2 \sin ax \quad \text{eigen function}$$

→ If any const. is attached with the eigen function it doesn't affect the eigen value.

eg. - $\frac{d}{dx} e^{5x} = 5 e^{5x}$

$$\frac{d}{dx} 100 e^{5x} = 5 \cdot 100 e^{5x}$$

$$\frac{d}{dx} 1000 e^{5x} = 5 \cdot 1000 e^{5x}$$

→ If const. is attached with operator, then it includes in eigen value

→ eg. $100 \frac{d}{dx} e^{5x} = 100 \cdot 5 e^{5x}$

$$= 500 e^{5x}$$

\downarrow
eigen value

DPP 2 Quantum Mechanics

1 Consider the statements

1) $(A+A^\dagger)$ is hermitian and $i(A-A^\dagger)$ is hermitian. **F**2) K_x, p_x and $K_x + p_x$ is hermitian operator. **T**3) e^{ax+b} is an eign function for an operator d/dx . **T**

The true statements above are (a) 1,2,3, (b) 2,3 (c) 1,2, (d) 2,3 (e) 3 (f) 1

2 Consider the statement

1) If ψ_1 and ψ_2 are the eignfunction of operator A with distinct eigenvalue than $c_1\psi_1 + c_2\psi_2$ is not an eign function of operator A. **T**2) The operator $L_x L_y + L_y L_x$ is Hermitian operator. **T**3) The operator $[x, (x, H)]$ is $-(\hbar^2/4\pi^2 m)$. **T** $L_x - \text{Hermitian}$
 $L_y - \text{Hermitian}$

$$L_x L_y + L_y L_x = H$$

The correct statement above are (a) 1,2 (b) 2,3 (c) 1,3 (d) 1,2,3

3. Consider the statements

1) Any two eignfunction of hermitian operator that belongs to different eigenvalue are orthogonal. **T**2) $-i(d/dx)$ is hermitian operator. **T**3) Commuting operator have common set of eignfunction. **T**

The correct statements above are (a) 1,2,3 (b) 2,3 (c) 1,3, (d) 3 only

5. $\{(-\hbar^2/8\pi^2 m)(d^2/dx^2) + (\hbar^2 \alpha^2 x^2)/2\pi^2 m\} e^{-\alpha x^2} = C(\hbar^2/4\pi^2) e^{-\alpha x^2}$ (\hbar, π, α, m constant), value of C is
(a) $2\alpha/m$ (b) $\alpha/2m$ (c) α/m (d) α^2/m IIT JAM6) 12 If an operator $\{(d^2/dx^2) - 16x^2\}$ is operated on an function e^{-2x^2} than corresponding eigenvalue is a) -2 b) -4 c) 2 d) 4 e) none IIT GATE7) The kinetic energy corresponding to given function $(1/L)^{0.5} \sin(\pi x/L)$ (for a particle in 1 D box of length $2L$ ($-L$ to $+L$)) is(a) $(\hbar^2 \pi^2 / 2ml^2)$ (b) $(\hbar^2 \pi^2 / ml^2)$ (c) $(\hbar^2 \pi^2 / 4ml^2)$ (d) $(\hbar^2 \pi^2 / 8ml^2)$ (e) none8) When the operator $-(\hbar^2/2m)(d^2/dx^2)$ operates on a function e^{-ikx} the result is
(a) $\hbar^2 k^2 e^{-ikx}$ (b) $i\hbar^2 k^2 e^{-ikx}$ (c) $i\hbar^2 e^{-ikx}$ (d) $\hbar^2 e^{-ikx}$ IIT GATE

9) Consider the statement regarding

1) Every function used in quantum mechanics should be an eignfunction. **F**2) The function $f=0$ is never allowed as eignfunction for a system. **T**3) All eignfunction of Hermitian operator must be real functions. **F**The correct statements above are (a) 1,2,3 (b) 2,3 (c) 1,3, (d) 1,2 **2**10) The value of $[x, p_x]$ is equal to(a) 0 (b) \hbar/i (c) $-i\hbar$ (d) \hbar/i

IIT JAM 2015

11) Consider the statements regarding operator ACSIR CHEM

i) The multiplication of operator A and its hermitian adjoint is always hermitian. **T**ii) The multiplication of operator A and its hermitian adjoint is nothermitian **F**iii) $AA^\dagger + A^\dagger A$ is hermitian but $AA^\dagger - A^\dagger A$ is anti hermitian **F**The correct statements above are (a) 1,2,3 (b) 2,3 (c) 1,3, (d) 1,2 **(c) 1**function can't be zero but
eigen value can be
zero
 $[x, L_x] = 0$

$AA^\dagger \rightarrow$ always Hermitian

12) If operator $A = -(d/dx) + x$ then **CSIR**

a) A is hermitian b) A is anti hermitian c) AA^\dagger is hermitian d) AA^\dagger is anti hermitian

13. Consider the statements

1. The normalization constant for function $e^{im\phi}$ of a rotating particle is $1/(2\pi)^{1/2}$. **T**

2. The normalized wave function is dimensionless. **T**

3. The probability of finding particle in 1 D box of length L between the limit 0 to L/3 in first excited state is 33%. **F**

The true statements above are (a) 1,2 (b) 1,2,3 (c) 1,3 (d) 1 only (e) 2 only (f) 3 only

14. Consider the statements

1. The normalization constant for a wave function $\sin\pi x$ between the limit 0 to 1 is $(2)^{1/2}$. **T**

2. The average value of momentum is 0 for a particle in 1 D box means, that momentum is 0.

3. Uncertainty in momentum for a particle in 1 d box of length l in ground state is $h/2l$. **T**

True statements above are (a) 1,2 (b) 2,3 (c) 1,3 (d) 1,2,3 (e) 1 only (f) 2 only (g) 3 only

15. Consider the statements

1. Larger the region of the box larger the uncertainty of finding the particle in the region.

2. The value of commutator $[L_y, p_z] = (ih/2\pi)p_x$ **T**

3. The average value of (momentum)² for a particle in 1 d box of length l is $n^2 h^2 / 4l^2$. **T**

Correct statements above are (a) 1,2 (b) 2,3 (c) 1,2,3 (d) 1 only (e) 2 only (f) 3 only

16. Consider the statement

1. If a function is normalized at $t=0$ it would be normalized at every time. **T**

2. For stationary state the probability density is independent of time but function is dependent on time. **T**

3. The complex conjugate and Hermitian adjoint of momentum operator give the same value. **F**

True statements above are (a) 1,2 (b) 2,3 (c) 1,3 (d) 1,2,3 (e) 1 only (f) 2 only (g) 3 only

17. Consider the statements

1. The uncertainty in kinetic energy for a particle in 1 d box of length is zero. **T**

2. The particle of mass m is confined to move in a 1d box of length 2 nm the uncertainty in position in ground state is independent of mass. **T**

3. The particle in 1 D box of length l have orthonormal set of wavefunction is orthonormal. **T**

True statements above are (a) 1,2 (b) 2,3 (c) 1,3 d) 1,2,3 (e) all (f) none (g) 1 (h) 2

18. For the particle in a box problem in (0,L), the value of $\langle x^3 \rangle$ in the $n \rightarrow \infty$ would be

a) $L^3/6$ (b) $L^3/3$ c) $L^3/4$ (d) $L^4/4$

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19) The angular momentum operator L_y would be

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a) $(-h/2\pi i)(y d/dz - z d/dy)$ b) $h/2\pi i(z d/dx - x d/dz)$ (c) $-ih/2m(d/dx)$ (d) none

20. The operator $S_\pm = S_x \pm iS_y$ Where S_x and S_y are components of spin angular momentum operator The commutator $[S_z, S_\pm]$ is

(a) $hS_\pm/2\pi$ (b) $hS_\pm/2\pi$ (c) $-hS_\pm/2\pi$ d) $-hS_\pm/2\pi$ (e) none

box $0 \rightarrow l$

$n \rightarrow \infty$

$$\langle x^n \rangle = \frac{1}{2} \int_0^l \frac{x^{n+1}}{n+1} dx$$

$$\langle x^3 \rangle = \frac{1}{2} \int_0^l \frac{x^4}{4} dx = \frac{1}{2} \left[\frac{x^4}{4} \right]_0^l$$

$$\frac{d}{dx^2} e^{-ax} = 4a^2 x^2 e^{-ax} - 2a e^{-ax}$$

DPP-2

⑥ $\left(\frac{d^2}{dx^2} - 16x^2\right) e^{-2x}$

$$= \frac{d^2}{dx^2} e^{-2x} - 16x^2 e^{-2x}$$

$$= 16x^2 e^{-2x} - 4e^{-2x} - 16x^2 e^{-2x}$$

$$= \boxed{-4} e^{-2x}$$

⑧ $-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} e^{-ikx}$

$$= -\frac{\hbar^2}{2m} \frac{d}{dx} \frac{d}{dx} e^{-ikx}$$

$$= -\frac{\hbar^2}{2m} \frac{d}{dx} (-ik e^{-ikx})$$

$$= \frac{\hbar^2}{2m} ik \frac{d}{dx} e^{-ikx}$$

$$= \frac{\hbar^2}{2m} ik (-ik e^{-ikx})$$

$$= \frac{\hbar^2}{2m} k^2 e^{-ikx}$$

⑤ $\left(-\frac{\hbar^2}{8\pi^2 m} \frac{d^2}{dx^2} + \frac{\hbar^2 \alpha^2 x^2}{2\pi^2 m}\right) e^{-\alpha x^2}$

$$-\frac{\hbar^2}{8\pi^2 m} \left[4\alpha^2 x^2 e^{-\alpha x^2} - 2\alpha e^{-\alpha x^2} \right] + \frac{\hbar^2 \alpha^2 x^2 e^{-\alpha x^2}}{2\pi^2 m}$$

$$-\frac{\hbar^2}{2\pi^2 m} \alpha^2 x^2 e^{-\alpha x^2} - \frac{\hbar^2 \alpha}{4\pi^2 m} e^{-\alpha x^2} + \frac{\hbar^2 \alpha^2 x^2 e^{-\alpha x^2}}{2\pi^2 m}$$

$$C(h^2/4\pi^2) e^{-\alpha x^2}$$

$$C = \frac{\alpha}{m}$$

$$(11) \quad (i) \quad (AA^\dagger)^\dagger = (A^\dagger)^\dagger A^\dagger \\ = AA^\dagger$$

$$(iii) \quad (AA^\dagger + A^\dagger A)^\dagger = (AA^\dagger)^\dagger + (A^\dagger A)^\dagger \\ = (A^\dagger)^\dagger A^\dagger + A^\dagger (A^\dagger)^\dagger \\ = AA^\dagger + A^\dagger A$$

$$(AA^\dagger - A^\dagger A)^\dagger = (AA^\dagger)^\dagger - (A^\dagger A)^\dagger \\ = AA^\dagger - \cancel{A^\dagger A} - \cancel{A^\dagger A} + A^\dagger A$$

(12)

$$A = -\frac{d}{dx} + x$$

$$(A)^\dagger = \frac{d}{dx} + x \quad \rightarrow \text{Not hermitian}$$

$$\left(-\frac{d}{dx} + x\right)^\dagger \left(\frac{d}{dx} + x\right)^\dagger = \left(-\frac{d}{dx} + x\right) \left(\frac{d}{dx} + x\right)$$

(20)

$$S_z = \frac{1}{2} \hbar \sigma_z$$

$$S_- = S_x - iS_y$$

$$[S_z, S_x - iS_y]$$

$$[S_z, S_x] - [S_z, -iS_y]$$

$$= i\hbar S_y - i[-i\hbar S_x]$$

$$= i\hbar S_y + \hbar S_x$$

★ Properties of Hermitian operator -

- ① Eigen value corresponding to Hermitian operator are always real.

Let us consider \hat{A} is an hermitian operator with eigen value

eqn
$$\hat{A}\psi = a\psi, \quad A^*\psi^* = a^*\psi^*$$

As \hat{A} is Hermitian

$$\int \psi^* A \psi d\tau = \int \psi A^* \psi^* d\tau$$

$$\int \psi^* a \psi d\tau = \int \psi a^* \psi^* d\tau$$

$$a \int \psi^* \psi d\tau = a^* \int \psi \psi^* d\tau$$

$$a = a^*$$

$\Rightarrow a$ is real

- ② Non-degenerate eigen function corresponding to Hermitian operator are orthogonal

Non-degenerate eigen function -

$$\hat{A}\psi_1 = a_1\psi_1$$

ψ_1 & ψ_2

$$\hat{A}\psi_2 = a_2\psi_2$$

are

non-degenerate

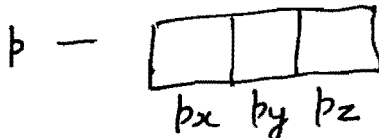
If $\hat{A}\psi_1 = a\psi_1$

ψ_1 & ψ_2

$$\hat{A}\psi_2 = a\psi_2$$

are degenerate function.

eg-



$$H\psi_{bx} = E\psi_{bx}$$

$$H\psi_{by} = E\psi_{by}$$

$$H\psi_{bz} = E\psi_{bz}$$

ψ_{bx} , ψ_{by} & ψ_{bz} are degenerate

→ Orthogonal -

function are vector quantity, then their dot product

is given by

$$\therefore \vec{\Psi}_1 \cdot \vec{\Psi}_2 = \Psi_1 \Psi_2 \cos \theta$$

$$\theta = 90^\circ \quad (\text{Orthogonal})$$

$$\vec{\Psi}_1 \cdot \vec{\Psi}_2 = 0$$

Two function Ψ_m & Ψ_n are said to be orthogonal only when

$$\int \Psi_m^* \Psi_n d\tau = 0$$

It may be conceptualized as functions are directional in nature & act as vector entity & two vector A & B are orthogonal only when

$$\vec{A} \cdot \vec{B} = 0$$

$$\vec{A} \cdot \vec{B} = AB \cos \theta$$

$$\theta = 90^\circ \quad (\text{for orthogonal})$$

$$\therefore \vec{A} \cdot \vec{B} = 0$$

UPSC

Let us consider two non-degenerate eigen function ~~the~~ corresponding to hermitian operator \hat{A} are Ψ_m & Ψ_n & the corresponding eigen values are a_m & a_n

$$\hat{A} \Psi_m = a_m \Psi_m$$

$$\Rightarrow a_m \neq a_n$$

$$\hat{A} \Psi_n = a_n \Psi_n$$

for Hermitian operators

$$\int \Psi_m^* \hat{A} \Psi_n d\tau = \int \Psi_n \hat{A}^* \Psi_m^* d\tau$$

$$\int \Psi_m^* a_n \Psi_n d\tau = \int \Psi_n a_m^* \Psi_m^* d\tau$$

$$a_n \int \psi_m^* \psi_n d\tau = a_m^* \int \psi_n \psi_m^* d\tau$$

$$a_n \int \psi_m^* \psi_n d\tau - a_m^* \int \psi_n \psi_m^* d\tau = 0$$

$$(a_n - a_m^*) \int \psi_m^* \psi_n d\tau = 0$$

But $a_n \neq a_m$

$$\therefore a_n - a_m^* \neq 0$$

$$\Rightarrow \int \psi_m^* \psi_n d\tau = 0$$

DPP-2

★

Sum of two degenerate eigen function is also a eigen function corresponding to same operator.

$$\hat{A} \psi_1 = a \psi_1$$

$$\hat{A} \psi_2 = a \psi_2$$

$$\hat{A} (\psi_1 + \psi_2) = a (\psi_1 + \psi_2)$$

→ But sum of two non-degenerate eigen function is not a eigen function.

$$\hat{A} \psi_1 = a_1 \psi_1$$

$$\hat{A} \psi_2 = a_2 \psi_2$$

$$\hat{A} (\psi_1 + \psi_2) = a_1 \psi_1 + a_2 \psi_2$$

③ (iii)

★ Two operators corresponding to same set of eigen ~~functi~~ ~~vect~~ function are commutative.

OR

Two commutative operators have common set of eigen function.

$$\hat{A} \psi_i = a_i \psi_i$$

$$\hat{B} \psi_i = b_i \psi_i$$

\hat{A} & \hat{B} are commutative

$$\hat{A} \hat{B} \psi_i = \hat{B} \hat{A} \psi_i$$

$$\hat{A} b_i \psi_i = \hat{B} a_i \psi_i$$

$$b_i \hat{A} \psi_i = a_i \hat{B} \psi_i$$

$$b_i a_i \psi_i = a_i b_i \psi_i$$

$$a_i b_i = b_i a_i$$

$$\Rightarrow \boxed{\psi_i = \psi_i}$$

$$\boxed{\text{LHS} = \text{RHS}}$$

$\Rightarrow \hat{A}$ & \hat{B} commute.

①

$$\left(\frac{1}{L}\right)^{0.5} \sin \frac{\pi x}{L}$$

$$K_x = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$$

$$-\frac{\hbar^2}{2m} \left(\frac{1}{L}\right)^{0.5} \frac{d^2}{dx^2} \sin \frac{\pi x}{L} \left[\frac{d^2}{dx^2} \sin ax = -a^2 \sin ax \right]$$

$$= -\frac{1}{\sqrt{L}} \frac{\hbar^2}{2m} \left(\frac{\pi}{L}\right)^2 \sin \frac{\pi x}{L}$$

$$= \left(\frac{\hbar^2 \pi^2}{2mL^2}\right) \left(\frac{1}{L}\right)^{0.5} \sin \frac{\pi x}{L}$$

③ A Real operator with multiplication as operation is always hermitian

eg- position - (x)

$$\int \psi^* x \psi d\tau = \int \psi x^* \psi^* d\tau$$
$$= \int \psi x \psi^* d\tau$$

- ④ The multiplication of two commutative hermitian operators is hermitian
- ⑤ The commutator of two hermitian operators is anti hermitian
- ⑥ Addition and subtraction of two hermitian operators is hermitian

★ Normalization & Probability -

Probability - Acc-to max Born interpretation of wavefunction the function doesn't determine the exact location of microscopic particle (e^-) during the motion in any system, it provides the probabilistic region in the form of mathematical expression

$$P = \int_a^b \psi^* \psi d\tau$$

a to b is desired region in which we have to determine the probability.

ψ is function. & ψ^* is complex conjugate.
 $d\tau$ is volume element

$d\tau$ for 1D = dx

for polar co-ordinates -

2D = $dx dy$

$$d\tau = r^2 dr \sin \theta d\theta d\phi$$

3D = $dx dy dz$

Normalization -

A function ψ is said to be normalized only when the probability of finding the particle over entire space of the system (for which function is determined) is equal to one

$$P = \int \psi^* \psi d\tau = 1$$

over entire
space.

If function is not normalized we have to make it Normalized.

Qus- Check that function $\psi(x) = x$ is normalized or not b/w the limit 0 to 1. If not normalized it.

Soln-

function $\psi(x)$ is normalized only when

$$= \int_0^1 \psi^*(x) \psi(x) dx = 1$$

$$= \int_0^1 x^* x dx$$

$$= \int_0^1 x^2 dx$$

$$\left[\frac{x^3}{3} \right]_0^1$$

$$= \left[\frac{1}{3} - 0 \right]$$

$$= \frac{1}{3} \neq 1 \quad \text{Not normalized}$$

★ How to Normalize -

$$\psi(x) = x$$

$$\int_0^1 \psi^* \psi dx = \frac{1}{3} \longrightarrow \frac{3}{1} \longrightarrow \sqrt{3}$$

Normalized -

$$\psi_{\text{norm}}(x) = \sqrt{3} x$$

$$\int_0^1 \sqrt{3} x \times \sqrt{3} x^* dx$$

$$= \int_0^1 3 x^2 dx$$

$$= 3 \left[\frac{x^3}{3} \right]_0^1$$

$$= 3 \left[\frac{1}{3} \right] = 1 \quad (\text{Normalized})$$

$$\int \psi \psi^* d\tau = 1$$

$$\int_0^1 \psi \psi dx = 1$$

Normalized $\longleftarrow \psi_n = N \psi_u \longrightarrow$ Unnormalized

\downarrow
Normalization Constant

$$\int_0^1 \psi_n \psi_n dx$$

$$\int_0^1 N \cdot \psi_u N \psi_u dx$$

$$N^2 \int_0^1 \psi_u \psi_u dx$$

$$N = \frac{1}{\sqrt{\int_0^1 \psi_u \psi_u dx}}$$

* To check a function OR To make a function normalized —

First of all we will determine $\int \psi^* \psi d\tau$
over entire space

if value is ① then it is Normalized

If it is not ① then whatever be the value of $\int \psi^* \psi d\tau$

we will reverse it and taking SQRT of the value and attach this value with the function.

$$\therefore N = \frac{1}{\sqrt{\int \psi \psi^* d\tau}}$$

Qus-1

Normalize the wave function -

$$\psi(x) = \sin \pi x$$

$$\int_0^1 \sin \pi x \sin \pi x dx$$
$$\int_0^1 \sin^2 \pi x dx$$

$$\sin^2 ax = \frac{1}{2} [x] - \frac{1}{4a} [\sin 2ax]$$

$$\frac{1}{2} [x]_0^1 - \frac{1}{4a} [\sin 2ax]_0^1$$

$$\frac{1}{2} [x]_0^1 - \frac{1}{4a} [\sin 2a - 0]$$

$$\frac{1}{2} - \frac{1}{4a} [\sin 2a]$$

$$= \frac{1}{2}$$

$$\psi_n(x) = \sqrt{2} \sin \pi x$$

② Normalize the wave function $\frac{1}{x}$ b/w the limit a to b

$$\psi(x) = \frac{1}{x}$$

$$\int_a^b \frac{1}{x} \cdot \frac{1}{x} dx$$

$$\int_a^b \frac{1}{x^2} dx$$

$$\left[-\frac{1}{x}\right]_a^b$$

$$= \left[-\frac{1}{b} + \frac{1}{a}\right] \neq 1$$

$$= \left[\frac{1}{a} - \frac{1}{b}\right]$$

$$= \frac{b-a}{ab}$$

$$\psi_n(x) = \sqrt{\frac{ab}{b-a}} \frac{1}{x}$$

③ Normalize the wave function $\psi(x) = \sin \frac{\pi x}{L}$ for a particle confined to a make in 0 to L

$$\psi(x) = \sin \frac{\pi x}{L}$$

$$\int_0^L \left(\sin \frac{\pi x}{L}\right)^2 \sin \frac{\pi x}{L} dx$$

$$= \int_0^L \sin^2 \frac{\pi x}{L} dx$$

$$= \frac{1}{2} [x]_0^L - \frac{L}{4\pi} \left[\sin 2\pi x\right]_0^L$$

$$= \frac{1}{2} [L-0] - \frac{L}{4\pi} \left[\sin \frac{2\pi}{L} L - \sin \frac{\pi}{L} 0\right]$$

$$= \frac{L}{2}$$

$$\psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{\pi x}{L}$$

$$\int \sin bx \cos bx \, dx = -\frac{1}{4b} [\cos 2bx]$$

$$\sin \theta \cos \theta = \frac{\sin 2\theta}{2}$$

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Qus.-

Normalize the wave function

$$\psi = \cos \frac{\pi x}{2l} \quad \text{b/w } -l \text{ to } l$$

$$\int \cos^2 bx \, dx = \frac{1}{2} [x] + \frac{1}{4b} [\sin 2bx]$$

$$\int \psi^* \psi \, d\tau = \int \cos \frac{\pi x}{2l} \cdot \cos \frac{\pi x}{2l} \, dx$$

Imp Qus - calculate the probability of finding the particle b/w 0 to $\frac{l}{4}$
 If particle is confined to move in 1D box of length 0 to l
 in ground state.

$$\psi_n = \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l}$$

$$P = \int \psi_n^* \psi_n \, d\tau$$

$$= \int_0^{\frac{l}{4}} \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l} \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l} \, dx$$

$$= \frac{2}{l} \int_0^{\frac{l}{4}} \sin^2 \frac{n\pi x}{l} \, dx$$

$$= \frac{2}{l} \left[\frac{1}{2} [x]_0^{\frac{l}{4}} - \frac{1}{4b} [\sin 2bx]_0^{\frac{l}{4}} \right]$$

$$\begin{aligned}
 & \frac{1}{2} \left[x \right]_{\frac{l}{4}}^{\frac{3l}{4}} - \frac{1}{2\pi b} \left[\sin^2 2bx \right]_{\frac{l}{4}}^{\frac{3l}{4}} \\
 &= \frac{1}{2} \left[\frac{l}{4} - 0 \right] - \frac{1}{2\pi b} \left[\sin^2 2b \frac{l}{4} \right] - \left[\sin^2 \frac{2b \cdot 0}{2} \right] \\
 &= \frac{l}{4} - \frac{1}{2\pi} \left[\sin^2 \frac{2\pi}{2} \times \frac{l}{4} \right] \\
 &= \frac{l}{4} - \frac{1}{2\pi} \left[\sin^2 \frac{\pi}{2} \right] \quad n=1
 \end{aligned}$$

$$P = \frac{l}{4} - \frac{1}{2\pi}$$

Setup a general expression to determine the probability within any region and for any state, of finding the particle that is confined to move in 1-D box of length l with normalized wave function

$$\psi = \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l} \quad (0 < x < l)$$

Solⁿ -

$$P = \int \psi_n^* \psi_n dx$$

$$P = \int \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l} \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l} dx$$

$$= \frac{2}{l} \int \sin^2 \frac{n\pi x}{l} dx$$

$$= \frac{2}{l} \left[\frac{x}{2} \right] - \frac{1}{4\pi} \left[\sin 2bx \right]$$

$$P = \frac{1}{2} \left[x \right] - \frac{1}{2\pi} \left[\sin \frac{2n\pi x}{l} \right]$$

$n=1$

$\frac{l}{4}$ to $\frac{3l}{4}$

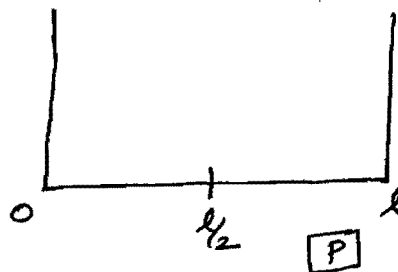
Put $n=1$ & limits in above result we obtained the desired result.

eg. - $\frac{1}{2} \left[x \right]_{\frac{l}{4}}^{\frac{3l}{4}} - \frac{1}{2 \times 1 \times \pi} \left[\sin \frac{2\pi}{l} x \right]_{\frac{l}{4}}^{\frac{3l}{4}}$

0 to $l/4$ $n=1$

$$\begin{aligned} & \frac{1}{2} [x]_0^{l/4} - \frac{1}{2\pi} \left[\sin \frac{2\pi x}{l} \right]_0^{l/4} \\ &= \frac{1}{2} \left[\frac{l}{4} \right] - \frac{1}{2\pi} \left[\sin \frac{2\pi x \times l}{l} \times \frac{l}{4} \right] \\ &= \frac{1}{2} \left[\frac{l}{4} \right] - \frac{1}{2\pi} \left[\sin \frac{\pi}{2} \right] \\ &= \frac{l}{4} - \frac{l}{2\pi} \end{aligned}$$

IMP. ★



① Left-half = 0 to $l/2$ = $\frac{l}{2}$ — 50%

② Right-half = $l/2$ to l = $\frac{l}{2}$ — 50%

③ Left quarter = 0 to $l/4$ \rightarrow $\frac{l}{4} - \frac{l}{2\pi}$

④ Right quarter = $3l/4$ to l \rightarrow $\frac{l}{4} - \frac{l}{2\pi}$ \rightarrow 0.09 \Rightarrow 9%

NET

⑤ middle half = $l/2 - l/2$ to $l/2 + l/2$
 $= \frac{l}{4}$ to $\frac{3l}{4}$ \rightarrow $\frac{l}{2} + \frac{l}{\pi} = 0.82 = 82\%$

⑥ middle $1/3$ rd = $\frac{l}{2} - \frac{l/3}{2}$ to $\frac{l}{2} + \frac{l/3}{2}$
 $l/3$ to $2l/3$ \rightarrow 60% $\frac{l}{3} + \frac{\sqrt{3}}{2\pi}$

⑦ middle quarter = $l/2 - \frac{l/4}{2}$ to $l/2 + \frac{l/4}{2}$
 $3l/8$ to $5l/8$ \rightarrow $\frac{l}{4} + \frac{l}{\sqrt{2}\pi} = 47\%$

⑧ left $1/3$ rd = 0 to $l/3$ \rightarrow 19.5%

⑨ Right one third ($1/3$) = $2l/3$ to l \rightarrow 19.5%

Calculate the probability of finding the particle in the ground state

between

(a) $-l/2$ to $0 = \frac{1}{4} + \frac{1}{2\pi}$

(b) 0 to $l/2 = \frac{1}{4} + \frac{1}{2\pi}$

(c) middle half of box $\Rightarrow -l/2$ to $l/2 = \frac{1}{2} + \frac{1}{\pi}$

for a particle confined to move in 1D box of length $-l$ to l with Normalized wave function

$$\Psi_n = \frac{1}{\sqrt{l}} \cos \frac{\pi x}{2l}$$

$$\frac{1}{l} \left[\frac{1}{2} [x] + \frac{1}{4b} [\sin 2bx] \right]$$

$$b = \frac{\pi}{2l}$$

★ Average value OR expectation value-

$$\langle M \rangle = \int \Psi^* \hat{M} \Psi d\tau$$

eg-

Translational momentum

$$\langle \text{momentum} \rangle = \int \Psi_{T_x}^* (\text{momentum}) \Psi_{T_x} d\tau$$

To determine the value of observable for any motion we operate the operator of observable on the function of motion & check that it follow eigen value eqn or not. If it follow then eigen value is considered as the value of observable

eg: Translational K.E. may be obtained by operating operator of K.E. on the wave function of translational motion (obtained from PIB model)

$$K_x \times \Psi_{T_x} = \text{eigenvalue } \Psi_{T_x}$$

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \left[\sqrt{\frac{2}{l}} \sin \frac{2n\pi x}{l} \right] = \frac{\hbar^2 \pi^2 n^2}{2ml^2} \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l}$$

↓
observable

value

If the operator of the observable and function of motion does not follow eigen value relationship then we use expectation value method to determine the value of observable by using operator of observable & function of motion. Observable value ($\langle M \rangle$) may be obtained as-

$$\langle M \rangle = \frac{\int \psi^* \hat{M} \psi d\tau}{\int \psi^* \psi d\tau}$$

If ψ is normalized

$$\int \psi^* \psi d\tau = 1$$

$$\langle M \rangle = \int \psi^* \hat{M} \psi d\tau$$

Qus. find the average value of x for wave function

$$\psi(x) = x$$

between the limit 0 to 1

$$\psi(x) = x$$

$$\psi_n(x) = \int_0^1 x dx = \frac{1}{3}$$

$$\psi_n(x) = \sqrt{3}x$$

$$\langle x \rangle = \int_0^1 \psi_n^* x \psi_n dx$$

$$= \int_0^1 \sqrt{3}x x \sqrt{3}x dx$$

$$= 3 \int_0^1 x^3 dx = 3 \left[\frac{x^4}{4} \right]_0^1 = \frac{3}{4}$$

It is conceptualised from the average value expression studied in elementary classes

$$\langle x \rangle = \frac{x_1 f_1 + x_2 f_2 + \dots}{f_1 + f_2 + \dots}$$

$$\frac{\sum x_i f_i}{\sum f_i}$$

$$\frac{\int x f dx}{\int f dx}$$

$$\langle x \rangle = \frac{\int f^* x f dx}{\int f^* f dx}$$

find the average value of $\langle x \rangle$, $\langle p_x \rangle$, $\langle x^2 \rangle$, $\langle p_x^2 \rangle$ for a particle confined to move in 1D box of length l with normalized wave function

$$\psi_n = \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l}$$

- (ii) By using above average value verify the Heisenberg uncertainty principle.
- (iii) Show that $\psi_n = \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l}$ is orthonormal set of wave function.

Soln-

$$\begin{aligned} \langle x \rangle &= \int \psi^* x \psi dx \\ &= \int_0^l \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l} x \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l} dx \\ &= \frac{2}{l} \int_0^l x \sin^2 \frac{n\pi x}{l} dx \\ &= \frac{2}{l} \int_0^l x \sin^2 \frac{n\pi x}{l} dx \\ &= \frac{2}{l} \times \frac{l^2}{4} = \frac{l}{2} \end{aligned}$$

Imp.

$$\langle x \rangle = \frac{l}{2}$$

$$\langle p_x \rangle = 0$$

$$\langle x^2 \rangle = \frac{l^2}{3} - \frac{l^2}{2n^2\pi^2}$$

$$\langle p_x^2 \rangle = \frac{n^2 h^2}{4l^2}$$

$$\langle K_x \rangle = \frac{h^2 \pi^2 n^2}{2ml^2}$$

$$\text{OR } \frac{h^2 h^2}{8ml^2}$$

$$\langle \hat{p}_x \rangle = \int_0^l \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l} \hat{p}_x \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l} dx$$

$$= \frac{2}{l} \int_0^l \sin \frac{n\pi x}{l} (-i\hbar \frac{d}{dx}) \sin \frac{n\pi x}{l} dx$$

$$= \frac{2}{l} (-i\hbar) \int_0^l \sin \frac{n\pi x}{l} \frac{d}{dx} \sin \frac{n\pi x}{l} dx$$

$$= \frac{2}{l} (-i\hbar) \int_0^l \sin bx \frac{d}{dx} \sin bx dx$$

$$= \frac{2}{l} (-i\hbar) \int_0^l \sin bx \cdot b \cos bx dx$$

$$= \frac{2}{l} (-i\hbar) b \int_0^l \sin bx \cos bx dx$$

$$= \frac{2}{l} (-i\hbar) b \left[-\frac{1}{4b} [\cos 2bx] \right]_0^l$$

$$= \frac{2}{l} (i\hbar) \times \frac{1}{4} [\cos 2bx]_0^l$$

$$= \frac{2}{4l} (i\hbar) [\cos 2 \frac{n\pi}{l} x]_0^l$$

$$= \frac{1}{2l} i\hbar \left[\cos 2 \frac{n\pi}{l} \times l - \cos 2 \frac{n\pi}{l} \times 0 \right]$$

$$= \frac{1}{2l} i\hbar [1-1]$$

$$\langle p_x \rangle = 0$$

$$b = \frac{n\pi}{l}$$

DPP 3 Quantum Mechanics

1. If an operator $\{(d^2/dx^2) - 16x^2\}$ is operated on an function e^{-2x^2} than corresponding eigenvalue is
 a) -2 b) -4 c) 2 d) 4 e) none **GATE EXAM**

2. When the operator $-(\hbar^2/2m)(d^2/dx^2)$ operates on a function e^{-ikx} the result is
 a) $\frac{\hbar^2 k^2}{2m} e^{-ikx}$ b) $i \frac{\hbar^2 k^2}{2m} e^{-ikx}$ c) $\frac{i \hbar^2 k^2}{2m} e^{-ikx}$ d) $\frac{\hbar^2 k^2}{2m} e^{-ikx}$ **IIT GATE**

3. Consider the statements regarding operator A

CSIR CHEM

i) The multiplication of operator A and its hermitian adjoint is always hermitian. **T**

ii) The multiplication of operator A and its hermitian adjoint is not hermitian **F**

iii) $AA^\dagger + A^\dagger A$ is hermitian but $AA^\dagger - A^\dagger A$ is anti hermitian **F**

The correct statements above are (a) 1,2,3 (b) 2,3 (c) 1,3, (d) 1,2 **C**

4. The angular momentum operator L_y would be

CSIRJRFNET

a) $(-h/2\pi i)(y d/dz - z d/dy)$ (b) $h/2\pi i(z d/dx - x d/dz)$ (c) $-ih/2m(d/dx)$ (d) none

5. The operator $S_\pm = S_x \pm iS_y$ Where S_x and S_y are components of spin angular momentum operator The commutator $[S_z, S_\pm]$ is

a) $\hbar S_\pm/2\pi$ (b) $\hbar S_\pm/2\pi$ (c) $-\hbar S_\pm/2\pi$ (d) $-\hbar S_\pm/2\pi$ (e) none

6. The value of $[x, (x, p_x)]$ is equal to **CSIR JRF**

a) $i\hbar/2\pi$ b) $-i\hbar/2\pi$ c) $i\hbar p_x$ d) 0

7. Consider the statement regarding

1) Every function used in quantum mechanics should be an eignfunction. **F**

2) The function $f=0$ is never allowed as eignfunction for a system. **T**

3) All eignfunction of Hermitian operator must be real functions. **F**

The correct statements above are (a) 1,2,3 (b) 2,3 (c) 1,3, (d) 1,2 **C**

8. Consider the statements

1. The normalization constant for a wave function $\sin \pi x$ between the limit 0 to 1 is $(2)^{-5}$. **T**

2. The average value of momentum is 0 for a particle in 1 D box means, that momentum is 0.

3. Uncertainty in momentum for a particle in 1 d box of length l in ground state is $h/2l$. **T**

True statements above are (a) 1,2 (b) 2,3 (c) 1,3 (d) 1,2,3 (e) 1 only (f) 2 only (g) 3 only

9. Consider the statements

1. The uncertainty in kinetic energy for a particle in 1 d box of length is zero. **T**

2. The particle in 1 D box of length l have orthonormal set of wavefunction **T**

3. The value of $[x, p_x]$ is equal to $i\hbar/2\pi$. **T**

True statements above are (a) 1,2 (b) 2,3 (c) 1,3 (d) 1,2,3 (e) 1 only (f) 2 only (g) 3 only

bcoz k.e. follow eigen value eqn \Rightarrow zero uncertainty

10. Consider the statement

1. If the wavefunction for system is an eignfunction of operator associated with observable A than $\langle A^n \rangle = \langle A \rangle^n$ **T**

2. The probability of finding the particle in 1 D box of length l within the middle half of the box in first excited state is 82%. **T**

3. The value of commutator $[L_x L_y, L_z]$ is $(i\hbar/2\pi)[L_x^2 - L_y^2]$. **T**

True statements above are (a) 1,2 (b) 2,3 (c) 1,3 (d) 1,2,3 (e) 1 only (f) 2 only (g) 3 only

$$(P+Q)(P-Q)$$

$$P^2 - Q^2$$

$$(\hat{P}+\hat{Q})(\hat{P}-\hat{Q})$$

$$\hat{P}\hat{P} - \hat{P}\hat{Q} + \hat{Q}\hat{P} - \hat{Q}\hat{Q}$$

$$\hat{P}^2 - \hat{P}\hat{Q} + \hat{Q}\hat{P} - \hat{Q}^2$$

11 Under what conditions do we find the same result of $(\hat{P} + \hat{Q})(\hat{P} - \hat{Q})$, as in the case of ordinary algebra ... $\hat{P}\hat{Q} = \hat{Q}\hat{P}$... CSIR JRF

12 Consider the statements

1. The normalization constant corresponding to wave function x between the limit 0 to 1 is $(3)^{0.5}$
2. The average value of x for a particle that is confined to move in 1D box (of length a to b) with wave function $1/x$ is $ab/4$
3. The average value of momentum for a particle that is confined to move in 1 d box of length l is zero, means momentum is zero. ?

True statements above are (a) 1,2 (b) 2,3 (c) 1,3 (d) 1,2,3 (e) 1 only (f) 2 only (g) 3 only

13 Consider the statements

1. Momentum and kinetic energy may be determined simultaneously but momentum and total energy can not be determined simultaneously. τ
2. The normalization constant for a particle that is confined to move in a box of length 800 nm is $0.2 \text{ (nm)}^{-1/2} = 0.05 \text{ (nm)}^{-1/2}$
3. A wave function becomes zero at infinite. τ

True statements above are (a) 1,2 (b) 2,3 (c) 1,3 (d) 1,2,3 (e) 1 only (f) 2 only (g) 3 only

14 The wavefunction for a quantum mechanical particle in a 1 dimensional box of length 'a' is given by $\psi = A \sin(\pi x/a)$. The value of A for a box of length 200 nm is IIT GATE

- (1) $4 \times 10^4 \text{ (nm)}^2$ (2) $10\sqrt{2} \text{ (nm)}^{1/2}$ (3) $\sqrt{2}/10 \text{ nm}^{-1/2}$ (4) $0.1 \text{ nm}^{-1/2}$

15 Suppose, the ground stationary state of a harmonic oscillator with force constant 'k' is given $\Psi_0 = \exp[-Ax^2]$ Then, A should depend on k as CSIR JRF

- (a) $A \propto k^{-1/2}$ (b) $A \propto k$ (c) $A \propto k^{1/2}$ (d) $A \propto k^{1/3}$

16 The probability of finding the particle in a one dimensional box of length 'L' in the region between $\frac{L}{4}$ and $\frac{3L}{4}$ for quantum number $n=1$ is CSIR JRF

- (a) $\frac{1}{2}$ (b) $\frac{1}{2} + \frac{1}{\pi}$ (c) $\frac{1}{2} - \frac{1}{\pi}$ (d) $\frac{2}{3}$

17 For any operator A and its adjoint A^\dagger , the INCORRECT statement is:

- (a) AA^\dagger is hermitian (b) $AA^\dagger + A^\dagger A$ is hermitian CSIR JRF
 (c) $A + A^\dagger$ is hermitian (d) $A - A^\dagger$ is hermitian

18 Fill in the blanks

1. The average value of x in the ground state for a particle that is confined to move in a one d box of length $-l$ to l is ... 0 ...

2. The uncertainty in position may be considered as deviation in position then expression of uncertainty in position is ... $\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$...

3. The uncertainty in position for a particle that is confined to move in 1 d box of length 2 nm is ... 0.36 ...

4. The normalization constant corresponding to wavefunction $\psi = \sin(\pi x/2a)$ between the limit $-a$ to a is ... $\frac{1}{\sqrt{a}}$...

$$\Delta x \Delta p_x \geq \frac{h}{4\pi} \quad \text{OR} \geq \frac{h}{2} \quad \text{OR} \geq 0.5h$$

$$\langle x \rangle = \frac{l}{2}$$

$$\langle x^2 \rangle = \frac{l^2}{3} - \frac{l^2}{2n^2\pi^2}$$

$$\langle p_x \rangle = 0$$

$$\langle p_x^2 \rangle = \frac{n^2 h^2 \pi^2}{l^2} = \frac{n^2 h^2}{4l^2}$$

$$\Delta M = \sqrt{\langle M^2 \rangle - \langle M \rangle^2}$$

ΔM → deviation

$$\Delta p_x = \sqrt{\langle p_x^2 \rangle - \langle p_x \rangle^2}$$

$$= \sqrt{\frac{n^2 \pi^2 h^2}{4l^2} - 0}$$

for $n=1$

$$= \frac{n\pi h}{2l}$$

$$\Delta p_x = \frac{\pi h}{2l}$$

Uncertainty in ~~position~~ momentum

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$$

$$= \sqrt{\frac{l^2}{3} - \frac{l^2}{2n^2\pi^2} - \frac{l^2}{4}}$$

$$= \sqrt{\frac{l^2}{12} - \frac{l^2}{2n^2\pi^2}}$$

Δx for $n=1$

$$\Delta x = l \sqrt{\frac{1}{12} - \frac{1}{2\pi^2}}$$

Uncertainty in ~~position~~ position

$$\Delta x \cdot \Delta p_x = \frac{\pi h}{2l} \times l \sqrt{\frac{1}{12} - \frac{1}{2\pi^2}} = 0.57h > 0.50h$$

$$\therefore \Delta x \cdot \Delta p_x \geq 0.50h$$

Postulates of Quantum mechanics -

① The state of a quantum mechanical system is completely specified by function $\psi(x,t)$ that depends on co-ordinate of the particle and on the time, this function is called state function OR wave function has the important property i.e.

$$\psi^*(x,t) \psi(x,t) dt$$

that the particle lies in volume element dt located at x at time t

function $\psi(x,t)$ is consisting of two part $\psi(x)$ & $\psi(t)$

The value of $\psi(x)$ is generally obtained by time independent schrodinger eqn & the value of $\psi(t)$ is obtained by using postulate ⑤ that describe the change in value of function w.r.t time.

② To every observable in classical mechanics there corresponds a quantum mechanical linear hermitian operator.

classical mechanics deals with quantity called dynamic variable such as position, momentum, angular momentum, energy.

A measurable dynamic variable is called observable

There is one-to-one relationship b/w operator and observable.

③ In any measurement of the observable associated with operator \hat{A} the only value that will be observed are eigen value, which satisfy the relation

$$\hat{A}\psi = a\psi$$

In postulate ① it is not mention that a system must be in a state described by an eigen function

Any well behaved function is a possible wave function

If we determine the value of energy of system that is in a state described by ψ that is not eigen function of H ?

Our observed value will be one of the value E_n which one of it will be can't be predicted with certainty

"If ψ is the som of schrodinger eqn $H\psi = E\psi$ then for exactly solvable system ψ is always eigen function corresponding to H .

④ If a system is in a state described by a normalized wave function ψ , then the average value of observable value corresponding to operator \hat{A} is

$$\langle x \rangle = \int \psi^* \hat{x} \psi d\tau$$

If an operator of observable & eqn of motion function follow eigen value eqn, then the value obtained by eigen function & OR obtained by average value method is always same.

⑤ Wave function or state function of a system evolve in time according to time dependent schrodinger wave eqn

$$\hat{H}\psi = i\hbar \frac{d}{dt} \psi$$

$$\hat{H}\psi = E\psi$$

$$i\hbar \frac{d}{dt} \psi = E\psi$$

$$\frac{d}{dt} \psi = \frac{E}{i\hbar} \psi$$

$$\int \frac{d\psi}{\psi} = \int \frac{E}{i\hbar} dt$$

$$\ln \psi = \frac{E}{i\hbar} t$$

$$\psi = e^{\frac{Et}{i\hbar}}$$

$$\psi(t) = e^{-iEt/\hbar}$$

$$\psi = \psi(x) \psi(t)$$

$$\psi_T = \psi(x) e^{-iEt/\hbar}$$

→ Probability density is time independent

$$\text{Probability density} = \psi_T^* \psi_T$$

$$= (\psi(x) e^{-iEt/\hbar})^* \psi(x) e^{-iEt/\hbar}$$

$$= \psi(x)^* e^{iEt/\hbar} e^{-iEt/\hbar} \psi(x)$$

$$= \psi(x)^* \psi(x)$$

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Function corresponding to stationary state is time dependent and probability corresponding to stationary state is time independent.

If function is normalized at $t=0$ it remains normalized at every time. The value of observable is also time independent

If node corresponding to wave changing with time - Travelling wave
 If node corresponding to wave is not changing with time - Stationary wave

Q.M. treatment of Schrodinger equation -

Schrodinger eqn is the eigen value eqn of energy means the eigen value eqn in which eigen value is energy and operator is Hamiltonian.

$$\hat{H}\psi = E\psi$$

$$H = K + V$$

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V$$

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V \right) \psi = E\psi$$

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

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

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = (E - V)\psi$$

$$\nabla^2 \psi = -\frac{2m}{\hbar^2} (E - V)\psi$$

$$\nabla^2 \psi + \frac{2m}{\hbar^2} (E - V) \psi = 0$$

↓
laplacian operator

$$\nabla^2 = \frac{d^2}{dx^2} \quad - \text{1D Cartesian}$$

$$\nabla^2 = \frac{d^2}{dx^2} + \frac{d^2}{dy^2} \quad - \text{2D "}$$

$$\nabla^2 = \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2} \quad - \text{3D "}$$

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Motion	Model	Limit	function	dE	n States	Energy
Translational Motion	Particle in Box	0 to L	$\psi = \sqrt{\frac{2}{L}} \sin n\pi x$	dx	n = 1	$E = \frac{n^2 h^2}{8mL^2}$
Vibrational Motion	Simple Harmonic Oscillator	$-\infty$ to ∞	$\psi_0 = \left(\frac{B}{\pi}\right)^{1/4} e^{-Bx^2/2}$ $B = \sqrt{\frac{mk}{\hbar}}$	dx	n = 0	$E = (n + \frac{1}{2}) h\nu$
Electronic Motion	Hydrogen atom	0 to ∞ 0 - ∞ 0 - π 0 - 2π	$\psi_{1s} = \frac{1}{\sqrt{\pi}} a_0^{3/2} e^{-r/a_0}$ $a_0 = \text{Bohr radius}$ $= \frac{4\pi \epsilon_0 \hbar^2}{me^2}$ $a_0 = 0.529 \text{ \AA}$	$0 < r < \infty$ $0 < \theta < \pi$ $0 < \phi < 2\pi$	n = 1	$E = -\frac{e^2}{8\pi\epsilon_0 a_0} \cdot \frac{Z^2}{n^2}$ $= -13.6 \frac{Z^2}{n^2} \text{ eV}$
Rotational Motion (Particle in ring)	Rigid rotor	0 to 2π	$\psi = \frac{1}{\sqrt{2\pi}} e^{im\phi}$	$0 < \phi < 2\pi$	m = 0	$E = BJ(J+1)$ $B = \frac{\hbar^2}{8\pi^2 I}$ $I = \mu R^2$

$$\int_0^{\pi} \sin^3 \theta d\theta = \frac{4}{3}, \quad \int_0^{\pi} \sin^2 \theta \cos^2 \theta d\theta = \frac{2}{3} \quad \text{www.chemistryABC.com}$$

★ Show that ψ_{1s} is normalized. $\psi_{1s} = \frac{1}{\sqrt{\pi}a_0^{3/2}} e^{-r/a_0}$

ψ_{1s} is normalized only when $\int \psi_{1s}^* \psi_{1s} d\tau = 1$

$$\int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} \frac{1}{\sqrt{\pi}a_0^{3/2}} e^{-r/a_0} \cdot \frac{1}{\sqrt{\pi}a_0^{3/2}} e^{-r/a_0} r^2 dr \sin \theta d\theta d\phi$$

$$\frac{1}{\pi a_0^3} \int_0^{\infty} e^{-r/a_0} e^{-r/a_0} r^2 dr \int_0^{\pi} \sin \theta d\theta \int_0^{2\pi} d\phi$$

(I) (II) (III)

$$\int_0^{\infty} r^2 e^{-2r/a_0} dr = \frac{n!}{(\alpha)^{n+1}} \quad \left[\begin{array}{l} n = \text{power of } r \\ \alpha = \text{power of } e \text{ excluding } (-r) \end{array} \right]$$

$$\int_0^{\pi} \sin \theta d\theta = -[\cos \theta]_0^{\pi} = -[-1 - 1] = 2$$

$$\int_0^{2\pi} d\phi = (\phi)_0^{2\pi} = 2\pi$$

$$\Rightarrow \frac{1}{\pi a_0^3} \times 4\pi \times \frac{2!}{\left(\frac{2}{a_0}\right)^{2+1}} = \frac{4}{a_0^3} \times \frac{2}{8} a_0^3 = 1$$

Qus. ★ Normalize the wave function e^{-r} for an e^- in $1s$ orbital of H-atom. and find the average value of r & r^2

Soln-

$$\int \psi \psi^* d\tau$$

$$\int_0^{\infty} e^{-r} e^{-r} r^2 dr \int_0^{\pi} \sin \theta d\theta \int_0^{2\pi} d\theta = 4\pi$$

$$4\pi \int_0^{\infty} r^2 e^{-2r} dr = 4\pi \times \frac{2!}{(2)^{2+1}} = 4\pi \times \frac{2}{8} = \pi$$

$$\psi_n(r) = \frac{1}{\sqrt{\pi}} e^{-r}$$

$$\begin{aligned} \langle r \rangle &= \int \psi_n^* r \psi_n d\tau \\ &= \int_0^{\infty} \frac{1}{\sqrt{\pi}} e^{-r} r \frac{1}{\sqrt{\pi}} e^{-r} r^2 dr \cdot 4\pi \\ &= \frac{4\pi}{\pi} \int_0^{\infty} r^3 e^{-2r} dr \\ &= \frac{4\pi}{\pi} \cdot \frac{3!}{(2)^{3+1}} \\ &= \frac{4\pi}{\pi} \frac{8 \times 2 \times 1}{16} \\ &= \frac{24}{16} = \frac{3}{2} \end{aligned}$$

$$\langle r \rangle = \frac{3}{2}$$

$$\langle r^2 \rangle = 3$$

$$\langle r^2 \rangle = 4 \int r^4 e^{-2r} dr = 3$$

★ If angular part also present in function

★ When we move from cartesian co-ordinate to polar co-ordinate then several changes takes place in the value of operator of observable & function of motion.

To study translational & vibrational motion we use Cartesian co-ordinate & to study rotational & electronic we use polar co-ordinates

x	r	$r \sin \theta \cos \phi$
y	r	$r \sin \theta \sin \phi$
z	r	$r \cos \theta$
p_x	$-i\hbar \frac{d}{dx}$	$p_x = -i\hbar \left(\frac{d}{dx} + \frac{1}{r} \right)$
K_x	$-\frac{\hbar^2}{2m} \nabla^2$ $= -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$	$K = -\frac{\hbar^2}{2m} \nabla^2$ $= -\frac{\hbar^2}{2m} \left[\frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} + \frac{1}{r^2 \sin \theta} \frac{d}{d\theta} \sin \theta \left(\frac{d}{d\phi} + \frac{1}{r^2 \sin^2 \theta} \frac{d^2}{d\phi^2} \right) \right]$
$V(x)$	$V(r)$ $(Tr) V = 0$ $(lib) V = \frac{1}{2} k r^2$	$V = -\frac{e^2}{4\pi\epsilon_0 r}$

$e^{-r} \sin \theta$

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} e^{-r} \sin \theta e^{-r} \sin \theta r^2 dr \sin \theta d\theta d\phi$$

$$\int_0^\infty r^2 e^{-2r} dr \int_0^\pi \sin^3 \theta d\theta \int_0^{2\pi} d\phi$$

\downarrow \downarrow \downarrow
 $\frac{n!}{(\alpha)^{n+1}}$ $\frac{4}{3}$ 2π

$e^{-r} \cos \theta$

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} e^{-r} \cos \theta e^{-r} \cos \theta r^2 dr \sin \theta d\theta d\phi$$

$$\int_0^\infty r^2 e^{-2r} dr \int_0^\pi \cos^2 \theta \sin \theta d\theta \int_0^{2\pi} d\phi$$

\downarrow \downarrow \downarrow
 $\frac{n!}{(\alpha)^{n+1}}$ $\frac{2}{3}$ 2π

★ find the average value of $\langle r \rangle$, $\langle r^2 \rangle$, $\langle \frac{1}{r} \rangle$, $\langle \frac{1}{r^2} \rangle$, $\langle \frac{1}{r^3} \rangle$, $\langle K \rangle$, $\langle V \rangle$ for an ψ in 1s orbital of H-atom.

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} a_0^{-3/2} e^{-r/a_0} \quad a_0 = \frac{4\pi\epsilon_0 \hbar^2}{me^2}, \quad a_0 = 0.529 \text{ \AA}$$

IMP Verify the virial theorem by using above result in case of H atom

$$\langle K \rangle = \frac{1}{2} \langle \text{Potential energy} \rangle$$

$$K = -\frac{1}{2} \langle V \rangle$$

OR

$$\langle T \rangle = -\frac{1}{2} \langle V \rangle$$

$$\langle r \rangle = \int_0^{\infty} \int_0^{\pi} \int_0^{2\pi} \frac{1}{\sqrt{\pi}} a_0^{-3/2} e^{-r/a_0} r \cdot \frac{1}{\sqrt{\pi}} a_0^{-3/2} r^2 dr \int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} d\phi$$

$$= \frac{1}{\pi a_0^3} \int_0^{\infty} r^3 e^{-2r/a_0} dr \cdot 4\pi$$

$$= \frac{4\pi}{\pi a_0^3} \int_0^{\infty} r^3 e^{-2r/a_0} dr \quad \begin{matrix} n=3 \\ \alpha = 2/a_0 \end{matrix}$$

$$= \frac{4}{a_0^3} \times \frac{3!}{\left(\frac{2}{a_0}\right)^{3+1}} = \frac{4}{a_0^3} \times \frac{3 \times 2 \times 1 \times a_0^4}{8} = \frac{3}{2} a_0$$

$$\langle r \rangle = \frac{3}{2} a_0$$

In the very same way

$$\langle r^2 \rangle = 3a_0^2$$

$$\langle p_r \rangle = \int_0^\infty \int_0^\pi \int_0^{2\pi} \frac{1}{\sqrt{\pi} a_0^{3/2}} e^{-r/a_0} \frac{1}{r} e^{-r/a_0} r^2 dr \sin\theta d\theta d\phi$$

$$= \frac{4\pi}{\pi a_0^3} \int_0^\infty e^{-r/a_0} \left[-i\hbar \left(\frac{d}{dr} + \frac{1}{r} \right) \right] e^{-r/a_0} r^2 dr$$

$$= -\frac{4}{a_0^3} i\hbar \int_0^\infty e^{-r/a_0} \left[\frac{d}{dr} + \frac{1}{r} \right] e^{-r/a_0} r^2 dr$$

$$\begin{aligned} \left(\frac{d}{dr} + \frac{1}{r} \right) e^{-r/a_0} &= \frac{d}{dr} e^{-r/a_0} + \frac{1}{r} e^{-r/a_0} \\ &= -\frac{1}{a_0} e^{-r/a_0} + \frac{1}{r} e^{-r/a_0} \end{aligned}$$

$$\begin{aligned} &= -\frac{4}{a_0^3} i\hbar \int_0^\infty e^{-r/a_0} \left(-\frac{1}{a_0} e^{-r/a_0} + \frac{1}{r} e^{-r/a_0} \right) r^2 dr \\ &= -\frac{4}{a_0^3} i\hbar \left[\int_0^\infty \frac{-1}{a_0} e^{-2r/a_0} r^2 dr + \int_0^\infty \frac{1}{r} e^{-2r/a_0} r^2 dr \right] \\ &= -\frac{4}{a_0^3} i\hbar \left[\left[-\frac{1}{a_0} \left(\frac{2}{a_0} \right)^{2+1} \right] + \left[\left(\frac{2}{a_0} \right)^2 \right] \right] \\ &= +\frac{4}{a_0^3} i\hbar \left[-\frac{1}{a_0} \times \frac{2}{8} a_0^3 + \frac{1}{4} a_0^2 \right] \\ &= -\frac{4i\hbar}{a_0^3} \left[-\frac{a_0^2}{4} + \frac{a_0^2}{4} \right] \\ &= 0 \end{aligned}$$

$$\langle x \rangle = \frac{3}{2} a_0$$

$$\langle x^2 \rangle = 3a_0^2$$

$$\langle p_x \rangle = 0$$

$$\langle p_x^2 \rangle = \frac{\hbar^2}{a_0^2}$$

$$\langle K \rangle = \frac{\hbar^2}{2ma_0^2}$$

$$\langle V \rangle = -\frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{a_0}$$

$$\langle x \rangle = 0$$

$$\langle y \rangle = 0$$

$$\langle z \rangle = 0$$

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$$

$$= \sqrt{3a_0^2 - \frac{9}{4}a_0^2}$$

$$\Delta x = \frac{\sqrt{3}}{2} a_0$$

$$\Delta p_x = \sqrt{\langle p_x^2 \rangle - \langle p_x \rangle^2}$$

$$= \sqrt{\frac{\hbar^2}{a_0^2}} = \frac{\hbar}{a_0}$$

→ Verify virial Theorem - Relation b/w $\langle E \rangle$, $\langle V \rangle$ & $\langle K \rangle$

It is applicable in atom, molecules etc.

$$\langle K \rangle = -\frac{1}{2} \langle V \rangle$$

$$\langle K \rangle = \frac{\hbar^2}{2ma_0^2}$$

$$= \frac{\hbar^2}{2ma_0 a_0}$$

$$= \frac{\hbar^2}{2ma_0} \times \frac{4\pi\epsilon_0 \hbar^2}{me^2}$$

$$= \frac{e^2}{8\pi\epsilon_0} \frac{1}{a_0}$$

$$\langle V \rangle = -\frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{a_0}$$

$$\left[a_0 = \frac{4\pi\epsilon_0 \hbar^2}{me^2} \right]$$

$$\frac{\langle K \rangle}{\langle V \rangle} = -\frac{1}{2}$$

$$\frac{\frac{e^2}{8\pi\epsilon_0} \frac{1}{a_0}}{-\frac{e^2}{4\pi\epsilon_0} \cdot \frac{1}{a_0}} = -\frac{1}{2}$$

(verified)

$$\langle E \rangle = \langle K \rangle + \langle V \rangle$$

$$= \langle K \rangle - 2\langle K \rangle$$

$$\langle E \rangle = -\langle K \rangle$$

Normalize the wave function

$$\int \psi^* \psi d\tau = 1$$

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$$\psi = e^{-r/3a_0 + i\phi} \cos\theta$$

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} (e^{-r/3a_0 + i\phi} \cos\theta)^* e^{-r/3a_0 + i\phi} \cos\theta r^2 dr \sin\theta d\theta d\phi$$

$$= \int_0^\infty r^2 e^{-2r/3a_0} dr \int_0^\pi \cos^2\theta \sin\theta d\theta \int_0^{2\pi} d\phi$$

$$\left(\frac{2!}{\left(\frac{2}{3a_0}\right)^{2+1}}\right) \cdot \frac{2}{3} \cdot 2\pi$$

$$= \frac{2 \times 9a_0^3}{8} \times \frac{2}{3} \times 2\pi$$

$$= 9a_0^3 \pi \neq 1$$

$$\psi_n = \frac{1}{\sqrt{9\pi} a_0^{3/2}} e^{-r/3a_0 + i\phi} \cos\theta$$

$$\psi_n = \frac{1}{\sqrt{\pi} 3a_0^{3/2}} e^{-r/3a_0 + i\theta} \cos\theta$$

DPP 4

(i)

2s

$n=2$

$z=1$

$$E = -\frac{0.5 \times z^2}{n^2} = -0.125 \text{ a.u.}$$

(ii)

$$E = -\frac{e^2}{8\pi\epsilon_0} \cdot \frac{1}{a_0} \frac{z^2}{h^2} = -13.6 \frac{z^2}{h^2} = -R_H h c \frac{z^2}{h^2}$$

$$= -0.5 \frac{z^2}{h^2} \text{ a.u.}$$

DPP 4 Quantum Mechanics

1. The average value of the radius $\langle r \rangle$ in the 1s state of the hydrogen atom is (a_0 is Bohr radius)

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- (a) a_0 (b) $1.5 a_0$ (c) $0.75 a_0$ (d) $0.5 a_0$

2 The ground state energy of hydrogen atom is -13.598 eV. The expectation values of kinetic energy, $\langle T \rangle$ and potential energy, $\langle V \rangle$, in unit of eV, are

June CSIR

- (a) $\langle T \rangle = 13.598, \langle V \rangle = -27.196$ (b) $\langle T \rangle = -27.196, \langle V \rangle = 13.598$
 (c) $\langle T \rangle = -6.799, \langle V \rangle = -6.799$ (d) $\langle T \rangle = 6.799, \langle V \rangle = -20.397$

$$E = -T$$

$$E = \frac{V}{2} \quad \boxed{V = 2E}$$

3. A set of N vectors X_1, X_2, \dots, X_n satisfy the eigenvalue equation for an operator A with scalar eigenvalues $\lambda_1, \lambda_2, \dots, \lambda_n$ (i.e. $A X_k = \lambda_k X_k$). The linear combination vector $\psi = \sum C_k X_k$ where C_k are non zero scalar coefficient

- a) is not an eigenvector of A
 b) is an eigenvector of A only if the λ_k are all distinct (no two eigenvalues are equal)
 c) is an eigenvector of A only if the λ_k are all equal
 d) is an eigenvector of only if C_k are equal

$$A X_k = \lambda_k X_k$$

4. If $\psi_{x,t}$ is considered as product of two function $f(x)g(t)$ where $f(x)$ has the form $e^{-iE\psi/\hbar}$ then it can be shown that probability of finding the particle between x and $x+dx$

- a) Equal to 1 b) is independent of time c) can be obtained by the solution of time dependent schrodinger equation d) can be obtained by the solution of time independent schrodinger equation

5. The mathematical expression $e^{i(kx - \omega t)}$ represents

$$e^{ikx} \cdot e^{-i\omega t}$$

- A) a wave stationary in space but oscillating in time
 B) a travelling wave moving in the positive x direction
 C) a wave stationary in time but periodically varying in space
 D) a travelling wave moving in the negative x direction

6 The vibrational Raman effect was first reported by Late Sir CV Raman in 1928. The intensity of the individual vibrational resonances observed in a Raman spectrum is proportional to

- i) Number of molecules ii) Polarizability of the bond iii) Wavelength of radiation used iv) a considerably weak scattering phenomena

Correct statement above are a) I,ii,iii b) I,ii,iv c) ii,iii,iv d) all

7 In a spherical polar coordinate system, a point A at (x, y, z) in the Cartesian coordinate system can be described by (r, θ, ϕ) where $r, \theta,$ and ϕ have their usual meaning. Expression for the volume of an infinitesimally small cube confined by $dx, dy,$ and dz in terms of the spherical coordinate system is given by

- A) $drd\theta d\phi$ B) $r \sin\theta drd\theta d\phi$ C) $r^2 \sin^2\theta drd\theta d\phi$ D) $r^2 \sin\theta drd\theta d\phi$

8 Consider the statements

- 1) The energy corresponding to 2s orbital of hydrogen atom is -0.125 a.u. τ
 2) The energy of hydrogenic atom is directly proportional to μZ^2 . τ
 3) The energy of 2s and 2p orbital of hydrogenic species is equal means they are degenerate according to schrodinger equation. τ

Correct statements above are (a) 1,,2 (b) 2,3 (c) 1,3 (d) 1,2,3 (e) none

$$E = \frac{-13.6 Z^2}{n^2} \text{ eV}$$

$$E = \frac{-0.5 Z^2}{n^2} \text{ a.u.}$$

$$1 \text{ a.u.} = 27.2 \text{ eV}$$

$$2s = 2p$$

$$n=2 \quad n=2$$

It is considered that -
 electric field & magnetic field are
 completely absent.

Fill in the blanks

- i) The normalisation constant corresponding to wave function $\psi = e^{-r/2a_0 + i\theta} \cos\theta$ is ... $\sqrt{\frac{3}{8\pi}} \cdot a_0^{-3/2}$
- ii) The virial theorem corresponding to hydrogenic atom is ... $\langle K \rangle = -\frac{1}{2} \langle V \rangle$
- iii) The average value of r for an electron in 2s orbital of hydrogen atom ... $6a_0$
- iv) Average value of kinetic energy for an electron in 2s orbital of hydrogen atom ... 3.4 eV

10 The correct statement about both the average value of position ($\langle x \rangle$) and momentum ($\langle p \rangle$) of a 1-d harmonic oscillator wave function is

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- a) $\langle x \rangle \neq 0$ and $\langle p \rangle \neq 0$
- b) $\langle x \rangle = 0$ but $\langle p \rangle \neq 0$
- c) $\langle x \rangle = 0$ and $\langle p \rangle = 0$
- d) $\langle x \rangle \neq 0$ but $\langle p \rangle = 0$

11. The energy of a harmonic oscillator in its ground state is $\frac{1}{2} \hbar\omega$. According to the virial theorem, the average kinetic (T) and potential (V) energies of the above are

- (a) $T = \frac{1}{4} \hbar\omega$; $V = \frac{1}{4} \hbar\omega$
- (b) $T = \frac{1}{8} \hbar\omega$; $V = \frac{3}{8} \hbar\omega$
- (c) $T = \hbar\omega$; $V = -\frac{1}{2} \hbar\omega$
- (d) $T = \frac{3}{8} \hbar\omega$; $V = \frac{1}{8} \hbar\omega$

$E = (n + \frac{1}{2}) \hbar\omega$
Dec CSIR $\frac{1}{2} \hbar\omega$
 $\frac{1}{2} \hbar\omega$
 $\frac{1}{2} \hbar\omega$

12. Show that wave function 1s and 2s are orthogonal to each other, for an electron in hydrogenic atom.

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} a_0^{-3/2} e^{-r/a_0} \quad \psi_{2s} = \frac{1}{4\sqrt{2\pi}} \left(2 - \frac{r}{a_0} \right) e^{-r/2a_0}$$

13. Consider the statements

- i) As electron move away far from the nucleus then velocity decreases. T
- ii) If we replace mass of the electron by the reduced mass in hydrogenic atom the bohr radius becomes $\frac{1}{4}$ of its initial value. F
- iii) Virial theorem apply on the the ground state only F

The correct statement above are a) I,ii b) ii,iii c) I,iii d) I,ii,iii e) I only f) ii only

14. For hydrogen-like atom with a nuclear charge Z, the energy of orbital with principal quantum number 'n' follows the relation.

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- (a) $E_n \propto n^2 Z^2$
- (b) $E_n \propto -\frac{Z^2}{n}$
- (c) $E_n \propto -\frac{Z}{n}$
- (d) $E_n \propto -\frac{Z^2}{n^2}$

15. Consider the statements

- i) The average value of r for an electron in 1S orbital of hydrogen atom is $.8 A^0$. T
 - ii) The energy corresponding to He^+ in 2s orbital is -0.5 a.u. T
 - iii) The value of potential energy for 2s orbital in Li^{2+} is -2.25 a.u. T
- The correct statement above are a) I,ii b) ii,iii c) I,iii d) I,ii,iii e) I only f) ii only

16. Fill in the blanks

- 1) i) The value of potential energy in case of Be^{3+} is ... 435.2 eV
- 2) The uncertainty in r for an electron in 1S orbital of H-atom is ... $\sqrt{3} a_0$
- 3) The commutator of two hermitian operator is ... (Hermitian/antihermitian)
- 4) The probability of finding the electron in 1S orbital of hydrogen atom within first bohr radius is ... 32%
- 5) Three 2 p wavefunction have (same/different) radial factor.
- 6) The zero value of energy is (possible / not possible) in quantum mechanics.
- 7) Uncertainty in momentum for an electron in 1 S orbital of hydrogen atom is
- 8) Virial theorem is applicable to Hydrogen atom Model and Simple Harmonic osc. model

with 1st bohr radius 0 to a_0

$$\int_0^{a_0} \int_0^\pi \int_0^{2\pi} \frac{1}{\sqrt{\pi} a_0^{3/2}} e^{-r/a_0} \frac{1}{\sqrt{\pi} a_0^{3/2}} e^{-r/a_0} r^2 dr d\theta \sin\theta d\phi$$

$$\frac{4}{a_0} \int_0^{a_0} r^2 e^{-2r/a_0} dr = 1 - \frac{5}{2} = 32\%$$

* Probability of 1S orbital
0 to Da_0
 $P = 1 - e^{-2D} (2D^2 + 2D + 1)$
0 to $1a_0 = 1 - 5e^{-2}$

$$V = -\frac{e^2}{4\pi\epsilon_0 a_0}$$

$$\langle V \rangle = -\frac{e^2}{4\pi\epsilon_0 a_0}$$

for (i)

$$\langle V \rangle = -\frac{e^2}{4\pi\epsilon_0 a_0} \frac{Z^2}{n^2} \quad (\text{for all orbitals})$$

$$\langle T \rangle = -\frac{e^2}{8\pi\epsilon_0 a_0}$$

$$E = \langle V \rangle + \langle T \rangle$$

$$= -\frac{e^2}{8\pi\epsilon_0} \frac{1}{a_0} \frac{Z^2}{n^2} \quad (\text{for all hydrogenic})$$

$$= -13.6 \frac{Z^2}{n^2} \text{ eV}$$

OR

$$-0.5 \frac{Z^2}{n^2} \text{ a.u.}$$

↓
 H
 He⁺
 Li²⁺
 Be³⁺

$a_0^{3/2}$

Pa

$\frac{1}{2} h\nu$

$\frac{1}{2} h\nu$

$\frac{1}{2} \frac{h}{2\pi} 2\pi$

$\frac{1}{2} h\nu$

(ii)

$$E = -\frac{e^2}{8\pi\epsilon_0} \frac{1}{a_0} \frac{Z^2}{n^2}$$

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{\mu e^2}$$

↳ reduced mass

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{\mu e^2}$$

$$E = -\frac{e^2}{8\pi\epsilon_0} \times \frac{\mu e^2}{4\pi\epsilon_0 \hbar^2} \frac{Z^2}{n^2}$$

$$\mu = \frac{m_p m_e}{m_p + m_e}$$

$$m_p \gg 1840 m_e$$

$$E \propto \mu Z^2$$

$$\mu = \frac{m_p m_e}{m_p} = m_e$$

del

L

★ Simple Harmonic Oscillator -

$$\textcircled{1} \quad \psi_0 = \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\beta x^2/2}$$

$$\beta = \frac{\sqrt{mK}}{\hbar}$$

$$\textcircled{2} \quad d\tau = dx$$

$$\textcircled{3} \quad \text{Limit } -\infty \text{ to } \infty$$

Show that ψ_0 is normalized -

$$\int_{-\infty}^{\infty} \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\beta x^2/2} \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\beta x^2/2} dx$$

$$\int x^n e^{-\beta x^2} dx$$

$n = \text{even}$

$n = \text{odd}$

0

$$\sqrt{\frac{n+1}{2}}$$

$$\beta^{n+1/2}$$

$$\sqrt{\frac{1}{2}} = \sqrt{\pi}$$

$$\sqrt{\frac{3}{2}} = \frac{1}{2} \sqrt{\pi}$$

$$\sqrt{\frac{5}{2}} = \frac{3}{2} \times \frac{1}{2} \sqrt{\pi}$$

$$\sqrt{\frac{7}{2}} = \frac{5}{2} \cdot \frac{3}{2} \cdot \frac{1}{2} \sqrt{\pi}$$

→ Normalize the wave function -

$$\psi = e^{-2x^2}$$

$$\int_{-\infty}^{\infty} \psi^* \psi dx$$

$$\int_{-\infty}^{\infty} e^{-2x^2} e^{-2x^2} dx$$

$$\int_{-\infty}^{\infty} e^{-4x^2} dx$$

$$\int_{-\infty}^{\infty} x^0 e^{-4x^2} dx$$

$$n=0$$

$$\beta=4$$

$$\frac{\sqrt{\frac{n+1}{2}}}{\beta^{\frac{n+1}{2}}} = \frac{\sqrt{\frac{1}{2}}}{\beta^{\frac{1}{2}}} = \frac{\sqrt{\frac{1}{2}}}{4^{\frac{1}{2}}} = \frac{\sqrt{\pi}}{2} \neq 1$$

$$\psi_n = \sqrt{\frac{2}{\sqrt{\pi}}} e^{-2x^2}$$

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$$N(2x^2-1)e^{-x^2/2}$$

$$\int_{-\infty}^{\infty} (2x^2-1)e^{-x^2/2} (2x^2-1)e^{-x^2/2} dx = 1$$

$$\int_{-\infty}^{\infty} (2x^2-1)^2 e^{-x^2} dx$$

$$\int_{-\infty}^{\infty} (4x^4 + 1 - 4x^2) e^{-x^2} dx$$

$$\int_{-\infty}^{\infty} 4x^4 e^{-x^2} dx + \int_{-\infty}^{\infty} x^0 e^{-x^2} dx + \int_{-\infty}^{\infty} -4x^2 e^{-x^2} dx$$

$$4 \frac{\sqrt{\frac{5}{2}}}{1^{5/2}} + \frac{\sqrt{\frac{1}{2}}}{1^{1/2}} - 4 \frac{\sqrt{\frac{3}{2}}}{1^{3/2}} = 4 \cdot \frac{3}{2} \cdot \frac{1}{2} \sqrt{\pi} + \sqrt{\pi} - 4 \cdot \frac{1}{2} \sqrt{\pi}$$

$$N = \frac{1}{\sqrt{2\sqrt{\pi}}} \left[\frac{1}{2\sqrt{\pi}} \right]^{1/2}$$

(a) find the average of $\langle x \rangle$, $\langle x^2 \rangle$, $\langle p_x \rangle$, $\langle p_x^2 \rangle$, $\langle K \rangle$, $\langle V \rangle$, $\langle \Delta x \rangle$, $\langle \Delta p_x \rangle$

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for 1D SHO in ground state

$$\psi_0 = \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\beta x^2/2}$$

(b) verify Heisenberg uncertainty principle

(c) verify virial Theorem

$$\langle K \rangle = \langle V \rangle$$

* Virial Theorem -

↓

Relation b/w $\langle V \rangle$ and $\langle K \rangle$

In case of -

H-atom model

→

$$\langle K \rangle = \langle T \rangle = -\frac{1}{2} \langle V \rangle$$

SHO - model

→

$$\langle K \rangle = \langle T \rangle = \langle V \rangle$$

But in case of -

PIB & Rigid rotor

$$V = 0$$

∴ No virial relation

$$E_n = (n + \frac{1}{2}) h\nu = (n + \frac{1}{2}) \frac{h}{2\pi} 2\pi h\nu$$

$$= (n + \frac{1}{2}) \hbar \omega$$

$$\langle x \rangle = \int_{-\infty}^{\infty} \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\beta x^2/2} x \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\beta x^2/2} dx$$

$$= \left(\frac{\beta}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} x e^{-\beta x^2} dx$$

$$= \frac{\sqrt{\frac{1+1}{2}}}{\beta^{\frac{1+1}{2}}} \quad x^1 \quad n=1 \text{ odd} = 0$$

$$\langle x \rangle = 0$$

$$\langle x \rangle = 0$$

$$\langle p_x \rangle = 0$$

$$\langle x^2 \rangle = \frac{1}{2B}$$

$$\langle p_x^2 \rangle = \frac{B\hbar^2}{2}$$

$$\langle K \rangle = \frac{\langle p^2 \rangle}{2m} = \frac{B\hbar^2}{4m}$$

$$\langle V \rangle = \frac{1}{2}k\langle x^2 \rangle = \frac{k}{4B}$$

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$$

$$= \sqrt{\frac{1}{2B} - 0} = \sqrt{\frac{1}{2B}}$$

$$\Delta p_x = \sqrt{\langle p_x^2 \rangle - \langle p_x \rangle^2} = \sqrt{\frac{B\hbar^2}{2}}$$

$$\Delta x \Delta p_x = \frac{\hbar}{2}$$

③

$$\langle K \rangle = \langle V \rangle$$
$$\frac{B\hbar^2}{4m} = \frac{k}{4B}$$

$$B = \frac{\sqrt{Bk}}{\hbar}$$

$$\langle K \rangle = \frac{\sqrt{Bk}}{\hbar} \cdot \frac{\hbar^2}{4m}$$

$$= \frac{1}{4} \cdot \frac{\hbar}{2\pi} \sqrt{\frac{k}{m}}$$

$$= \frac{1}{4} \cdot \hbar \cdot \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

$$= \frac{1}{4} h\nu$$

$$(ii) \quad v = \frac{k}{4B} = \frac{k}{4} \frac{\hbar}{\sqrt{Bk}} = \frac{1}{4} \hbar \sqrt{\frac{k}{m}}$$
$$= \frac{1}{4} \cdot h \cdot \frac{1}{2\pi} \sqrt{\frac{k}{m}} = \frac{1}{4} h\nu$$

$$\therefore \langle K \rangle = \langle V \rangle$$

③ ②

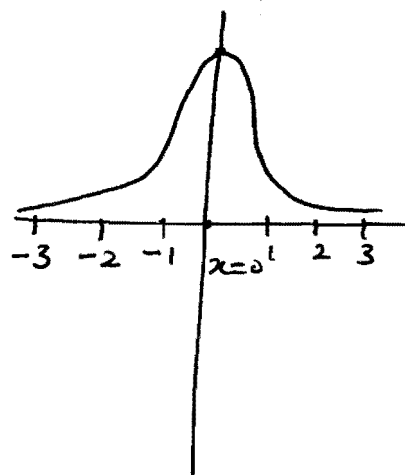
$$\psi_0 = \left(\frac{B}{\pi}\right)^{1/4} e^{-Bx^2/2}$$

$$e^{-Bx^2/2} = 1 = e^0$$

$$\frac{Bx^2}{2} = 0$$

$$x = 0$$

Maximum

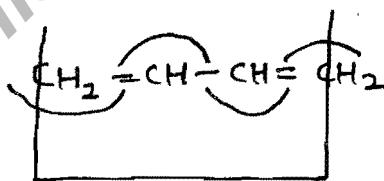


Gaussian function

★ Particle in Box Model —

To study the translational motion of particle in bounded region this model was proposed.

For example - In chemistry the movement of πe^- in conjugated system from one end of the carbon to other end of carbon.



* In physics -

movement of microscopic particle in solid (Band theory)

Acc. to Born-Oppenheimer

To study the translation motion of microscopic particle we keep it independent of other motion i.e. Rot, vib. & electronic motion

Let us consider a free particle is confined to move in a 1D-box of length $[0 < x < L]$ particle is free.

{ Particle is free ~~no~~ particle, no force is acting on it potential energy is const. and to avoid mathematical complication put $v=0$ } $v=0$

$$T = e^{-2 \sqrt{2m_e(E-V)} \cdot L} = e^{-\dots}$$

$$T = e^{-2 \sqrt{2 \times 1840 m_e (E-V)} \cdot L} = e^{-\sqrt{1840} \dots}$$

$$= e^{-857}$$

DPP 5 Quantum mechanics

Q1 Tunneling is a quantum mechanical phenomenon, consider the statements about it

- 1) On increasing mass of the particle and height of the barrier tunneling decreases T
- (2) Particle with energy close to the height of barrier have more tendency to cross the barrier T
- (3) If tunneling corresponding to electron is e^{-20} then corresponding to proton is e^{-480} F

Correct statements above are (a) 1,2 (b) 1,3 (c) 2,3 (d) 1,2,3 (e) none

Q2 Consider the statement

- (1) Virial theorem are applicable to atom and molecule both. T
- (2) According to virial energy contributed by potential energy and kinetic energy are equal. F
- (3) For first excited state in SHO the energy contributed by kinetic energy is $.75 h \nu$. T

Correct statements above are (a) 1,2 (b) 2,3 (c) 1,3 (d) 1,2,3 (e) none

Q3 Consider the statements

- 1) The value of $\langle x \rangle$ and $\langle p_x \rangle$ in case of 1D SHO is zero. T
- 2) The wavefunction corresponding to ground state in 1 D sho is symmetric and decreases rapidly if mass of the atom is more. T
- 3) The energy gap between SHO is always equal. T

Correct statements above are (a) 1, 2 (b) 2,3 (c) 1,3 (d) 1,2,3 (e) none

↓
Property of gaussian function

Q4 Consider the statements

4 Consider the statements

(1) A standing wave has nodes that are at fixed distances independent of time, whereas the nodes move in time for a traveling wave. T

(2) For the ground state, it is much more likely that the particle is found near the center of the box than at the edges T

Correct statements above are (a) 1, (b) 2, (c) 1,2 (d) none

Q5. The transmission probability of a particle encountering the barrier is e^{-10} if mass is reduced by $\frac{1}{2}$ and width of the barrier is doubled, tunneling probability would be CSIR-JRF

- (a) $e^{-10\sqrt{2}}$ (b) e^{-20} (c) $e^{-20\sqrt{2}}$ (d) does not change

Q6 Consider the statements

- (a) quantization is the result of boundary condition. T
- (b) As number of node increases the value of energy increase in 1 D box model. T $E \propto n^2$
- (c) The length of the box is the integral multiple of half of the wavelength $L = n \cdot \frac{\lambda}{2}$
- (d) As we move towards higher value of n quantum and classical prediction are same T

True statements are (1) a,b (2) b,c (3) a,b,c (4) a,b,c,d (5) none

↓ Bohr's Correspondance principle

Q7 Consider the statement

1. the condition that $V=0$ inside the box is the result that we are using free particle T
- 2 $V=\infty$ is considered elsewhere to avoid tunneling T
- 3 The energy of quantum mechanical particle in PIB model increases with increases in mass. F

True statements above are

- (a) 1,2 (b) 2,3 (c) 1,3 (d) 1,2,3

Q8 A particle is confined to move in 1 D box of length l, if the boundary of the box is removed than

- (a) noquantisation (b) quantisation retains (c) particle remains within the same region (d) none

Q9 Consider the statements

$$\frac{\Delta E}{E} = \frac{(2n+1) \frac{h^2}{8ml^2}}{\frac{n^2 h^2}{8ml^2}} = \frac{2n+1}{n^2} \xrightarrow{n \rightarrow \infty} 0$$

i) bound state give quantized energy level ^T ii) Quantum number in PIB model is a restriction rather than assumption as in bohr theory of hydrogen atom ^T iii) the probability of finding the particle in the left half of the box in every state is equal to half. The true statement above are a) i and ii b) i, iii c) ii, iii ~~d) i, ii, iii~~ e) none ^T

10. Consider the statement

- i) $\Delta E/E$ becomes a smaller fraction of the energy as $n \rightarrow \infty$. This result shows that the energy spectrum becomes continuous for large n . ^T
- ii) zero point energy approaches zero as l approaches infinity. In this limit, the particle becomes free. ^T
- iii) probability of finding the particle in the central third of the box if it is in its ground state is 0.6. ^T

True statement above are a) i, ii b) i and iii c) ii and iii d) i, ii, iii

11. consider the statements

- i) For sufficiently small l , the energy E may become greater than the depth of the potential well. such a well will not hold the microparticle. ^T *E > Tunnelling Res*
- ii) The wavefunction of a heavy particle decays more rapidly inside a barrier than that of a light particle. ^T
- iii) that two wavefunctions belonging to different energies are orthogonal. ^T

The true statement above are (a) i, ii (b) ii, iii (c) i, ii, iii (d) none



12. Consider the statement

- i) the uncertainty principle requires a particle to possess kinetic energy if it is confined to a finite region. ^T *K.E. = 0 => Delta x = infinity => particle unbound*
- ii) Energy is quantized but other observable are not quantized in quantum mechanics. ^F
- iii) PIB model is the basis of the treatment of the electronic structure of metals and a treatment of conjugated molecules. ^T

True statements above are (a) i, ii (b) ii, iii (c) I, iii (d) I, ii, iii (e) none

13. Consider the statement

- i) Tunneling is a real, detectable quantum phenomenon. It is not predicted by classical mechanics ^T
- ii) The average value of the position of the particle in a box is $a/2$ for any value of the quantum number n . ^T
- *iii) Heisenberg does have restriction on knowing average values of the position or the momentum also ^F

True statements above are (a) I, ii (b) ii, iii (c) I, ii, iii (d) none

* 14. Write the formulae for probability of finding the particle between 0 to $a/2$ for a particle in box for n th state is ^T

15. Uncertainty in position for a particle confined to move in a box of length 0.2 nm is 0.037 nm. The wave function corresponds to $n=2$ for a particle in a box of length l ($-l/2$ to $+l/2$) is ^T ** $\sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l}$*

(ii) (iii) *max उत्तर → Tunnelling कम → Transmission कम*
 \downarrow
psi barrier में decay हुआ ← psi की value कम

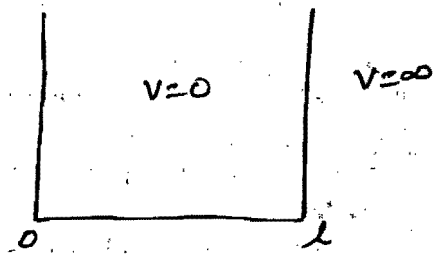
$V = \infty$ elsewhere [To avoid tunnelling, tunnelling is a quantum mechanical phenomenon www.chemistryABC.com]

Microscopic particle having energy less than the energy of potential barrier have the tendency to cross the barrier of finite width is known as tunnelling
 e.g- ejection of α -particle from radioactive nuclei is example of tunnelling

If microscopic particle mass = m Energy = E

Pot. barrier = V barrier width = L
 height

$E < V$ $T = e^{-2\sqrt{\frac{2m(V-E)}{\hbar^2}} \cdot L}$
 If $V = \infty$ $T = 0$



Schrodinger eqn

$$\nabla^2 \psi + \frac{2m}{\hbar^2} (E - V) \psi = 0$$

for 1D-system Cartesian co-ordinates $\nabla^2 = \frac{d^2}{dx^2}$

$$\frac{d^2 \psi}{dx^2} + \frac{2m}{\hbar^2} (E - V) \psi = 0$$

$V = 0$ inside the box

$$\frac{d^2 \psi}{dx^2} + \frac{2m}{\hbar^2} E \psi = 0$$

$$\frac{d^2 \psi}{dx^2} + k^2 \psi = 0$$

$$\frac{2mE}{\hbar^2} = k^2$$

This differential eqn have two solutions

$$\psi = Ae^{ikx} + Be^{-ikx}$$

$$\psi = A \sin kx + B \cos kx \quad \text{--- (1)}$$



Applying Boundary conditions -

① $x=0$ ② $x=l$

③ $\psi=0$ ④ $\psi=0$

$$0 = A \sin k \cdot 0 + B \cos k \cdot 0$$

$$0 = 0 + B \cdot 1$$

$$B = 0$$

Putting in eqn ① $B=0$,

$$\psi = A \sin kx$$

Applying 2nd boundary condition

$$x=l \quad \psi=0$$

$$0 = A \sin kl$$

$$\text{So } \sin kl = 0 = \sin n\pi$$

$$k = \frac{n\pi}{l}$$

$$n = 1, 2, 3, \dots$$

$$\psi = A \sin kx + B \cos kx$$

$$\psi = A \sin \frac{n\pi x}{l}$$

[$n=0$ is mathematically allowed but not quantum mechanically quantum mech. restrictions imposed on a no. n called Quantum no.]

Apply Normalization conditions

$$\int \psi^* \psi dx = 1$$

$$\int_0^l A \sin \frac{n\pi x}{l} A \sin \frac{n\pi x}{l} dx = 1$$

$$A^2 \int_0^l \sin^2 \frac{n\pi x}{l} dx = 1$$

$$A = \sqrt{\frac{2}{l}}$$

$$\Psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$$

$$k^2 = \frac{2mE}{\hbar^2}$$

↓

$$\left(\frac{n\pi}{L}\right)^2 = \frac{2mE}{\hbar^2}$$

$$E = \frac{n^2 \pi^2 \hbar^2}{2mL^2}$$

Factors affecting Tunnelling -

$$T = e^{-2\sqrt{\frac{2m(V-E)}{\hbar}} \cdot L}$$

If $\sqrt{\frac{2m(V-E)}{\hbar}} \cdot L$ is more Tunnelling is less.

If $\left. \begin{array}{l} V \uparrow \\ m \uparrow \\ L \uparrow \end{array} \right\} T \downarrow$

If $E \uparrow \} T \uparrow$ OR $E \downarrow, T \downarrow$

$E \rightarrow$ energy of particle

$V \rightarrow$ Barrier height

$L \rightarrow$ Barrier width

$m \rightarrow$ mass of particle

★ Plot of ψ & ψ^2 -

$$\psi = \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l}$$

for $n=1$

$$\psi_1 = \sqrt{\frac{2}{l}} \sin \frac{1\pi x}{l}$$

→ ψ is maximum when $\sin \frac{1\pi x}{l}$ is maximum

$$\sin \frac{1\pi x}{l} = +1$$

$$\sin \frac{1\pi x}{l} = \sin \frac{\pi}{2}$$

$$\frac{\pi x}{l} = \frac{\pi}{2}$$

$$x = \frac{l}{2}$$

$$\sin \frac{\pi}{2} = +1$$

$$\sin \frac{5\pi}{2} = +1$$

$$\sin \frac{9\pi}{2} = +1$$

But

$$\sin \frac{1\pi x}{l} = \sin \frac{5\pi}{2}$$

$$\Rightarrow x = 2.5l \text{ (out of boundary)}$$

Not accepted)

→ ψ is zero when -

$$\sin \frac{1\pi x}{l} = 0$$

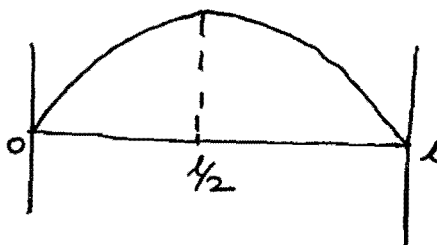
$$\sin \frac{1\pi x}{l} = \sin \pi$$

$$\frac{\pi x}{l} = \pi$$

$$x = l$$

boundary

⇒ No node



for $n=2$

$$\psi_2 = \sqrt{\frac{2}{l}} \sin \frac{2\pi x}{l}$$

ψ_2 is maximum when $\sin \frac{2\pi x}{l}$ is maximum

$$\sin \frac{2\pi x}{l} = \sin \frac{\pi}{2}$$

$$\frac{2\pi x}{l} = \frac{\pi}{2}$$

$$x = \frac{l}{4}$$

ψ_2 is zero when

$$\sin \frac{2\pi x}{l} = \sin \pi$$

$$\frac{2\pi x}{l} = \pi$$

$$x = \frac{l}{2}$$

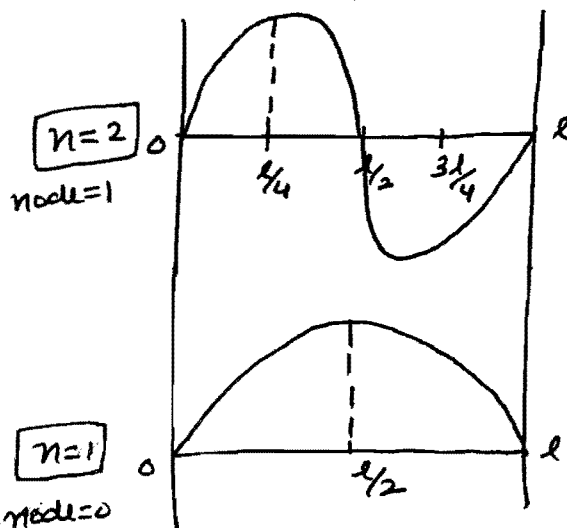
ψ_2 is minimum when

$$\sin \frac{2\pi x}{l} = -1$$

$$\sin \frac{2\pi x}{l} = \sin \frac{3\pi}{2}$$

$$\frac{2\pi x}{l} = \frac{3\pi}{2}$$

$$x = \frac{3l}{4}$$



→ First maxima for n th state -

$$\psi = \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l}$$

ψ is maximum when $\sin \frac{n\pi x}{l} = +1 = \sin \frac{\pi}{2}$

$$\frac{n\pi x}{l} = \frac{\pi}{2}$$

$$x = \frac{l}{2n}$$

$$n=1 = \frac{l}{2}$$

$$n=2 = \frac{l}{4}$$

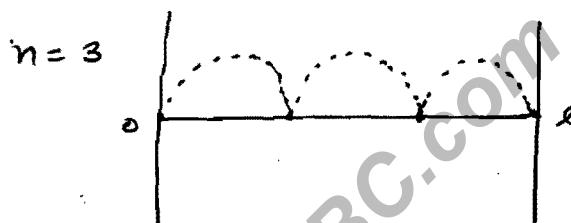
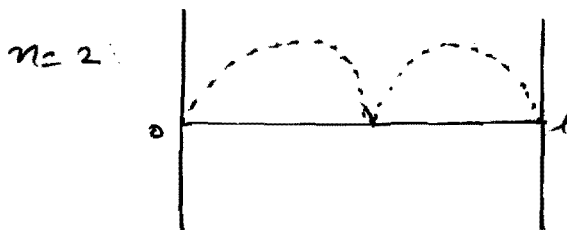
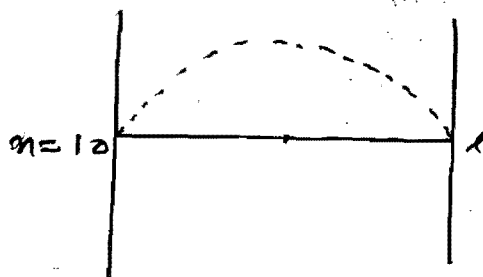
$$n=3 = \frac{l}{6}$$

$$\vdots$$

* → No. of nodes = $(n-1)$

$n=1$	$\frac{l}{2}$ first maxima	$\frac{l}{2} + \frac{l}{2} = l$ boundary	
$n=2$	$\frac{l}{4}$ "	$\frac{l}{4} + \frac{l}{4} = \frac{l}{2} = \text{node}$	
$n=3$	$\frac{l}{6}$ "	$\frac{l}{6} + \frac{l}{6} = \frac{2l}{6} \rightarrow \text{node}$ $\frac{l}{6} + \frac{l}{6} + \frac{l}{6} = \frac{3l}{6}$ minima	
		$\frac{l}{6} + \frac{l}{6} + \frac{l}{6} + \frac{l}{6} = \frac{4l}{6} = \frac{2l}{3}$ (node)	

$\psi^2 \rightarrow$ always +ve
(Probability)



★ Features of PIB model-

- ① From the relation b/w length of the box & the wavelength it is clear that length of the box is integral multiple of $\lambda/2$

as -

$$E = \frac{n^2 h^2}{8ml^2}$$

$$K.E = \frac{p^2}{2m}$$

$$\lambda = \frac{h}{p} \quad p = \frac{h}{\lambda}$$

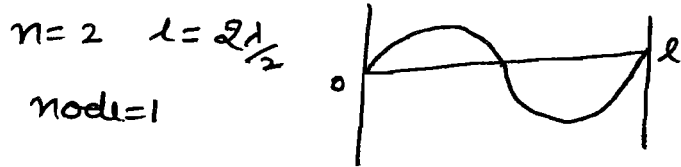
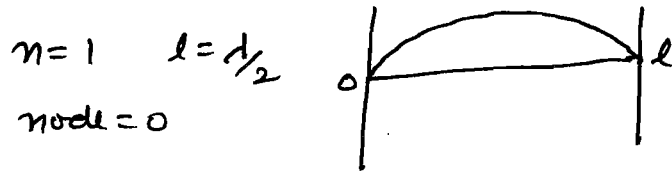
$$K.E = \frac{h^2}{2m\lambda^2}$$

$$\frac{n^2 h^2}{8ml^2} = \frac{h^2}{2m\lambda^2}$$

$$\boxed{\lambda = \frac{2l}{n}}$$

If $l = \frac{nd}{2}$ then function become zero b/w limit 0 to l as $n \rightarrow \infty$ because after every $d/2$ function becomes zero.

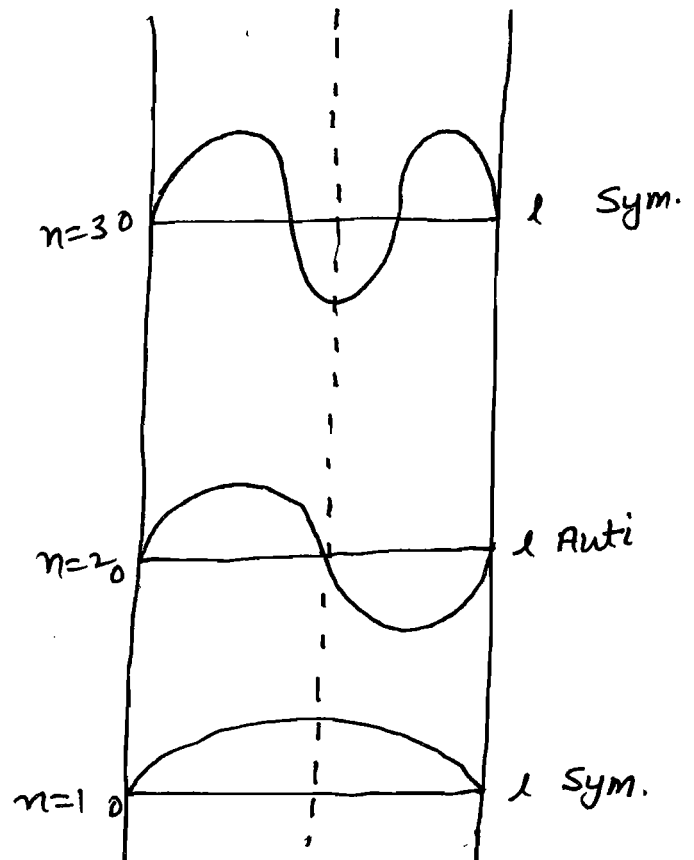
$$\text{No. of nodes} = \text{Translational q. No} - 1$$



②

function ψ_1, ψ_3, ψ_5 are symmetric w.r.t. Centre of the box
 \Downarrow
 $(\psi(+x) = \psi(-x))$

& function ψ_2, ψ_4, ψ_6 are Anti-symmetric w.r.t. Centre of box
 $(\psi(+x) = -\psi(-x))$



③ As the value of node \uparrow value of increases Energy \uparrow . www.chemistryABC.com

$$\text{node} = n - 1$$

$$n = \text{node} + 1$$

$$E = \frac{n^2 h^2}{8mL^2}$$

④ In the ground state particle spends most of the time within the middle region means non-uniformity in distribution of the particle in the lower level. As the value of $n \uparrow$ the uniformity in the distribution. & at very high value of n particle spends almost equal time at every region of probability means continuity generates, classical behaviour energies Hence Bohr correspondence principle verify (At very high value of n the prediction made by quantum mechanics is same as classical mechanics predicts)

(i) 0 to l $\psi = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$ $E_n = \frac{n^2 h^2 \pi^2}{8mL^2} = \frac{n^2 h^2}{8mL^2}$

$$E_{n+1} - E_n = \left[(n+1)^2 - n^2 \right] \frac{h^2}{8mL^2}$$

$$= \frac{(2n+1)h^2}{8mL^2}$$

(ii) 0 to $2l$ $\psi = \sqrt{\frac{2}{2l}} \sin \frac{n\pi x}{2l}$ $E = \frac{n^2 h^2}{8m(2l)^2}$

$$= \frac{n^2 h^2}{32mL^2}$$

(iii) $-l$ to $+l$ $\psi_n = \sqrt{\frac{1}{l}} \sin \frac{n\pi x}{2l} \rightarrow n = \text{even}$ $E = \frac{n^2 h^2}{8m(2l)^2}$ $\langle x \rangle = 0$
 $\psi_n = \sqrt{\frac{1}{l}} \cos \frac{n\pi x}{2l} \rightarrow n = \text{odd}$ $= \frac{n^2 h^2}{32mL^2}$ $\langle p \rangle = 0$
 $\langle x^2 \rangle = ?$

$$\langle p^2 \rangle = \frac{n^2 h^2}{16L^2}$$

$$\Delta E \cdot \Delta t \geq \frac{\hbar}{2}, \quad \Delta J \cdot \Delta \phi \geq \frac{\hbar}{2}, \quad \Delta x \cdot \Delta p_x \geq \frac{\hbar}{2}$$

$$\Delta T \geq \frac{\hbar}{2(V-E)}$$

DPP6 Quantum Mechanics

1. Consider an electron with energy E , mass m tunneling through a barrier of height $V > E$ and width w , the total time t electron spends inside the barrier **TIFR**

- a) $\hbar/(V-E)$ b) $w \times (2m/E)^{0.5}$ c) $\{2m(V-E)/\hbar\}^{0.5}$ d) $\{4m^2(V-E)/\hbar\}^{0.5}$

2. Consider the statements

(1) If the total energy can be written as a sum of independent terms corresponding to different degrees of freedom, then the wave function is a product of individual terms, each corresponding to one of the degrees of freedom. **T**

(2) number of states, each represented by a distinct eigenfunction, that have the same energy is the **degeneracy** of the level. **T**

(3) the wavelength of the light emitted when an electron in a one-dimensional box of length 5.0 nm makes a transition from $n=7$ to $n=6$ is 6.34×10^{-6} m. **T**

Correct statements above are (a) 1,2 (b) 2,3 (c) 1,3 (d) 1,2,3

3. The smallest observed frequency for a transition between states of an electron in a one-dimensional box is $3 \times 10^{13} \text{ s}^{-1}$ the length of the box is

- (a) 3 nm (b) 30 nm (c) 300 nm (d) 130 nm (d) none

4. The movement of π electron in a conjugated system is considered as a free-electron model. Using the same argument, ~~show that~~ the length of hexatriene can be estimated to be 867 pm.

Show that the first electronic transition is predicted to occur at $2.8 \times 10^4 \text{ cm}^{-1}$.

5. The difference in the ground state energies (kJ/mol) of an electron in one-dimensional boxes of lengths 0.2 nm and 2 nm is _____ **GATE Chem**

6. Consider a particle is confined to move in a 1D box under the potential $V=0$ [$0 < x < l$] and $V=\infty$ elsewhere. **GATE Chem**

i) When the particle in its lowest energy state the average value of momentum $\langle p_x \rangle$ is

- a) 0 b) $\hbar/2a$ c) $\hbar/2\pi a$ d) \hbar/a

ii) The uncertainty in momentum Δp_x in its lowest energy state is

- a) 0 b) $\hbar/2a$ c) $\hbar/2\pi a$ d) \hbar/a

7. The lifetime of molecule in an excited electronic state is 10^{-10} s The uncertainty in its energy in eV approximately is **GATE Chem**

- a) 2×10^{-5} b) 3×10^{-6} c) 0 d) 10^{-14}

8. A particle is confined in a 1D box of length 1 mm if length is changed by 10^{-9} the percent change in energy is **GATE Chem**

- a) 2×10^{-4} b) 2×10^{-7} c) 2×10^{-2} d) 0

9. If $[x, p] = i\hbar$ then the value of commutator $[x^3, p]$ is **GATE Phy**

- a) $2i\hbar x^2$ b) $-2i\hbar x^2$ c) $3i\hbar x^2$ d) $-3i\hbar x^2$

10. A particle of mass m is confined in the ground state of one dimensional box extending from $-2L$ to $+2L$ The wave function of particle in box is $\psi_x = \psi_0 \cos(\pi x/4L)$ where ψ_0 is constant

i) The normalization constant ψ_0 of the function is **GATE Phy**

- a) $(2/L)^{0.5}$ b) $(1/4L)^{0.5}$ c) $(1/2L)^{0.5}$ d) $(1/L)^{0.5}$

ii) The energy eigenvalue corresponding to this state is

- a) $[\hbar^2 \pi^2 / 2mL^2]$ b) $[\hbar^2 \pi^2 / 4mL^2]$ c) $[\hbar^2 \pi^2 / 16mL^2]$ d) $[\hbar^2 \pi^2 / 32mL^2]$

iii) The expectation value of operator p^2 (p is momentum operator) is

- a) 0 b) $[\hbar^2\pi^2/32L^2]$ c) $[\hbar^2\pi^2/16L^2]$ d) $[\hbar^2\pi^2/8L^2]$

11 A particle is confined to move in a 1d box of length $-a$ to $+a$ the wavefunction corresponding to ground state is $\psi_n = \frac{1}{\sqrt{L}} \cos \frac{n\pi x}{2L}$ GATE Chem ~~Wave function~~ excited state = $\psi_n = \frac{1}{\sqrt{L}} \sin \frac{n\pi x}{2L}$

12 Calculate the wave length corresponding to lowest energy excitation of an electron confined to move in a 1 D box of length 1nm. IIT JAM $11.03 \times 10^{-7} \text{m}$

13 Given three systems, A, B, and C, what could be they if the spacing between the neighbouring energy levels in A decreases with increasing energy, while that for B is constant, and that for C increases with increasing energy? TIFR 2013

- A) A= particle in a one-dimensional box, B= harmonic oscillator, C=electron in hydrogen atom
 B) A= electron in hydrogen atom, B= harmonic oscillator, C= particle in a one-dimensional box
 C) A= particle in a one-dimensional box, B= electron in hydrogen atom, C= harmonic oscillator
 D) A= electron in hydrogen atom, B= particle in a one-dimensional box, C= harmonic oscillator

14 Consider the statement

1. Probability of finding the particle in right half of box is 0.5, if the box length is $2l$ ($-l$ to $+l$). T
 2. The maximum value of function for a particle in 1D box of length 2 nm (0 to 2nm) is 1 nm^{-5} .
 3. Stabilization because of resonance and Red shift in conjugated may be explained by PIB model.
 The correct statements above are (a) 1,2 (b) 2,3 (c) 1,2,3 (d) none

15 The location of node for a particle that is confined to move in a 1 D box of length 3 nm in the second excited state is (a) $0.5 \text{ nm}, 1.5 \text{ nm}$ (b) $1 \text{ nm}, 0.66 \text{ nm}$ (c) $0.5 \text{ nm}, 0.66 \text{ nm}$ (d) none

16 Zero point energy of a particle confined to move in 1D box of length l ($-l/2$ to $+l/2$) is

- (a) $n^2\hbar^2/8ml^2$ (b) $\hbar^2/8ml^2$ (c) 0 (d) $\hbar^2/32ml^2$ (e) none

17 Using Heisenberg uncertainty principle derive an expression for ground state energy of particle of mass m in 1D box of length l . IIT JAM

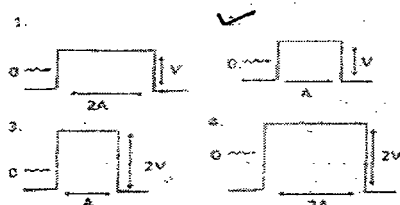
18 If π electron in butadiene molecule behave particle in box model and length is taken l the total ground state energy of π electrons in the ground state is

- (i) $9\hbar^2/4ml^2$ (b) $7\hbar^2/8ml^2$ (c) $5\hbar^2/4ml^2$ (d) $2\hbar^2/8ml^2$ (e) none

19 For a particle of mass m confined in a box of length L assume $\Delta x=L$, assume further that $\Delta p_{\min}=(p^2)^{1/2}$, Use the uncertainty principle to obtain the estimate of ground state energy of the particle. The value will be CSIR Chem

- a) $[\hbar^2/8mL^2]$ b) $[\hbar^2/8mL^2]$ c) $[\hbar^2/32mL^2]$ d) $[\hbar^2/2mL^2]$

20. A quantum mechanical particle with energy $E_0 < V$ is allowed to strike the following four barrier separately The Transmission probability is maximum in CSIR Chem



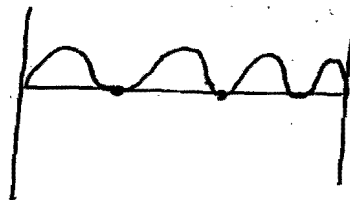
(19) $\Delta x \cdot \Delta p = \frac{\hbar}{2}$
 $\Delta p = \frac{\hbar}{2L}$
 $(p^2)^{1/2} = \frac{\hbar}{2L}$
 $E = \frac{p^2}{2m} = \frac{\hbar^2}{8mL^2}$

Qus. → For the energy level $\frac{2^2 h^2}{ma^2}$ the probability for a particle of mass m over the length a of 1D box is depicted by -

$$\frac{2^2 h^2}{ma^2} = \frac{n^2 h^2}{8ma^2}$$

$$n = 4$$

$$\text{node} = 3$$



★ $-l$ to l ($2l$)

$$V = 0 \text{ (inside)}$$

$$V = \infty \text{ elsewhere}$$

$$\frac{d^2\psi}{dx^2} + \frac{2M}{\hbar^2} (E - V)\psi = 0$$

$$V = 0 \text{ (inside)}$$

$$\frac{d^2\psi}{dx^2} + \frac{2M}{\hbar^2} E \psi = 0 \quad = \quad \frac{d^2\psi}{dx^2} + k^2 \psi = 0$$

Soln of eqn is -

$$\psi = A \sin kx + B \cos kx \quad \text{--- (1)}$$

Boundary conditions -

$$x = -l \quad \psi = 0$$

$$A \sin k(-l) + B \cos k(-l) = 0$$

$$-A \sin kl + B \cos kl = 0 \quad \text{--- (2)}$$

$$\textcircled{2} \quad x = l \quad \psi = 0$$

$$A \sin kl + B \cos kl = 0 \quad \text{--- (3)}$$

$$\textcircled{2+3} \quad 2B \cos kl = 0 \quad \text{--- (4)}$$

$$\textcircled{3-2} \quad 2A \sin kl = 0 \quad \text{--- (5)}$$

A & B simultaneously never be equal to zero otherwise function becomes zero, either $A = 0$ OR $B = 0$

If $A=0$ $B \neq 0$

$$\psi = A \sin kx + B \cos kx$$

$$\psi = B \cos kx$$

from eqn (4)

$$B \cos kl = 0$$

$$B \neq 0 \Rightarrow \cos kl = 0$$

$$\cos kl = \cos \frac{n\pi}{2} \quad n = 1, 3, 5, \dots$$

$$kl = \frac{n\pi}{2}$$

$$k = \frac{n\pi}{2l}$$

$$\psi = B \cos \frac{n\pi x}{2l}$$

$$n = 1, 3, 5, \dots$$

If $B=0$ $A \neq 0$

$$\psi = A \sin kx + B \cos kx$$

$$\psi = A \sin kx$$

from eqn (5)

$$A \sin kl = 0$$

$$A \neq 0$$

$$\sin kl = 0 = \sin \frac{n\pi}{2}$$

$$n = 2, 4, 6, \dots$$

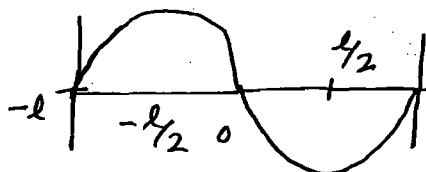
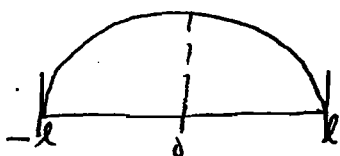
$$k = \frac{n\pi}{2l}$$

$$\psi = A \sin \frac{n\pi x}{2l}$$

$$n = 2, 4, 6, \dots$$

$$k^2 = \frac{2ME}{\hbar^2}$$

$$E = \frac{n^2 \pi^2 \hbar^2}{8ml^2} = \frac{n^2 h^2}{32ml^2}$$



★ $-\frac{l}{2}$ to $\frac{l}{2}$ (1)

$$\psi_n = \sqrt{\frac{2}{l}} \cos \frac{n\pi x}{l}$$

$$n = \text{odd} = 1, 3, 5, \dots$$

$$\psi_n = \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l}$$

$$n = \text{even} = 2, 4, 6, \dots$$

$$E = \frac{h^2 \pi^2 n^2}{8m(l/2)^2} = \frac{n^2 h^2}{8ml^2}$$

Particle in 2-D Box -

Let us consider a free particle is confined to move in a 2-D box $0 < x < l(x)$, $0 < y < l(y)$. Particle is free $v=0$ $v=\infty$ elsewhere.

Schrodinger eqn -

$$\nabla^2 \psi + \frac{2m}{\hbar^2} (E - V) \psi = 0$$

∇^2 for 2D-system

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

Then

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) \psi(x,y) + \frac{2m}{\hbar^2} (E - V) \psi(x,y) = 0$$

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) \psi(x,y) + \frac{2m}{\hbar^2} E \psi(x,y) = 0$$

$$\frac{\partial^2 \psi(x,y)}{\partial x^2} + \frac{\partial^2 \psi(x,y)}{\partial y^2} + \frac{2m}{\hbar^2} E \psi(x,y) = 0$$

function $\psi(x,y)$ represents the motion of particle in more than one spatial dimension.

$$\psi(x,y) = \psi(x)\psi(y)$$

$$E(x,y) = E_x + E_y$$

→ function represents the wave ⇒ multiplicative & energy is extensive property ⇒ additive

Replace $\Psi(x,y) = \Psi(x) \cdot \Psi(y)$ & $E(x,y) = E(x) + E(y)$ in eqn

$$\frac{\partial^2 \Psi(x)\Psi(y)}{\partial x^2} + \frac{\partial^2 \Psi(x)\Psi(y)}{\partial y^2} + \frac{2m}{\hbar^2} [E(x) + E(y)] \Psi(x)\Psi(y) = 0$$

$$\Psi(y) \frac{\partial^2 \Psi(x)}{\partial x^2} + \Psi(x) \frac{\partial^2 \Psi(y)}{\partial y^2} + \frac{2m}{\hbar^2} [E(x) + E(y)] \Psi(x)\Psi(y) = 0$$

To separate the variable divide by $\Psi(x)\Psi(y)$ we get

$$\frac{1}{\Psi(x)} \frac{\partial^2 \Psi(x)}{\partial x^2} + \frac{1}{\Psi(y)} \frac{\partial^2 \Psi(y)}{\partial y^2} + \frac{2m}{\hbar^2} (E_x + E_y) = 0$$

$$\frac{1}{\Psi(x)} \frac{\partial^2 \Psi(x)}{\partial x^2} + \frac{1}{\Psi(y)} \frac{\partial^2 \Psi(y)}{\partial y^2} = -\frac{2m}{\hbar^2} E_x - \frac{2m}{\hbar^2} E_y \quad \text{--- (2)}$$

Motion of the particle in one dimension is independent of motion of particle in other dimension.

So term on left side of eqn (2) is equal to 1st term on right side of eqn

$$\frac{1}{\Psi(x)} \frac{\partial^2 \Psi(x)}{\partial x^2} = -\frac{2m}{\hbar^2} E(x) \quad \text{--- (3)}$$

&

$$\frac{1}{\Psi(y)} \frac{\partial^2 \Psi(y)}{\partial y^2} = -\frac{2m}{\hbar^2} E(y) \quad \text{--- (4)}$$

eqn (3) may be written as-

$$\frac{\partial^2 \Psi(x)}{\partial x^2} + \frac{2m}{\hbar^2} E(x) \Psi(x) = 0$$

The soln of above eqn is -

$$\Psi(x) = \sqrt{\frac{2}{L(x)}} \sin \frac{n\pi x}{L(x)}$$

$$E = \frac{n^2 \hbar^2}{m(L(x))^2}$$

DPP 7 Quantum chemistry **Imp**

1. The degeneracy corresponding to energy of 2D square box with energy $10\pi^2 \hbar^2/2ml^2$ is
 (a) 2 (b) 3 (c) 4 (d) 5

2. The lowest energy level that exist both in 1 D box and 2 D square box of length l is
 (a) $25\hbar^2\pi^2/2ml^2$ (b) $25\hbar^2\pi^2/8ml^2$ (c) $5\hbar^2\pi^2/2ml^2$ (d) $\hbar^2\pi^2/ml^2$

3. The degeneracy of quantum mechanical particle of a cubic box having energy four times that of the ground state energy is **IIT GATE**

a) 3 b) 6 c) 1 d) 4

4. The degeneracy of quantum mechanical particle of a cubic box having energy two times than the ground state energy is **CSIR JRF**

a) 3 b) 6 c) 1 d) 4

5. If cyclobutadiene molecule is treated as particle in 2D square box of 1 nm, then the energy required for the transition from HOMO to LUMO, write also the wave function corresponding to degenerate state. **IIT JAM**

6. The porphyrin molecule (considered planar and treated as 2D square box) has 26 π electrons. If we approximate the length of the molecule is 1000 pm, then what is the predicted lowest energy absorption of the porphyrin molecule. $\frac{5h^2}{8ml^2} = 2.9 \times 10^{-19} \text{ J}$

7. For a particle undergoing quantum mechanical tunneling **TIFR**

i) the amplitude of the wavefunction after passing through the barrier decreases with increases in width. **T**

ii) Tunneling barrier height increases the tunneling probability decreases **T**

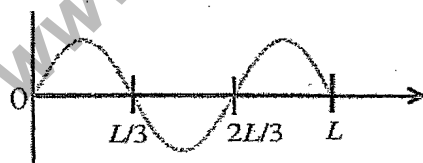
iii) The energy of the particle after the crossing decreases with increases in distance. **F**

The correct statements above are (a) i,ii (b) ii,iii (c) i,iii (d) i,ii,iii (e) none (f) all

8. A proton is confined to a cubic box, whose sides have length 10^{-12} m . What is the minimum kinetic energy of the proton? The mass of proton is $1.67 \times 10^{-27} \text{ kg}$ and Planck's constant is $6.6 \times 10^{-34} \text{ J-sec}$. **(1,1,1) $\frac{3h^2}{8m}$**

a) $1.1 \times 10^{-17} \text{ J}$ b) $3.3 \times 10^{-17} \text{ J}$ c) $9.9 \times 10^{-17} \text{ J}$ d) $6.6 \times 10^{-17} \text{ J}$ **Gate PHY**

9. A free particle of mass m is confined to move in a region of length L . The de Broglie wave associated with particle is sinusoidal in nature as given in the figure the energy of the particle is **IIT JAM PHY**



$$\text{nodes} = 2 \Rightarrow \text{nodes} + 1 = n = 3$$

$$E = \frac{n^2 h^2}{8ml^2} = \frac{(3)^2 \times h^2}{8ml^2} = \frac{9h^2}{8ml^2}$$

10. A particle is confined in a one d box of length $2a$ with potential $v = \infty$ for $x < -a$, $x > a$ and $v = 0$ inside the box. Energy difference between the level $n=3$ and $n=2$ is **-a to a**

a) $5h^2/8ma^2$ b) $9h^2/8ma^2$ c) $9h^2/32ma^2$ d) $5h^2/32ma^2$ **CSIR JRF CH**

11. The probability of finding the particle in one dimensional box of length L in the region between $L/4$ and $3L/4$ for quantum number $n=1$ is **CSIR JRF CH**

a) $1/2$ b) $(1/2) + (1/\pi)$ c) $(1/2) - (1/\pi)$ d) $2/3$

$$\psi = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$$

12. A particle in 3d cubic box of length l has the energy $14h^2/8ml^2$. The degeneracy of the state is **CSIR JRF CH**

a) 2 b) 3 c) 6 d) 9

13 For the eigenstates of the hydrogen atom which of the following relation between the expectation value Kinetic energy and potential energy is true **CSIR JRF CH**

- a) $\langle T \rangle = \langle V \rangle$ b) $2\langle T \rangle = -\langle V \rangle$ c) $2\langle T \rangle = V$ d) $\langle T \rangle = -2\langle V \rangle$

14 An electron of mass m confined to a one dimensional box of length b make a radiative transition from second excited state to ground state the frequency of the photon emitted is
 a) $9h/8mb^2$ b) $3h/8mb^2$ c) h/mb^2 d) $2h/8mb^2$ **IIT GATE**

15 The ground state energy of the Hydrogen atom is -13.6 eV. The energy of the second excited state is a) -27.2 eV b) -6.8 eV c) -1.5 eV d) -4.5 eV

16 A particle of mass m is confined in a two dimensional square well potential of dimension a . This potential $V(x, y)$ is given by $V(x, y) = 0$ for $-a < x < a$ and $-a < y < a$, $V = \infty$ elsewhere The energy of the first excited state for this particle is given by, **Gate physics**

- a) $\hbar^2\pi^2/ma^2$ b) $2\hbar^2\pi^2/ma^2$ c) $5\hbar^2\pi^2/8ma^2$ d) $4\hbar^2\pi^2/ma^2$

17 A particle of mass m is in a cubic box of size a . The potential inside the box ($0 \leq x < a, 0 \leq y < a, 0 \leq z < a$) is zero and infinite outside. If the particle is in an eigenstate of energy $14\hbar^2\pi^2/ma^2$ its wavefunction is **CSIR Phy**

- a) $\psi = (2/a)^{3/2} \sin(3\pi x/a) \sin(5\pi y/a) \sin(6\pi z/a)$ b) $\psi = (2/a)^{3/2} \sin(7\pi x/a) \sin(4\pi y/a) \sin(3\pi z/a)$
 c) $\psi = (2/a)^{3/2} \sin(4\pi x/a) \sin(8\pi y/a) \sin(2\pi z/a)$ d) $\psi = (2/a)^{3/2} \sin(\pi x/a) \sin(2\pi y/a) \sin(3\pi z/a)$

18 A particle is in the ground state of an infinite square well potential given by, $v = 0$ inside the box $-a < x < a$ and $v = \infty$ otherwise The probability to find the particle in the interval between $-a/2$ and $a/2$ is (a) $1/2$ (b) $(1/2) + (1/\pi)$ (c) $(1/2) + (1/\pi)$ (d) $1/\pi$ **CSIR Phy**

IMP. 19 An electron is in the ground state of a hydrogen atom. The probability that it is within the Bohr radius is approximately equal to (a) 0.60 (b) 0.90 (c) 0.16 (d) 0.32 **CSIR Phy**

IMP. 20 A particle is moving in a two dimensional potential well $V=0$ $0 < x < L, 0 < y < 2L$, $V = \infty$ elsewhere which of the following statements about the ground state energy E_1 and ground state eigenfunction ϕ_0 are true? **MSQ IIT JAM Phy**

- a) $E_1 = \hbar^2\pi^2/mL^2$ b) $E_1 = 5\hbar^2\pi^2/8mL^2$
 c) $(2^{1/2}/L) \sin(\pi x/L) \sin(\pi y/2L)$ d) $(2/L) \sin(\pi x/L) \cos(\pi y/2L)$

21 The operator $[(d/dx) - x] [(d/dx) + x]$ is equivalent to **JEST Phy**

- a) $(d^2/dx^2) - x^2$ b) $(d^2/dx^2) - x^2 + 1$ c) $(d^2/dx^2) - 2x(d/dx) + 1$ d) none

22 The zero point energy of a particle of mass m confined to move in a one dimensional box of length l is (a) 0 b) $\hbar^2\pi^2/mL^2$ c) $\hbar^2\pi^2/2mL^2$ d) $3\hbar^2\pi^2/2mL^2$

23 The lowest energy level that is the example of accidental degeneracy, for a particle confined to move in a 3D cubic box of length a is

- i) $12\hbar^2\pi^2/ma^2$ ii) $12\hbar^2\pi^2/8ma^2$ iii) $27\hbar^2\pi^2/ma^2$ iv) $27\hbar^2\pi^2/8ma^2$

24 Fill in the blanks

1) The degeneracy corresponding to quantum mechanical particle in a 3D box of length 'a' with energy $E = 33\hbar^2\pi^2/mL^2$ is ... **12** ... $7^2 + 4^2 + 1, 8^2 + 1^2 + 1^2, 5^2 + 5^2 + 1^2$

2) The wave function corresponding to ground state of a particle in a 2d box of length $0 < x < 2l$ and $0 < y < 2l$ is ... $\sqrt{\frac{1}{2l}} \sin \frac{\pi x}{2l} \sqrt{\frac{1}{2l}} \sin \frac{\pi y}{2l}$

3) Average value of momentum for a quantum mechanical particle of mass m in a 3D cubic box is

similarity eqn (4)

$$\frac{d^2\psi(y)}{dy^2} + \frac{h^2}{2m} E_y \psi(y) = 0$$

$$\psi(y) = \sqrt{\frac{2}{l_y}} \sin \frac{n_y \pi}{l_y} y$$

$$E_y = \frac{(n_y)^2 h^2}{8m(l_y)^2}$$

$$\psi_{2D} = \psi = \sqrt{\frac{2}{l_x}} \sin \frac{n_x \pi}{l_x} x \sqrt{\frac{2}{l_y}} \sin \frac{n_y \pi}{l_y} y$$

$$E_{2D} = E_{(x)} + E_{(y)} = \frac{n_x^2 h^2}{8m l_x^2} + \frac{n_y^2 h^2}{8m l_y^2}$$

In the very same way -

$$\psi_{3D} = \sqrt{\frac{2}{l_x}} \sin \frac{n_x \pi}{l_x} x \sqrt{\frac{2}{l_y}} \sin \frac{n_y \pi}{l_y} y \sqrt{\frac{2}{l_z}} \sin \frac{n_z \pi}{l_z} z$$

$$E_{3D} = \frac{n_x^2 h^2}{8m l_x^2} + \frac{n_y^2 h^2}{8m l_y^2} + \frac{n_z^2 h^2}{8m l_z^2}$$

DPP - 7

(2b)

$$0 < x < L$$

$$0 < x < 2L$$

$$E_{(D)x} = \frac{n_x^2 h^2}{8m l^2} = \frac{1^2 h^2}{8m l^2}$$

$$E_{(D)y} = \frac{n_y^2 h^2}{8m (2L)^2} = \frac{h^2}{32m l^2}$$

★ Concept of degeneracy -

Same eigen value different function

↓ energy value ↓ state

In the energy level diagram of one-D system for every energy level only one state (one-spatial function)

For a 2D OR higher spatial dimensional system if we introduce the symmetry in the PIB model then there may be more than one state OR more than one function for the same value of energy

Degeneracy (Systematic) is the result of introduction of symmetry in PIB model.

When we introduce the symmetry in 2-D box, it becomes 2D-square box as $l_x = l_y = l$

$$E_{\text{SQR}}^{(2D)} = \frac{n_x^2 h^2}{8ml^2} + \frac{n_y^2 h^2}{8ml^2} = \frac{(n_x^2 + n_y^2) h^2}{8ml^2}$$

$$\psi_{\text{SQR}}^{(2D)} = \sqrt{\frac{2}{l}} \sin n_x \frac{\pi x}{l} \sqrt{\frac{2}{l}} \frac{n_y y}{l}$$

$$= \frac{2}{l} \sin n_x \frac{\pi x}{l} \cdot \sin n_y \frac{\pi y}{l}$$

$$= \frac{2}{\sqrt{A}} \sin n_x \frac{\pi}{l} x \sin n_y \frac{\pi}{l} y$$

$$[l^2 = A]$$

↓
Area

Energy level diagram of 2D-Square box -

$$E = \frac{(n_x^2 + n_y^2) h^2}{8ml^2}$$

$$\psi = \frac{2}{l} \sin \frac{n_x \pi x}{l} \sin \frac{n_y \pi y}{l}$$

_____ (3,3) $\frac{18h^2}{8ml^2}$

(4,1) _____ (1,4) $E = 17h^2/8ml^2$

(2,3) _____ (3,2) $E = 13h^2/8ml^2$

(1,3) _____ (3,1) = $\frac{10h^2}{8ml^2}$

$E = \frac{8h^2}{8ml^2}$ _____ 2,2

$E = \frac{5h^2}{8ml^2}$

(1,2)

(2,1)

$\psi_{2,1} = \frac{2}{l} \sin \frac{2\pi x}{l} \sin \frac{\pi y}{l}$

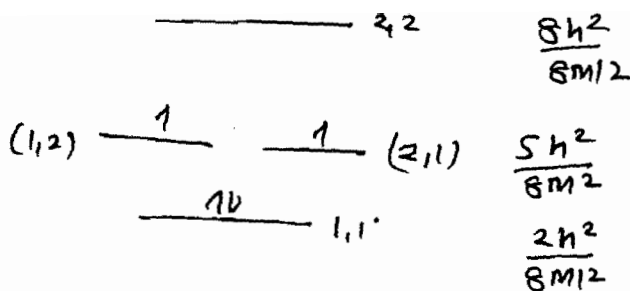
$\psi_{1,2} = \frac{2}{l} \sin \frac{\pi x}{l} \sin \frac{2\pi y}{l}$

(1,1)

$\psi = \frac{2}{l} \sin \frac{\pi x}{l} \sin \frac{\pi y}{l}$

$E = \frac{(1^2 + 1^2) h^2}{8ml^2} = \frac{2h^2}{8ml^2}$

DPP-7



$$\Delta E = [E_{2,2} - E_{(2,1)} = E_{(1,2)}]$$

$$= \frac{3h^2}{8ml^2} = \frac{3 \times (6.6 \times 10^{-34})^2}{8 \times 9.1 \times 10^{-31} \times (1 \times 10^{-9})^2}$$

$l = 1 \text{ nm}$

$\psi_{(1,2)} = \frac{2}{l} \sin \frac{\pi x}{l} \sin \frac{2\pi y}{l} = 2 \sin \pi x \sin 2\pi y \text{ (nm}^{-1}\text{)}$

$\psi_{(2,1)} = \frac{2}{l} \sin \frac{2\pi x}{l} \sin \frac{\pi y}{l} = 2 \sin 2\pi x \sin \pi y \text{ (nm}^{-1}\text{)}$

①

$$\frac{10 \pi^2 h^2}{8mL^2} = \frac{(n_x^2 + n_y^2) \pi^2 h^2}{8mL^2}$$

$$n_x^2 + n_y^2 = 10$$

$$3^2 + 1^2 = 10$$

$$g=2 \quad (3,1) (1,3)$$

★ when we introduce symmetry in 3-D box

$$l_x = l_y = l_z = l$$

The box is considered as 3D-cubic box

$$E = \frac{n_x^2 h^2}{8mL^2} + \frac{n_y^2 h^2}{8mL^2} + \frac{n_z^2 h^2}{8mL^2}$$

$$= \frac{(n_x^2 + n_y^2 + n_z^2) h^2}{8mL^2}$$

★ Spin includes degeneracy becomes double

Fermions - only 2 in one state

Bosons - Any no. in one state.

$$\Psi = \sqrt{\frac{2}{l}} \sin \frac{n_x \pi x}{l} \sqrt{\frac{2}{l}} \sin \frac{n_y \pi y}{l} \sqrt{\frac{2}{l}} \sin \frac{n_z \pi z}{l}$$

$$= \sqrt{\frac{8}{l^3}} \sin \frac{n_x \pi}{l} x \sin \frac{n_y \pi}{l} y \sin \frac{n_z \pi}{l} z$$

$$\downarrow$$

$$\sqrt{\frac{8}{V}} \quad [\because l^3 = V = \text{volume}]$$

(g=6) $\overline{(1,2,3)}$ $\overline{(1,3,2)}$ $\overline{(3,1,2)}$ $\overline{(2,1,3)}$ $\overline{(2,3,1)}$ $\overline{(3,2,1)}$ $E = \frac{14h^2}{8mL^2}$

g=1 $\overline{(2,2,2)}$ $E = \frac{12h^2}{8mL^2}$

g=3 $\overline{(1,3,1)}$ $\overline{(1,1,3)}$ $\overline{(3,1,1)}$ $E = \frac{11h^2}{8mL^2}$

g=3 $\overline{(2,2,1)}$ $\overline{(2,1,2)}$ $\overline{(1,2,2)}$ $E = \frac{9h^2}{8mL^2}$

g=3 $\overline{(1,1,2)}$ $\overline{(1,2,1)}$ $\overline{(2,1,1)}$ $E = \frac{6h^2}{8mL^2}$ $\Psi_{2,1,1}, \Psi_{1,2,1}, \Psi_{1,1,2}$

g=1 $\overline{(1,1,1)}$ $E = \frac{3h^2}{8mL^2}$ $\Psi_{1,1,1}$

~~Accidental~~★ Accidental degeneracy -

When two degenerate state [same energy different state]

does not have any common no. then it is called accidental degeneracy

$$E = \frac{50h^2}{8ml^2} \quad \text{have 3 degeneracy with state}$$

$$\left. \begin{array}{l} (7,1) \\ (1,7) \\ (5,5) \end{array} \right\} \text{Common degeneracy}$$

 $(7,1)(5,5) \text{ \& } (1,7)(5,5) \rightarrow \text{Accidental degeneracy}$
in 3D

$$\frac{27h^2}{8ml^2} = \frac{(n_x^2 + n_y^2 + n_z^2) h^2}{8ml^2}$$

$$n_x^2 + n_y^2 + n_z^2 = 27$$

(3,3,3), (5,1,1) are accidental degeneracy.

★

DPP-7 19★ Probability of 1s orbital of Hydrogen0 to D_0

$$P = 1 - e^{-2D} (2D^2 + 2D + 1) \quad e = 2.7$$

0 to 1D

$$= 1 - e^{-2} (2 + 2 + 1)$$

$$= 1 - 5e^{-2}$$

$$= 1 - 5(2.7)^{-2}$$

★ Hydrogenic Atom -

\Downarrow (Hydrogen or Hydrogen like)	H	He ⁺	n=1 z=2
		Li ⁺⁺	z=3
		Be ⁺⁺⁺	z=4
		B ^{u+}	z=5
		⋮	

In 3-D motion of polar co-ordinate the laplacian operator ∇^2 is obtained by replacing

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

$$y = r \sin \theta \sin \phi$$

$$z = r \cos \theta$$

In laplacian operator of cartesian co-ordinates, we get

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

Then function will be,

If our operator is containing of r, θ & ϕ co-ordinates our functions also depends on r, θ, ϕ co-ordinates

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V$$

$$V = -\frac{ze^2}{4\pi\epsilon_0 r}$$

& schrodinger eqn becomes

$$\nabla^2 \psi + \frac{2m}{\hbar^2} (E - V) \psi = 0$$

$$\left(\frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \psi(r, \theta, \phi) + \frac{2m}{\hbar^2} \left(E + \frac{ze^2}{4\pi\epsilon_0 r} \right) \psi(r, \theta, \phi) = 0$$

Summary-

To describe quantum mech. state of hydrogen like species we need a function Ψ which depends on 6 independent variables (3-co-ordinates of nucleus & 3 for e^-)

$$\Psi = \Psi_n \Psi_e$$

Ψ_n depends on co-ordinate of centre of mass & Ψ_e is considered as internal co-ordinates. Schrodinger eqn separates into two part one for nucleus & one for e^- .

The schrodinger eqn of e^- involve 3 polar co-ordinates r, θ & ϕ . The function R depends on r . These radial parts of wave function

$$\Psi(r, \theta, \phi) = R(r) Y(\theta, \phi)$$

$$R(r) = R_{n,l}$$

$$\Rightarrow \Psi_{n,m,l} = R_{n,l} Y_{l,m}$$

$$Y(\theta, \phi) = Y_{l,m}$$

depends on n & l , permitted value of n is 1, 2, 3, ... & l is 0 to $n-1$

& the value of $R_{n,l}$ is proportional to

$$R_{n,l} \propto \left(\frac{2Zr}{na_0} \right)^l e^{-Zr/na_0} L_{n-l}^{2l+1}$$

Where $L_{n-l}^{2l+1} \rightarrow$ Legendre polynomial $= \frac{d^{2l+1}}{d^{2l+1}}$ L_{n-l}

$$L_{n-l} = e^x \frac{d^{n-l}}{d^{n-l}} e^{-x}$$

$$= e^{-x} \frac{d^{n-l}}{dx^{n-l}} e^x$$

$$1s- \quad n=1 \quad l=0 \quad L_{1+0}^{2 \times 0 + 1} = L_1^1 = \text{const}$$

$$2s- \quad n=2 \quad l=0 \quad L_{2+0}^{2 \times 0 + 1} = L_2^1 = \left(2 - \frac{2Zr}{na_0} \right)$$

$$2p- \quad n=2 \quad l=1 \quad L_3^3 = \text{const}$$

Radial part of 1s for H-atom-

$$n=1$$

$$l=0$$

$$R_{(1,0)} \propto \left(\frac{2 \cdot 1 \cdot \hbar}{1 \cdot a_0} \right)^0 e^{-1\hbar/a_0}$$

$$R_{(1,0)} \propto e^{-\hbar/a_0}$$

$$R = N e^{-\hbar/a_0}$$

Radial part of 2s —

$$n=2$$

$$l=0$$

$$R_{2,0} \propto \left(\frac{2 \cdot 2 \cdot \hbar}{2 a_0} \right)^0 e^{-1 \cdot \hbar / 2 a_0} \left(2 - \frac{2 \cdot 1 \cdot \hbar}{2 a_0} \right)$$

$$R_{2,0} \propto \left(\frac{2 - \hbar}{a_0} \right) e^{-\hbar/2a_0}$$

Radial part of 2p-

$$n=2$$

$$l=1$$

$$R_{2,1} \propto \left(\frac{2 \cdot 1 \cdot \hbar}{2 a_0} \right)^1 e^{-1 \cdot \hbar / 2 a_0}$$

$$R_{2,1} = N \frac{\hbar}{a_0} e^{-\hbar/2a_0}$$

DPP 8 Quantum mechanics

1. Compare the difference of energies of the first excited and ground states of a particle confined in (i) a 1-d box (Δ_1), (ii) a 2-d square box (Δ_2) and (iii) a 3-d cubic box (Δ_3). Assume the length of each of the boxes is the same. The correct relation between the energy differences Δ_1 , Δ_2 , Δ_3 for the three cases is

June CSIR

(1) $\Delta_1 > \Delta_2 > \Delta_3$

~~(2) $\Delta_1 = \Delta_2 = \Delta_3$~~

(3) $\Delta_3 > \Delta_2 > \Delta_1$

(4) $\Delta_3 > \Delta_1 > \Delta_2$

2 Consider a two-dimensional harmonic oscillator with potential energy $V(x, y) = \frac{1}{2}k_x x^2 + \frac{1}{2}k_y y^2$. If $\Psi_{nx}(x)$ and $\Psi_{ny}(y)$ are the eigensolutions and E_{nx} and E_{ny} are the eigenvalues of harmonic oscillator problem in x and y direction with potential $\frac{1}{2}k_x x^2$ and $\frac{1}{2}k_y y^2$, respectively, the wave function and eigenvalues of the above two-dimensional harmonic oscillator problem are

Dec CSIR

(a) $\Psi_{nx,ny} = \Psi_{nx}(x) + \Psi_{ny}(y)$
 $E_{nx,ny} = E_{nx} + E_{ny}$

~~(b) $\Psi_{nx,ny} = \Psi_{nx}(x)\Psi_{ny}(y)$
 $E_{nx,ny} = E_{nx}E_{ny}$~~ $E_{nx} + E_{ny}$

(c) $\Psi_{nx,ny} = \Psi_{nx}(x) + \Psi_{ny}(y)$
 $E_{nx,ny} = E_{nx} + E_{ny}$

(d) $\Psi_{nx,ny} = \Psi_{nx}(x)\Psi_{ny}(y)$
 $E_{nx,ny} = E_{nx}E_{ny}$

3 The difference in energy levels of $n = 2$ and $n = 1$ of a particle in a one dimensional box is 6 units of energy. In the same units, what is the difference in energy levels on $n = 3$ and $n = 2$ for the above system?

June CSIR

- (a) 4 (b) 5 (c) 9 (
- ~~(d) 10~~
-)

4 The energy of a hydrogen atom in a state is $-\frac{hcR_H}{25}$ ($R_H = \text{Rydberg constant}$). The degeneracy of the state will be

Dec CSIR

- (a) 5 (b) 10 (
- ~~(c) 25~~
-) (d) 50

5 The energy of 2s and 2p orbitals is the same for

Dec CSIR

- (a) Li (
- ~~(b) Li^{2+}~~
-) (c)
- Be^{2+}
- (d) H

6 If the ionization energy of H atom is x, the ionization energy of Li^{2+} , is

June CSIR

- (a) 2x (b) 3x (c) 9x (d) 27x

7 Which of the following is true for the radial part of the hydrogen atom wavefunctions $R_{nl}(r)$ (n) principal quantum number and the nodes associated with them? Dec CSIR

- (~~(a)~~) The radial part of only s function is non-zero at the origin and has (n-1) nodes.
 (b) The radial part of s function is zero at the origin and has n number of nodes.
 (c) All radial functions have values of zero at the origin and have (n-1) nodes.
 (d) The radial parts of all s functions are zero at the origin and have no nodes.

$$n-l-1$$

$$l=0$$

$$\Rightarrow n-1$$

8 The most probable value of 'r' for an electron in 1s orbital of hydrogen atom is

- (a) $a_0/2$ (b) a_0 (c) $\sqrt{2}a_0$ (d) $3a_0/2$

Dec CSIR

9 The orbital with two radial and two angular nodes is

- (a) 3p (b) 5d (c) 5f (d) 8d

Dec CSIR

Imp. 10 The hydrogenic orbital with the form of the radial function

June CSIR

$$r^2(\alpha_1 - r)(\alpha_2 - r) \exp[-\beta r], \text{ where } \alpha_1, \alpha_2 \text{ and } \beta = 0$$

Are constants, May be identified as a

- (a) 3d orbital (b) 4f orbital (c) 5d orbital (d) 5f orbital

11 A hydrogenic orbital with radial function of the form $r^\alpha \exp[-\beta r]$ and ϕ - part as $\exp[-3i\phi]$ corresponds to

June CSIR

- (a) $n > 4, \ell > 3, m = 3$ (b) $n > 4, \ell = 3, m = -3$
 (c) $n > 4, \ell = 3, m = 3$ (d) $n = 4, \ell = 3, m = -3$

12 The angular momentum operator $L_z = -i\hbar \frac{\partial}{\partial \phi}$ has eigen functions of the form $\exp[iA\phi]$. The

condition that a full rotation leaves such an eigen function unchanged is satisfied for all the values of A.

Dec CSIR

(a) $0, \pm \frac{1}{3}, \pm \frac{2}{3}, \pm 1, \pm \frac{4}{3}, \dots$ (b) $0, \pm 1, \pm 2, \pm 3, \dots$

(c) $0, \pm \frac{1}{2}, \pm 1, \pm \frac{3}{2}, \dots$ (d) $0, \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$

$A = m$
 $m = 0, \pm 1, \pm 2, \dots$

13. If the angular part of wavefunction is $\sin^2 \Theta \cos \Theta e^{2i\phi}$ then the value of l and m respectively are Gate chem

- a) 3,3 b) 3,2 c) 2,3 d) 2,2

Imp. 14 The un-normalized wavefunction of a particle in a spherically symmetric potential is given by $\psi = zf(r)$ where $f(r)$ is a function of the radial variable r . The eigenvalue of the operator L^2 (namely the square of the orbital angular momentum) is Phy

- (a) $\hbar^2/4$ (b) 0 (c) $\hbar^2/2$ (d) $2\hbar^2$

15 Given that operator $p_r = -i\hbar[(\delta/\delta r) + (1/r)]$ the uncertainty Δp_r in the ground state of hydrogen atom is

- a) \hbar/a_0 b) $\hbar/2a_0$ c) $2\hbar/a_0$ d) 0 Phy

16 The normalized ground state wave function of a hydrogen atom is given by

$\psi = (1/\sqrt{4\pi})(2/a)^{3/2} e^{-r/a}$ where a is the Bohr radius and r is the distance of electron from the nucleus the expectation value of $\langle 1/r^2 \rangle$ is Phy

- a) $4/a^2$ b) $2/a^2$ c) $4\pi/a^2$ d) $2\pi/a^2$

17. Consider the statements

i) The normalisation constant for radial part of the wave function for the ground state of wave function is $N = \dots \frac{2}{a_0^{3/2}}$

ii) The normalisation constant for the angular part of wave function of p_z orbital is

iii) The presence of radial node in 2s orbital of hydrogen atom is at $r = \dots 2a_0 \dots$

(3) The magnetic quantum No. m describe (2) component of angular momentum through the eqn -

$$L_z = m\hbar$$

$$\hat{L}_z = -i\hbar \frac{d}{d\phi}$$

To verify this value $L_z = m\hbar$ apply $\hat{L}_z \psi_{l,m}$

$$\begin{aligned}\hat{L}_z \psi_{l,m} &= -\frac{i\hbar}{d\phi} \left[\sin^{|m|} \theta \cos^{\ell-|m|} \theta e^{im\phi} \right] \\ &= \sin^{|m|} \theta \cos^{\ell-|m|} \theta -i\hbar \left(\frac{d}{d\phi} e^{im\phi} \right) \\ &= m\hbar \left(\sin^{|m|} \theta \cos^{\ell-|m|} \theta e^{im\phi} \right) \\ &= m\hbar \psi_{l,m}\end{aligned}$$

$$L_z = m\hbar$$

DPP-8

(14)

$$\psi = z f(r)$$

$$z = r \cos \theta$$

$$\psi = r \cos \theta f(r)$$

$$\sin^0 \theta \cos^1 \theta e^{i0\phi} = \sin^{|m|} \theta \cos^{\ell-|m|} \theta e^{im\phi}$$

$$l=1$$

Imp Qus-

for the wave function

$$\psi = r(r-a)e^{-r/a_0} \sin\theta \cos\theta e^{i\phi}$$

find the value of

$$E$$

$$L^2$$

$$L_z$$

no. of Radial node

no. of angular node

Possible Hydrogenic species Name

Soln →

$$n = 4$$

$$l = 2$$

$$m = 1$$

Radial node $(r-a) = 0$

$$r = a$$

$$n - l - 1 = 1$$

$$n = 4$$

$$E = -13.6 \frac{Z^2}{n^2}$$

$$= -13.6 \frac{(4)^2}{(4)^2}$$

$$= -13.6 \text{ eV}$$

$$e^{-Zr/na_0} = e^{-r/a_0}$$

$$-\frac{Zr}{na_0} = -\frac{r}{a_0}$$

$$Z = 4$$

$$n = 2$$

$$L^2 = l(l+1)\hbar^2$$

$$= 2(2+1)\hbar^2$$

$$L^2 = 6\hbar^2$$

$$L_z = m\hbar = 1\hbar$$

$$L_z = \hbar$$

$$\text{No. of angular node} = l$$

$$l = 2$$

Radial nodes - To check the position or no. of radial nodes put radial part of wave function = 0 & get

for 1s -

$$R_{1,0} = 0$$

$$N e^{-r/a_0} = 0$$

$$N \neq 0$$

$$\Rightarrow e^{-r/a_0} = 0$$

$$e^{-r/a_0} = e^{-\infty}$$

$$r/a_0 = \infty$$

$$r = \infty \rightarrow \text{Boundary}$$

No node

for 2s -

$$R_{2,0} = 0$$

$$N \left(2 - \frac{r}{a_0} \right) e^{-r/2a_0} = 0$$

$$2 - \frac{r}{a_0} = 0$$

$$\boxed{r = 2a_0} \rightarrow \text{Node in 2-s orbital}$$

&

$$e^{-r/2a_0} = e^{-\infty}$$

$$\Rightarrow \boxed{r = \infty} \text{ no radial node}$$

One radial node for 2-s

for 2-p -

$$R_{2,1} = 0$$

$$N \frac{r}{a_0} e^{-r/2a_0} = 0$$

$$r = 0 \text{ boundary}$$

$$r = \infty \text{ boundary}$$

No radial node.

When we extend this series for radial part of wave function for various orbital, we get that radial part of function becomes zero $(n-l-1)$ times

$$\therefore \text{Radial node} = n-l-1$$

From the relation -

$$R_{n,l} \propto \left(\frac{2Zr}{na_0}\right)^l e^{-Zr/na_0} \quad \begin{matrix} \alpha^{n+1} \\ L_{n+1} \end{matrix}$$

If $l=0$ (for s orbital)

at $r=0$

$R_{n,l} \neq 0 \Rightarrow$ Radial part of function is non-zero at origin.

If $l=1, 2, 3, \dots$ ($l \neq 0$, ~~at~~ p, d, f orbitals)

at $r=0$

$$R_{n,l} = 0$$

\Rightarrow Radial part of function is zero at origin.

DPP-8

(10)

$$r^2(\alpha_1-r)(\alpha_2-r)e^{-Br} = 0$$

if $r=0$

if $\alpha_1-r=0 \quad r=\alpha_1$

if $\alpha_2-r=0 \quad r=\alpha_2$

if $e^{-Br}=0 \quad r=\infty$

2 nodes,

★ Normalization Const. for radial part of wave function for ground state -

www.chemistryABC.com

$$R_{1,0} \propto e^{-r/a_0}$$

$$R_{1,0} = N e^{-r/a_0}$$

$$\int R_{1,0} R_{1,0} d\tau = 1$$

$$\int N e^{-r/a_0} N e^{-r/a_0} d\tau = 1$$

$$N^2 \int_0^{\infty} e^{-2r/a_0} r^2 dr = 1$$

$$N^2 \frac{2!}{\left(\frac{2}{a_0}\right)^3} = 1$$

$$N^2 \frac{2}{8} a_0^3 = 1$$

$$N^2 = \frac{4}{a_0^3}$$

$$N = \frac{2}{a_0^{3/2}}$$

GATE-2001

$$\psi_{n,l,m} = R_{n,l} Y_{l,m}$$

$$R_{2,0} \propto \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$$

$$Y = \frac{1}{\sqrt{4\pi}}$$

$$\left(2 - \frac{r}{a_0}\right) e^{-r/2a_0} = 0$$

$$r = 2a_0$$

Angular part of wave function $\Psi(\theta, \phi)$ is dependent on θ & ϕ
 θ part of wave function depend on l & $|m|$ & ϕ part of wave function depends on m only.

θ function depends only on magnitude of m , does not describe the direction, while ϕ is proportional to

$$Y_{l,m} \propto \sin^{|m|} \theta \cos^{\lambda-|m|} \theta e^{im\phi}$$

$$Y_{l,m} \propto \sin^{|m|} \theta \cos^{\lambda-|m|} \theta e^{im\phi}$$

for ① $l=0, m=0$ - S-orbital

$$Y_{0,0} = \frac{1}{\sqrt{4\pi}} \rightarrow \text{Angular function for s-orbital}$$

$$\Psi_{\text{total}} = \Psi_{n,l,m} = R_{n,l} Y_{l,m} = \frac{2}{a_0^{3/2}} e^{-r/a_0} \cdot \frac{1}{\sqrt{4\pi}}$$

$$\Psi_{1,0,0} = \frac{1}{\sqrt{\pi}} a_0^{-3/2} e^{-r/a_0}$$

$n=1$
 $l=0$
 $m=0$

$$\Psi_{1s} = \frac{1}{\sqrt{\pi}} a_0^{-3/2} e^{-r/a_0}$$

② for

$l=1, m=0$	(angular) p_0	$= \sin^0 \theta \cos^{1-0} \theta e^{i0\phi} \propto \cos \theta$
$l=1, m=+1$	(angular) p_1	$= \sin^1 \theta \cos^{1-1} \theta e^{i \cdot 1 \cdot \phi} \propto \sin \theta e^{i\phi}$
$l=1, m=-1$	(angular) p_{-1}	$= \sin^{1-1} \theta \cos^{1-1-1} \theta e^{i(-1)\phi} \propto \sin \theta e^{-i\phi}$

$$Y_{1,1} = N \sin \theta e^{i\phi}$$

$$\int Y_{1,1}^* Y_{1,1} d\tau$$

p_0	$l=1, m=0$
p_1	$l=1, m=-1$
p_{+1}	$l=1, m=+1$
d_1	$l=2, m=1$
d_{-1}	$l=2, m=-1$
d_2	$l=2, m=2$
d_{-2}	$l=2, m=-2$
d_0	$l=2, m=0$

$Y_{1,0} \propto \cos\theta$
$Y_{1,-1} \propto \sin\theta e^{-i\phi}$
$Y_{1,1} \propto \sin\theta e^{i\phi}$
$Y_{2,1} \propto \sin\theta \cos\theta e^{i\phi}$
$Y_{2,-1} \propto \sin\theta \cos\theta e^{-i\phi}$
$Y_{2,2} \propto \sin^2\theta e^{2i\phi}$
$Y_{2,-2} \propto \sin^2\theta e^{-2i\phi}$
$Y_{2,0} \propto 3\cos^2\theta - 1$

Qus- find the value of n, l, m , for the function

Soln - $\Psi_{n,l,m} \propto \left(2 - \frac{r}{a_0}\right) e^{-Rr} \cos\theta$
 \downarrow
 $m=0$
 $l=1$

$2 - \frac{r}{a_0} = 0$

$r = 2a_0$

① radial nodes

$\Rightarrow n - l - 1 = 1$
 $n - 1 - 1 = 1$
 $n = 3$

$n=3$
 $m=0$
 $l=1$

3 p_0

DPP-8

(11)

$r \propto e^{-Br} e^{-3i\phi}$
 $e^{im\phi}$

$m = -3$

$r=0, l=0, r=\infty$ } Nonode

$l=3$ $\cos^{l-|m|} \theta = \cos^0 \theta$

$n - l - 1 = 0$
 $n - 3 - 1 = 0$ $n = 4$

* Significance of n, l, m -

(i) The principal quantum no. (n) describe the energy of e^- in Hydrogen like species and is given by

$$E = -\frac{e^2}{8\pi\epsilon_0} \cdot \frac{1}{a_0} \cdot \frac{Z^2}{n^2}$$

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{me^2}$$

$$E = -13.6 \frac{Z^2}{n^2}$$

$$E = -0.5 \frac{Z^2}{n^2}$$

$$E = -R_H hc \frac{Z^2}{n^2}$$

$$R_H hc = \frac{me^4}{8\pi\epsilon_0 (4\pi\epsilon_0) \hbar^2}$$

$n=1$	1s	—	1 state
$n=2$	2s 2p	—	4 state
$n=3$	3s 3p 3d	—	9 state
$n=4$	4s 4p 4d 4f		

$$\text{for } n = n^2 \text{ states}$$

Energy is completely dependent on (n)

\therefore 2s & 2p have same value of energy \Rightarrow degeneracy

Energy of e^- in Hydrogenic atom depends only on (n) not on l & m . Thus all ψ_e (electronic function) with same value of n but different value of l & m are degenerate i.e. they have same energy.

Thus the degeneracy of orbital for given value of n is n^2

When $n=1$ 1s $E = -\frac{e^2}{8\pi\epsilon_0 a_0} Z^2$

$n=2$ 2s 2p $E = -\frac{e^2}{32\pi\epsilon_0 a_0} Z^2$

$n=3$ 3s 3p 3d $E = -\frac{e^2}{72\pi\epsilon_0 a_0} Z^2$

The degeneracy $g_n = n^2$ exist in the system only when it is considered that electric field & magnetic field are completely absent.

If spin of the e^- also included then degeneracy become double

$$g_n = 2n^2$$

eg- (He^+) - 2.0 a.u (given)

$$\begin{aligned} -2.0 \text{ a.u} &= \frac{-0.5 \text{ a.u} \cdot Z^2}{n^2} \\ &= \frac{-0.5 \times (2)^2}{n^2} \end{aligned}$$

$$n^2 = 2$$

$$g_n = 1$$

eg- (H) - 3.4 eV (given)

$$-3.4 \text{ eV} = \frac{-13.6 (1)^2}{n^2}$$

$$n^2 = 4$$

$$g_n = n^2 = 4$$

② The azimuthal quantum No. describe the total angular momentum of e^- through the expression

$$L^2 = l(l+1)\hbar^2$$

The value of l → derived from spectroscopic Term

0	s	Sharp
1	p	principal
2	d	diffuse
3	f	fundamental
4	g	
5	h	
6	i	

The value of L^2 i.e. $L(L+1)\hbar^2$ may be verified by operating the operator of L^2 on the wave function $\Psi_{n,l,m}$ OR $Y_{l,m}$

The corresponding value is $L(L+1)\hbar^2$

$$L^2 = \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right]$$

$$Y_{0,0} = 0 \quad Y_{1,0} = 0(0+1)\hbar^2 Y_{1,0}$$

$$l=0 \\ m=0$$

$$Y_{1,0} = 2\hbar^2 Y_{1,0} = 1(1+1)\hbar^2 Y_{1,0}$$

$$l=1 \\ m=0$$

$$Y_{2,0} = 6\hbar^2 Y_{2,0} = 2(2+1)\hbar^2 Y_{2,0}$$

$$l=2 \\ m=0$$

By using $Y_{1,0} = N \cos\theta$ verify that $L^2 = L(L+1)\hbar^2$

$$-\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right] N \cos\theta$$

$$-\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin\theta \frac{\partial}{\partial\theta} \cos\theta \right]$$

$$= -N\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} (\sin^2\theta) \right]$$

$$= N\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \sin^2\theta \right]$$

$$= N\hbar^2 \left[\frac{1}{\sin\theta} 2\sin\theta \cos\theta \right]$$

$$= 2\hbar^2 [N \cos\theta] \rightarrow \text{given function}$$

↓ eigen value

DPP 9 Quantum mechanics

1. In a spherical polar coordinate system, a point A at (x, y, z) in the Cartesian coordinate system can be described by (r, θ , ϕ) where r, θ , and ϕ have their usual meaning. Expression for the volume of an infinitesimally small cube confined by dx, dy, and dz in terms of the spherical coordinate system is given by TIFR 2012

A) $rdrd\theta d\phi$ B) $r\sin\theta drd\theta d\phi$ C) $r^2 \sin^2\theta drd\theta d\phi$ D) $r^2 \sin\theta drd\theta d\phi$

2 The degeneracy of the energy level $12h^2/8ma^2$ of a particle in a three dimensional cube of length "a" is A) 1 B) 3 C) 6 D) 12 TIFR 2012

3 What is the degeneracy of the energy level with $n=6$ (n being the principal quantum number) in a hydrogenic atom or ion? A) 16 B) 9 C) 36 D) 25 TIFR 2013 $g_n = n^2$

4 Which of the following statement is not true TIFR 2015

i) The state function $\psi(x,t)$ is always equal to a function of time multiplied by a function of coordinate. F

ii) If f_1 and f_2 are eigen functions of operator B then $C_1 f_1 + C_2 f_2$ must always be an eigenfunction of B. where C_1 and C_2 are constants. F

iii) The operator L^2 commute with $L_x + L_y$. T

a) i,iii (b) i,ii (c) ii,iii (d) only iii

5 Four particles of mass m each are inside a two dimensional square box of side L. If each state obtained from the solution of the Schrodinger equation is occupied by only one particle, the minimum energy of the system in units of h^2/ml^2 is

(a) 2 (b) 5/2 (c) 11/2 (d) 25/4 IIT JAM Physics

6 The ground state energy of a particle of mass m in a three dimensional cubical box of side L is not zero but $3h^2/8mL^2$. This is because TIFR Physics 2015

(a) The ground state has no nodes in the interior of the box. (b) This is the most convenient choice of the zero level of potential energy. (c) Position and momentum cannot be exactly determined simultaneously. (d) The potential at the boundaries is not really infinite, but just very large.

7 A particle is confined in a 3D cubic well of width L with impenetrable wall

i) The sum of the energy of third and fourth energy level is Gate P

a) $10\pi^2\hbar^2/mL^2$ b) $10\pi^2\hbar^2/3mL^2$ c) $11\pi^2\hbar^2/2mL^2$ d) $15\pi^2\hbar^2/2mL^2$

ii) The degeneracy of fourth level is given by

a) 1 b) 2 c) 3 d) 4

8 In an hydrogen atom the coulomb degeneracy for the $n=4$ state is Gate P

a) 4 b) 16 c) 18 d) 32

9 An atomic state of hydrogen atom is represented as $\psi = (1/2a_0)^{3/2} [1 - (r/2a_0)] e^{-r/2a_0} \cos\theta$ Where a_0 is a constant value The quantum number of the state are Gate P

a) $l=0, m=0, n=1$ b) $l=1, m=1, n=2$ c) $l=1, m=0, n=3$ d) $l=1, m=1, n=3$

10 A particle of mass m is confined in a two dimensional square well potential of dimension a. This potential is given by $V=0$ for $0 < x < a$ and $0 < y < a$, $V=\infty$ elsewhere

The energy of the first excited state is Jam P

5

a) $\pi^2 \hbar^2 / ma^2$ b) $2\pi^2 \hbar^2 / ma^2$ c) $5\pi^2 \hbar^2 / 2ma^2$ d) $4\pi^2 \hbar^2 / 2ma^2$

11 The ground state wavefunction ψ of hydrogen atom in spherical coordinates has no angular dependence but only radial dependence. The ψ is an eigen function of Gate P

- a) L_x, L_y and L_z simultaneously b) L_z but not of L_x and L_y
 c) none of L_x, L_y and L_z d) p_z only

12 The energy of second excited state of the hydrogen atom is

a) -27.2 eV b) -6.8 eV c) -1.5 eV d) -4.5 eV

13 The one electron states for non interacting electron confined in a cubic box of side a are $E_0 < E_1 < E_2 < E_3$ etc

i) the energy of the lowest state is

a) 0 b) $\pi^2 \hbar^2 / 2ma^2$ c) $\pi^2 \hbar^2 / ma^2$ d) $3\pi^2 \hbar^2 / 2ma^2$ Gate P

ii) The degeneracy (including spin) of the level E_3 is

a) 2 b) 4 c) 6 d) 8

14 An electron in the Li^{2+} atom is in a state whose energy is -3.4 eV the degeneracy of the state is a) 4 b) 16 c) 36 d) none

15. The number of radial node of the radial wavefunction for an atomic electron $R(r) = A[27 - 18r + 2r^2] e^{-r/3}$ is

a) 0 b) 1 c) 2 d) 3

16 The radial wavefunction of the electron in the state $n=1, l=0$ in hydrogen atom is $R_{10} = (2/a_0^{3/2}) e^{-r/a_0}$

i) The most probable radius for r in 1s Orbital of hydrogen atom is Gate P, C

a) a_0 b) $2a_0$ c) $4a_0$ d) $8a_0$

17. Consider the statements

i) the radial part of wave function of S orbital of hydrogenic atom is nonzero at origin because radial part is containing of r^l terms. T

ii) The degeneracy corresponding to energy value $-e^2/72\pi\epsilon_0 a_0$ for an electron in an orbital of hydrogen atom is 9. T

iii) If angular part is containing of only $\cos\theta$ term than the value of $l=0$. F

The correct statements above are a) I,ii b) ii,iii c) I,iii d) all e) none

18 Which of the following function is acceptable for an electron in hydrogenic atom which motion is governed by polar coordinate (r, θ, ϕ)

a) e^{-r}/r b) $e^{-r} \cos \theta \sin \theta \sin(\phi/2)$
 c) $e^{-r} \sin(h\phi)$ d) $e^{-r} \cos \theta \sin \theta \sin \phi$

19 Fill in the blanks

i) The eigenvalue corresponding to kinetic energy operator for an electron in 2S orbital of hydrogen atom is 3.4 eV.

ii) The most probable radius for an electron in 2p orbital of hydrogen atom is $4a_0$..

iii) The average value of radius for an electron in 2p orbital is (higher/lower) than the average value of radius for an electron in 2S orbital of hydrogen atom

20 Find the most probable radius for an electron in 2s orbital of hydrogen atom wave function corresponding to 2s orbital is given to you. $2a_0$

imc
 cor
 fu
 for
 g.pw

F

⑤

$$\begin{array}{ccc}
 \text{---} \cdot \text{---} & (2,2) & \frac{h^2}{8ma^2} \\
 (1,2) \text{---} \cdot \text{---} & & \\
 \text{---} \cdot \text{---} & (2,1) & \frac{5h^2}{8ma^2} \\
 \text{---} \cdot \text{---} & & \\
 \text{---} \cdot \text{---} & (1,1) & \frac{8h^2}{8ma^2}
 \end{array}$$

$$\frac{2h^2}{8ma^2} + \frac{2 \times 5h^2}{8ma^2} + \frac{8h^2}{8ma^2} = \frac{20h^2}{8ma^2} = \frac{5}{2} \frac{h^2}{8a^2}$$

Designation of orbital ($A_s, p_x, p_y, p_z, \dots$) -

Pictorial representation of the angular part of wave function with $m \neq 0$ becoz it contain imaginary part in it.

So to represent spatial representation we have to remove imaginary part by taking linear combination of wave function concept into consideration (summation or subtraction of two eigen function is eigen functions of corresponding operators) degenerate
 for example we take the linear combination of $\psi_{1,1}$ & $\psi_{1,-1}$ to remove g. part as $\psi_{1,1} + \psi_{1,-1} = \sin\theta e^{i\phi} + \sin\theta e^{-i\phi}$

$$\begin{aligned}
 &= \sin\theta (e^{i\phi} + e^{-i\phi}) \\
 &= \sin\theta \cos\phi
 \end{aligned}$$

$$\begin{aligned}
 \psi_{1,1} - \psi_{1,-1} &= \sin\theta (e^{i\phi} - e^{-i\phi}) \\
 &= \sin\theta \sin\phi
 \end{aligned}$$

From this combination we may anticipate

$$\begin{array}{l}
 e^{im\phi} = \cos m\phi \\
 e^{-im\phi} = \sin m\phi
 \end{array}$$

$$\begin{array}{l}
 e^{im\phi} = \cos m\phi \\
 e^{-im\phi} = \sin m\phi
 \end{array}$$

$$p_1 \rightarrow \psi_{1,1} \propto \sin\theta e^{i\phi}$$

$$\sin\theta \cos\phi - p_x$$

$$\begin{aligned} x &= r \sin\theta \cos\phi \\ y &= r \sin\theta \sin\phi \\ z &= r \cos\theta \end{aligned}$$

$$p_0 \rightarrow \psi_{1,0} \propto \cos\theta - p_z$$

$$p_{-1} \rightarrow \psi_{1,-1} \propto \sin\theta e^{-i\phi} - \sin\theta \sin\phi - p_y$$

$$d_0 \rightarrow \psi_{2,0} \propto 3\cos^2\theta - 1 - dz^2$$

$$d_1 \rightarrow \psi_{2,1} \propto \sin\theta \cos\theta e^{i\phi} - \sin\theta \cos\theta \cos\phi = dxz$$

$$d_{-1} \rightarrow \psi_{2,-1} \propto \sin\theta \cos\theta e^{-i\phi} - \sin\theta \cos\theta \sin\phi = dyz$$

$$d_2 \rightarrow \psi_{2,2} \propto \sin^2\theta e^{2i\phi} - \sin^2\theta \cos 2\phi \rightarrow dx^2 - y^2$$

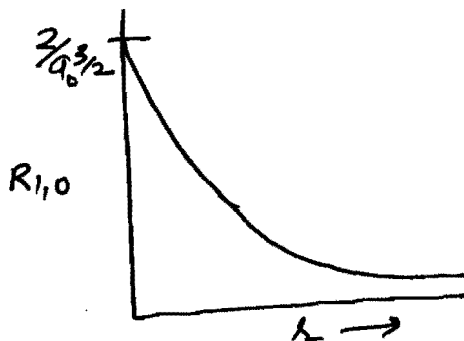
$$d_{-2} \rightarrow \psi_{2,-2} \propto \sin^2\theta e^{-2i\phi} - \sin^2\theta \sin 2\phi - d_{xy}$$

Azimuthal Q.N.	Magnetic Q.N.	Angular part of wave function	Linear Combination	Identification of orbital	Angular part of orbital designation
1	0	$\psi_{1,0} \propto \cos\theta$	not needed	$z = r \cos\theta$	$(p_z)_{ang} \propto \cos\theta$
1	+1	$\psi_{1,1} \propto \sin\theta e^{i\phi}$	$\psi_{1,1} + \psi_{1,-1} \propto \sin\phi \cos\phi$	$x = r \sin\theta \cos\phi$	$\psi_{p_x} \propto \sin\theta \cos\phi$
1	-1	$\psi_{1,-1} \propto \sin\theta e^{-i\phi}$	$\psi_{1,1} - \psi_{1,-1} \propto \sin\phi \sin\phi$	$y = r \sin\theta \sin\phi$	$\psi_{p_y} \propto \sin\theta \sin\phi$
2	0	$\psi_{2,0} \propto 3\cos^2\theta - 1$	not needed	$\cos^2\theta$ tends to z^2	$(\psi_{d_{z^2}})_{ang} \propto 3\cos^2\theta - 1$
2	1	$\psi_{2,1} \propto \sin\theta \cos\theta e^{i\phi}$	$\psi_{2,1} + \psi_{2,-1} \propto \sin\theta \cos\theta \cos\phi$	$\sin\theta \cos\theta \propto z$	$(\psi_{d_{xz}})_{ang} \propto \sin\theta \cos\theta \cos\phi$
2	-1	$\psi_{2,-1} \propto \sin\theta \cos\theta e^{-i\phi}$	$\psi_{2,1} + \psi_{2,-1} \propto \sin\theta \cos\theta \sin\phi$	tends to yz	$(\psi_{d_{yz}})_{ang} \propto \sin\theta \cos\theta \sin\phi$
2	+2	$\psi_{2,2} \propto \sin^2\theta e^{2i\phi}$	$\psi_{2,2} + \psi_{2,-2} \Rightarrow x^2 - y^2$	$\Rightarrow x^2 - y^2$	$(\psi_{d_{x^2-y^2}})_{ang} \propto \sin^2\theta \cos 2\phi$
2	-2	$\psi_{2,-2} \propto \sin^2\theta e^{-2i\phi}$	$\psi_{2,2} - \psi_{2,-2}$		$(\psi_{d_{xy}})_{ang} \propto \sin^2\theta \sin 2\phi$

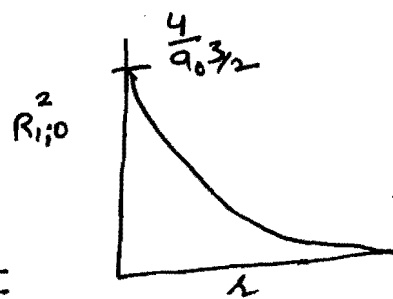
★ Plot of radial part of wave function -

(i) $R_{1,0}$ vs r

$$(R_{1,0}) = \frac{2}{a_0^{3/2}} e^{-r/a_0}$$



(ii) $R_{1,0}^2$ vs r (Density)



When we plot the graph of radial part of function vs r we get that $R_{1,0}$ and the density $R_{1,0}^2$ is maximum at $r=0$ (at origin (or for an e^- in 1s orbital))

But it does not describe the real picture.

To describe the probability of finding an e^- in any orbital we plot a graph b/w radial distribution function ($r^2 R_{1,0}^2$) v/s r

As we know radial probability of finding e^-



$$\int P(r) dr = \int R(r) R(r) dr = \int r^2 R^2 dr$$

$$P(r) = r^2 R^2$$

Most probable distance (The distance at which the probability of finding an e^- in an orbital is maximum) may be

obtained by applying maxima and minima condition on RDF

$P(r)$ is maximum in term of r only when,

$$\frac{dP(r)}{dr} = 0$$

$$\frac{d(r^2 R^2)}{dr} = 0$$

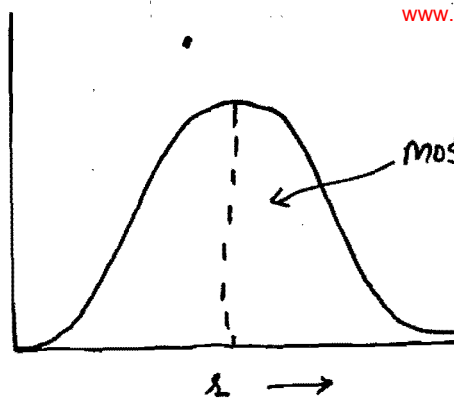
→ Radial distribution function -

RDF

$r^2 R_{1,0}^2$ v/s r

$r^2 R_{1,0}^2$

↑



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$$r^2 R_{1,0}^2 = \frac{4}{a_0^3} r^2 e^{-2r/a_0}$$

If $r=0$ $r^2 R_{1,0}^2 = 0$

$$r^2 R_{1,0}^2 = \frac{4}{a_0^3} r^2 e^{-2r/a_0}$$

↑ ↑
w.r.t w.r.t.
↑es ↓es

$$\frac{d}{dr} r^2 R_{1,0}^2 = 0$$

$$\frac{d}{dr} \frac{4}{a_0^3} r^2 e^{-2r/a_0} = 0$$

$$\frac{4}{a_0^3} \frac{d}{dr} r^2 e^{-2r/a_0} = 0$$

$$r^2 \frac{d}{dr} e^{-2r/a_0} + e^{-2r/a_0} \frac{d}{dr} r^2 = 0$$

$$r^2 \left(-\frac{2}{a_0} e^{-2r/a_0} \right) + e^{-2r/a_0} \cdot 2r = 0$$

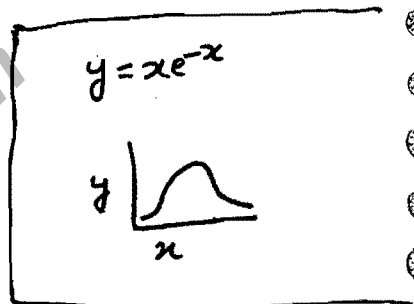
$$2r e^{-2r/a_0} \left[-\frac{r}{a_0} + 1 \right] = 0$$

$$-\frac{r}{a_0} + 1 = 0$$

$$r = a_0$$

most probable radius,

$$r_{m.p} = a_0$$



(*)

$$R_{2,0} \text{ v/s } r$$

$$\Psi_{2,0,0} = \frac{1}{4\sqrt{2\pi} a_0^{3/2}} \left(2 - \frac{r}{a_0} \right) e^{-r/2a_0}$$

$$\Psi_{2,0,0} = R_{2,0} Y_{0,0}$$

$$R_{2,0} = \frac{\Psi_{2,0,0}}{Y_{0,0}} = \sqrt{4\pi} \Psi_{2,0,0}$$

$$= \frac{\sqrt{4\pi}}{4\sqrt{2\pi} a_0^{3/2}} \left(2 - \frac{r}{a_0} \right) e^{-r/2a_0}$$

$$R_{2,0} = \frac{1}{\sqrt{8} a_0^{3/2}} \left(2 - \frac{r}{a_0} \right) e^{-r/2a_0}$$

$$r=0 = \frac{1}{\sqrt{8} a_0^{3/2}} (2-0) e^0 + \frac{1}{\sqrt{8} a_0^{3/2}}$$

$$(R_{2,0})_{\max} = \frac{1}{\sqrt{8} a_0^{3/2}}$$

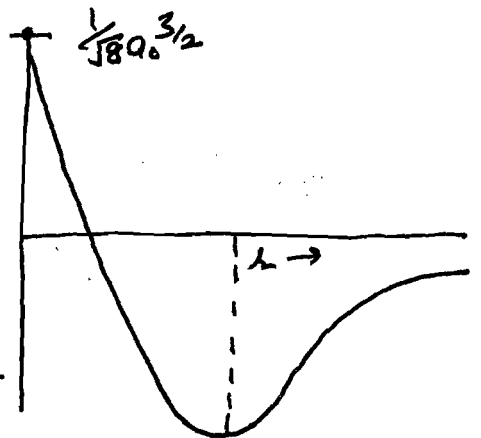
$$R_{2,0} = 0$$

$$N \left(2 - \frac{r}{a_0} \right) e^{-r/2a_0} = 0$$

↓

$$2 - \frac{r}{a_0} = 0$$

$$r = 2a_0 \quad \text{node}$$



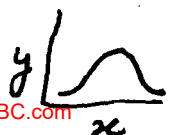
↓

$$(R_{2,0}) = 2e^{-r/2a_0} - \frac{r}{a_0} e^{-r/2a_0}$$

↓
+ve

↓
-ve

$$y = x e^{-x}$$



→ most probable radius -

$$\frac{d}{dr} (R_{2,0}) = 0$$

$$\lambda^2 R_{2,0}^2 \text{ v/s } \lambda \quad (2s\text{-orbital})$$

Most probable distance for $R_{2,0}$ may be obtained by -

$$\frac{d}{d\lambda} \lambda^2 R_{2,0}^2 = 0$$

When we solve it we get

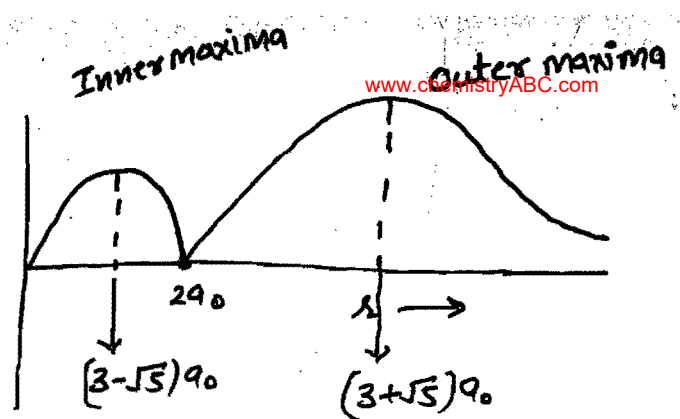
$$\lambda = 0$$

$$\lambda = (3 - \sqrt{5})a_0 \text{ — (inner maxima)}$$

$$\lambda = (3 + \sqrt{5})a_0 \text{ — (outer maxima)}$$

$$\lambda = 2a_0$$

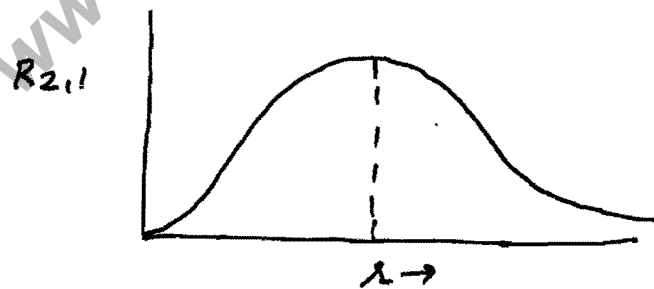
$$\lambda^2 R_{2,0}^2$$



$$R_{2,1} \text{ v/s } \lambda \text{ — (p-orbital)}$$

$$R_{2,1} \propto \frac{\lambda}{a_0} e^{-\lambda/2a_0}$$

$$R_{2,1} = N \frac{\lambda}{a_0} e^{-\lambda/2a_0}$$



$$\lambda = 0$$

$$R_{2,1} = 0$$

$$[R_{2,1}]_{\max} = \frac{d(R_{2,1})}{d\lambda} = 0$$

$$r^2 R_{2,1}^2 \text{ v/s } r$$

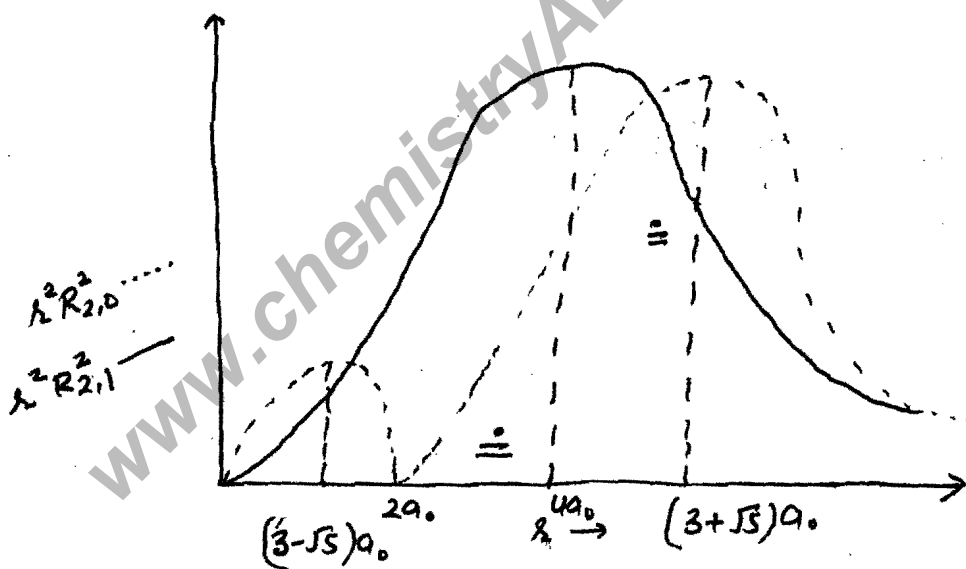
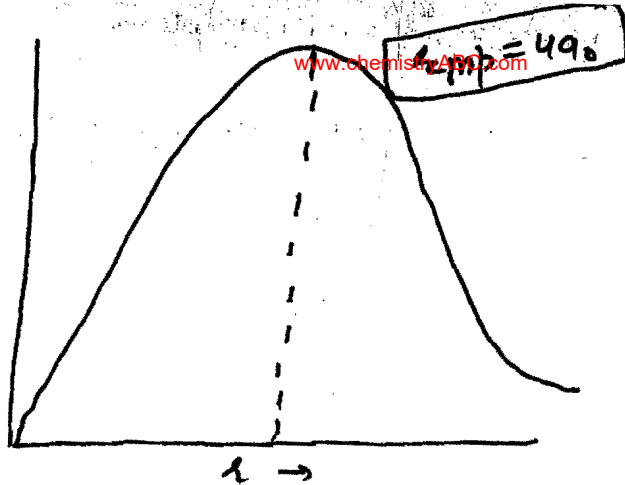
$$r^2 R_{2,1}^2 = N^2 \frac{r^3}{a_0^2} e^{-r/a_0}$$

$$\frac{d}{dr} r^2 R_{2,1}^2 = 0$$

$$r = 4a_0$$

$$r_{mp} = 4a_0$$

- 2p - orbital



Inner maxima explain the closeness of \bar{r} corresponding to 2s orbital near the nucleus.

$$\textcircled{=} \longrightarrow \psi = \psi_{2s} + \psi_{2p}$$

Superposition principle in Q.M.

By Schrödinger Cat expt.

Superposition Principle -

IMP

* Direct formula for $\langle r \rangle$ -

$$\left. \begin{array}{l} \langle r \rangle_{2s} \\ \langle r \rangle_{2p} \\ \langle r \rangle_{3s} \end{array} \right\}$$

$$\langle r \rangle_{n,l} = \frac{n^2 a_0}{Z} \left[1 + \frac{1}{2} \left(1 - \frac{l(l+1)}{n^2} \right) \right]$$

for $\langle r^2 \rangle$

$$\langle r^2 \rangle = \frac{n^4 a_0^2}{Z^2} \left[1 + \frac{3}{2} \left(1 - \frac{l(l+1)}{n^2} - \frac{1}{3} \right) \right]$$

Superposition Principle - (Schrodinger cat experiment)

It is the fundamental principle of QM.

the state of a quantum mechanical system is generally described by linear combination of various possible states in which system can be described individually.

let us consider function ψ is the linear combination of orthonormal set of wave function ϕ_1 & ϕ_2 as

$$\psi = c_1 \phi_1 + c_2 \phi_2$$

$$\int \phi_1 \phi_2 d\tau = 0$$

$$\int \phi_1 \phi_1 d\tau = 1$$

$$\int \phi_2 \phi_2 d\tau = 1$$

Quantum mechanics

1. The relation between average radius $\langle r \rangle$ of orbital 2s, 2p, 3s respectively are

- a) $\langle r \rangle_{2s} > \langle r \rangle_{2p} > \langle r \rangle_{3s}$ b) $\langle r \rangle_{2s} < \langle r \rangle_{2p} < \langle r \rangle_{3s}$
 c) $\langle r \rangle_{2s} > \langle r \rangle_{3s} > \langle r \rangle_{2p}$ d) none of these

2. The average value of $\langle r \rangle^2$ for an electron in 3d orbital of hydrogen atom is

- a) $3a_0^2$ b) $6a_0^2$ c) $4a_0^2$ d) none of these

3) The wavefunction ψ is the linear combination of function ϕ_1 and ϕ_2 as given below

$$\Psi = (1/\sqrt{2}) \phi_1 + (1/\sqrt{2}) \phi_2$$

The probability of finding the particle in state 1 (i.e. ϕ_1) is
 a) $1/2$ b) $1/4$ c) 1 d) none

Imp. 4) The Normalised wavefunction of hydrogen atom is denoted by $\Psi_{n,l,m}$ where n, l and m are respectively the principle, orbital and magnetic quantum number respectively now consider the electron in mixed state

$$\Psi = (1/3) \Psi_{1,0,0} + (2/3) \Psi_{2,1,0} + (2/3) \Psi_{3,2,-2}$$

$$c_1^2 + c_2^2 + c_3^2 = \frac{9}{9} = 1$$

The expectation value of energy $\langle E \rangle$ of this electron in eV will be approximately is

- a) -1.5 eV b) -3.7 eV c) -13.6 eV d) -80.1 eV e) none = $(\frac{1}{3})^2 (-13.6) + (\frac{2}{3})^2 (-\frac{13.6}{4}) + (\frac{2}{3})^2 (-\frac{13.6}{9})$

5) A hydrogen atom is in the state

$$\Psi = (\sqrt{8/21}) \Psi_{2,0,0} - (\sqrt{3/7}) \Psi_{2,1,0} + (\sqrt{4/21}) \Psi_{3,2,1}$$

where n, l and m are respectively the principle, orbital and magnetic quantum number respectively
 The average value of L^2 corresponding to function Ψ is $2 \dots \dots \hbar^2$.

6) An energy eigenstate of hydrogen atom has the wavefunction

$$\psi = (1/81\sqrt{\pi})(1/a_0)^{1.5} e^{-(r/3a_0)+i(\phi)} \cos \Theta \sin \Theta$$

- Find the value of energy, total angular momentum and z component of angular momentum
 - find the value of n, l, m. -1.5 eV $6 \hbar^2$ $\downarrow \hbar$ $n=3$
 $m=1$
 $l=2$
 - Find the degeneracy, number of radial node and number of angular node
- 7) Fill in the blank $\rightarrow 9$ $\rightarrow 0$ $\rightarrow 2$

8) Normalised wavefunction of hydrogen atom is denoted as

$$\Psi = (1/2) \Psi_{1s} + (1/\sqrt{2}) \Psi_{2s} + C_{3s} \Psi_{3s}$$

Then energy corresponding to function Ψ is -0.209 u .

ii) The uncertainty in position r in case of an electron in 2p orbital of hydrogen atom ... $5a_0$...

iii) Magnetic quantum number corresponding to p_x orbital is $(m=1)$...

Tu

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2 disc

Co²⁺

2

2

Average

PPP

2, 2, 2

Then ψ is normalized only when

$$C_1^2 + C_2^2 = 1$$

-OR-

* C_1 & C_2 can be imaginary

$$\therefore C_1 C_1^* + C_2 C_2^* = 1$$

Probability
① P_1

② P_2

① P_1

② P_2

C_1^2 describes the probability of finding the system corresponding to state ①

C_2^2 - state ②

$$\begin{aligned} P_1 &= \int C_1 \phi C_1 \phi, d\tau \\ &= C_1^2 \int \phi_1 \phi_1 d\tau \\ &= C_1^2 (1) \\ &= C_1^2 \end{aligned}$$

Average value of observable corresponding to function ψ

$$\psi = C_1 \phi_1 + C_2 \phi_2$$

$$\langle \text{observable} \rangle = P_1 (\text{observable})_1 + P_2 (\text{observable})_2$$

$$\langle E \rangle = P_1 E_1 + P_2 E_2$$

$$\langle L_z \rangle = P_1 L_{z1} + P_2 L_{z2}$$

$$\begin{aligned} P_1 &= C_1^2 \\ P_2 &= C_2^2 \end{aligned}$$

$$\textcircled{4} \quad \psi = \frac{1}{3} \psi_{1,0,0} + \frac{2}{3} \psi_{2,1,0} + \frac{2}{3} \psi_{3,2,-2}$$

$$E_1 + \left(\frac{2}{3}\right)^2 E_2 + \left(\frac{2}{3}\right)^2 E_3 = \left(\frac{1}{3}\right)^2 (-13.6) + \left(\frac{2}{3}\right)^2 \left(-\frac{13.6}{22}\right) + \left(\frac{2}{3}\right)^2 \left(-\frac{13.6}{32}\right)$$

=

① ①

$$\frac{1}{2} \psi_{1s} + \frac{1}{\sqrt{2}} \psi_{2s} + c_{3s} \psi_{3s}$$

$$c_1^2 + c_2^2 + c_3^2 = 1$$

$$\frac{1}{4} + \frac{1}{2} + c_3^2 = 1$$

$$c_3^2 = \frac{1}{4}$$

$$\boxed{c_{3s} = \frac{1}{2}}$$

$$E = \left(\frac{1}{2}\right)^2 (-0.5) + \left(\frac{1}{\sqrt{2}}\right)^2 \left(-\frac{0.5}{4}\right) + \left(\frac{1}{2}\right)^2 \left(-\frac{0.5}{9}\right)$$

$$= \frac{1}{4} (-0.5) + \frac{1}{2} \left(-\frac{0.5}{4}\right) + \frac{1}{4} \left(-\frac{0.5}{9}\right) \text{ in a.u.}$$

$$= -\frac{0.5}{4} - \frac{0.5}{8} - \frac{0.5}{36}$$

If c_1 & c_2 are imaginary

$$c_1 c_1^* + c_2 c_2^* = 1$$

$$c_1 - c_1^*$$

$$c_2 - c_2^*$$

$$c_1^2 + c_2^2 = 1$$

$$\int \psi^* \psi d\tau = 1$$

$$\int (c_1 \phi_1 + c_2 \phi_2)^* (c_1 \phi_1 + c_2 \phi_2) d\tau = 1$$

$$\int (c_1^* \phi_1^* + c_2^* \phi_2^*) (c_1 \phi_1 + c_2 \phi_2) d\tau = 1$$

$$c_1 c_1^* \int \phi_1^* \phi_1 d\tau + \int c_1^* \phi_1 c_2 \phi_2 + c_2^* c_2 \int \phi_2^* \phi_2 d\tau + c_2^* c_1 \int \phi_2^* \phi_1 d\tau = 1$$

$$\boxed{c_1 c_1^* + c_2 c_2^* = 1}$$

Probability corresponding to state ①

$$P_1 = \int (C_1 \phi_1)^* C_1 \phi_1 d\tau$$
$$= C_1^* C_1 \int \phi_1^* \phi_1 d\tau$$

$$P_1 = C_1^* C_1$$

Probability corresponding to state ②

$$P_2 = \int (C_2 \phi_2)^* C_2 \phi_2 d\tau$$
$$= C_2^* C_2 \int \phi_2^* \phi_2 d\tau$$

$$P_2 = C_2^* C_2$$

DPP ②

$$P_1 = \left(\frac{3}{5}\right)^2 = \frac{9}{25}$$

$$P_2 = \frac{1}{25}$$

$$P_3 = \frac{15}{25}$$

$$\frac{1}{16} + \frac{5}{16} + \frac{10}{16} \rightarrow$$

(N)

$$L_x^2 + L_y^2 + L_z^2 = L^2$$

$$L_x^2 + L_y^2 = L^2 - L_z^2$$

$$= \lambda(\lambda+1)\hbar^2 - (m\hbar)^2$$

$$= \lambda(\lambda+1)\hbar^2 - m^2\hbar^2$$

$$L_x^2 + L_y^2 = P_1 (L_x^2 + L_y^2)_1 + P_2 (L_x^2 + L_y^2)_2 + P_3 (L_x^2 + L_y^2)_3$$

③

5

$$C_1^2 + C_2^2 + C_3^2 + C_4^2 = 1$$

$$1 + 4 + 9 + 2 = 1$$

(16)

$$\psi = \frac{1}{\sqrt{16}} \psi_{2,0,0} + \frac{2}{\sqrt{16}} \psi_{2,1,1} + \frac{3}{\sqrt{16}} \psi_{2,1,0} + \frac{\sqrt{2}}{\sqrt{16}} \psi_{2,1,-1}$$

$$= \frac{1}{16} (0)\hbar + \frac{4}{16} \hbar + \frac{9}{16} (0)\hbar + \frac{2}{16} (-1)\hbar$$

$$= \frac{4}{16} - \frac{2}{16} \hbar$$

$$= \frac{\hbar}{8}$$

6

$$\langle z \rangle = \int \psi^* z \psi d\tau$$

$$= \int_0^{2\pi} \int_0^{\pi} \int_0^{\infty} (A e^{-r/a_0} \cos\theta) (A e^{-r/a_0} r^2 dr \sin\theta d\theta d\phi)$$

$$= A^2 \int_0^{\infty} r^3 e^{-2r/a_0} dr \int_0^{\pi} \cos\theta \sin\theta d\theta \int_0^{2\pi} d\phi$$

$$\downarrow$$

$$= 0$$

$$= 0$$

$$\frac{1}{36} + \frac{5}{36} + \frac{10}{36} + \frac{2}{3}$$

11

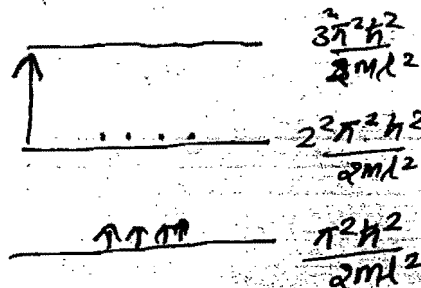
$$\text{Spin} = \frac{3}{2}$$

$$\text{No. of } e^- \text{ in one state} = \frac{3}{2} \times 2 + 1 = 4$$

$$\frac{1}{36} - \frac{10}{36} + \frac{20}{36}$$

$$\frac{10}{36} = \frac{5}{18}$$

$$\frac{1+4}{8} = \frac{5}{8}$$



$$\psi_0 = \frac{1}{2}$$

$$\frac{1}{8} + 12$$

Q.1
Q.2
Q.3
Q.4
Q.5
Q.6
Q.7
Q.8

Q.1 - If $\Psi_{n,l,m}$ denotes the eigenfunction of Hamiltonian with a potential $V = \dots$ then expectation value of the operator $L_x^2 + L_y^2$ in the state $\Psi = \frac{1}{5} [3\Psi_{2,1,1} + \Psi_{2,1,0} - \sqrt{15}\Psi_{2,1,-1}]$ is $L^2 = l(l+1)\hbar^2$
 $L_x^2 + L_y^2 + L_z^2 = L^2$
 $L_x^2 + L_y^2 = l(l+1)\hbar^2 - m^2$

- (a) $\frac{39\hbar^2}{25}$ (b) $\frac{13\hbar^2}{25}$ (c) $2\hbar^2$ (d) $\frac{26\hbar^2}{25}$

Q.2 - If an electron is in the ground state of Hydrogen atom is -13.6 eV . The ground state of Li^{2+} atom is $-13.6 \times 9 = -122.4 \text{ eV}$

Q.3 - If an electron is in the ground state of the hydrogen atom, the probability that its distance from the proton is more than one Bohr radius is approximately $1 - e^{-2} [2 \times 1^2 + 2 \times 1 + 1] = 1 - \frac{5}{e^2} = 0.32$

- (a) 0.68 (b) 0.48 (c) 0.28 (d) 0.91

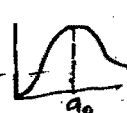
Q.4 - Let $\Psi_{n,l,m}$ denote the eigenfunction of a Hamiltonian for a spherically symmetric potential $V(r)$. The wavefunction $\Psi = \frac{1}{7} [\Psi_{2,1,0} + \sqrt{5}\Psi_{2,1,-1} + \sqrt{10}\Psi_{2,1,1}]$ is eigenfunction of $n=2, l=1$. $M \neq$ not same. (a) H, L^2 and L_z (b) H and L_z (c) H and L^2 (d) L^2 and L_z

Q.5 - The wavefunction of state of H-atom is given by $\Psi = \Psi_{200} + 2\Psi_{2,1,1} + 3\Psi_{2,1,0} + \sqrt{2}\Psi_{2,1,-1}$. Where $\Psi_{n,l,m}$ denotes the eigenfunction of the state with quantum number n, l, m in the usual notation. The expectation value of L_z in the state Ψ is

- (a) $\frac{15\hbar}{16}$ (b) $\frac{11\hbar}{16}$ (c) $\frac{3\hbar}{8}$ (d) $\frac{\hbar}{8}$

Q.6 - The expectation value of z coordinate (z), in the ground state of Hydrogen atom (wavefunction $\Psi_{100}(r) = A e^{-r/a_0}$ where A is normalisation const. and a_0 is Bohr radius) is

- (a) a_0 (b) $\frac{a_0}{2}$ (c) $\frac{a_0}{4}$ (d) 0

Q.7 - The ground state wavefunction of the hydrogen atom is given by $\Psi_{1,0,0} = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$ where a_0 is Bohr radius. The plot of radial probability distribution function for the hydrogen in the ground state is 

Q.8 - The azimuthal wavefunction for the hydrogen atom is $\phi(\varphi) = A e^{im\varphi}$ where m is the magnetic quantum no. If $\phi(\varphi)$ is Normalised the value of normalisation constant A is $\frac{1}{\sqrt{2\pi}}$

- (a) $\frac{1}{\sqrt{2\pi}}$ (b) $\frac{1}{\sqrt{2\pi}}$ (c) $\frac{1}{\sqrt{2\pi}}$ (d) $\frac{1}{\sqrt{2\pi}}$

Q.9 Let Ψ_{nlm} denotes the eigenfunction of a Hamiltonian for a spherically symmetric potential $V(r)$. The expectation value of L_z in the state

$$\Psi = \frac{1}{6} [\Psi_{200} + \sqrt{5} \Psi_{210} + \sqrt{10} \Psi_{21-1} + \sqrt{20} \Psi_{211}]$$

- (a) $-\frac{5}{18} \hbar$ (b) $\frac{5}{6} \hbar$ (c) \hbar (d) $\frac{5}{18} \hbar$

Q.10 A particle of mass m is confined in the $V(x) = \frac{1}{2} m \omega^2 x^2$. Let the wavefunction of particle is given by

$$\Psi(x) = -\frac{1}{\sqrt{5}} \Psi_0 + \frac{2}{\sqrt{5}} \Psi_1 + \frac{1}{5} \left(\frac{1}{2} \hbar \omega \right) + \frac{4}{5} \left(\frac{3}{2} \hbar \omega \right)$$

where Ψ_0 and Ψ_1 are the eigenfunctions of ground state and first excited state respectively. The expectation value of energy is

Q.11 Consider a system of eight non interacting, identical quantum particles of spin $\frac{3}{2}$ in one d box of length L . The minimum excitation energy of the system in units of $\frac{\pi^2 \hbar^2}{2mL^2}$ is

(a) $\frac{31}{10} \hbar \omega$ (b) $\frac{25}{10} \hbar \omega$ (c) $\frac{13}{10} \hbar \omega$ (d) $\frac{11}{10} \hbar \omega$

Fermions (Indistinguishable)
 Distinguishable \rightarrow B-E Statistics
 Indistinguishable \rightarrow F-D Statistics

Q.12 The ground state energy of four non interacting isotropic simple harmonic oscillator by ω

- (a) $3\hbar\omega$ (b) $6\hbar\omega$ (c) $\hbar\omega$ (d) None

Q.13 Consider the statements

- (i) At very high value of quantum no two large maximum at the extremum of vibration occur in simple harmonic oscillator.
 - (ii) Tunnelling probability in SHO is independent of mass and force constant.
 - (iii) SHO model is an ideal situation, in reality the vibration that take place is anharmonic in nature.
- The True statement above are (a) i, ii (b) ii, iii (c) i, ii, iii (d) i, iii

Q.14 Which of the following is not a feature of quantum mechanical SHO

- (i) The energy level spacing of SHO is constant τ
- (ii) The wavefunction of harmonic oscillator is either symmetric or anti-symmetric under the reflection $x=0$.
- (iii) Thermal decomposition of molecule may be explained by SHO.
- (iv) The harmonic oscillator has finite energy even in ground state τ

Q.15 Write T/F in front of given statement

- (i) In SHO, Each wavefunction is orthogonal to all other function even if the symmetry of two function is same.
 - (ii) In particle in a box, function differ from harmonic oscillator function because in PIB model Tunnelling phenomenon does not exist but in SHO it exists.
- ... the amplitude of the wave function after passing through

★ Simple Harmonic oscillator — To study vibrational motion of microscopic particle. www.chemistryABC.com

$$\psi_0 = \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\beta x^2/2}$$

$$E_0 = \frac{1}{2} h\nu$$

$$E_n = (n + \frac{1}{2}) h\nu$$

$$\langle x \rangle = 0$$

$$\langle p_x \rangle = 0$$

$$\langle x^2 \rangle = \frac{1}{2\beta}$$

$$\langle p_x^2 \rangle = \frac{\beta \hbar^2}{2}$$

$$\langle K \rangle = \frac{1}{4} h\nu$$

$$\langle V \rangle = \frac{1}{4} h\nu$$

The Schrödinger eqn is

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} (E - V)\psi = 0$$

To obtain the vibrational energy of the vib. motion of microscopic particle we take the Schrödinger eqn of 1-D system in form of cartesian co-ordinates, as

$$V = \frac{1}{2} kx^2 \quad (\text{SHO})$$

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} \left(E - \frac{1}{2} kx^2 \right) \psi = 0$$

$$\frac{d^2\psi}{dx^2} + \left(\frac{2mE}{\hbar^2} - \frac{2m}{\hbar^2} \frac{1}{2} kx^2 \right) \psi = 0$$

$$\frac{2mE}{\hbar^2} = \alpha$$

$$\frac{2m}{\hbar^2} \frac{1}{2} k = \beta$$

$$\frac{d^2\psi}{dx^2} + (\alpha - \beta^2 x^2)\psi = 0$$

$$\alpha = \frac{2mE}{\hbar^2}$$

$$\beta^2 = \frac{mk}{\hbar^2}$$

$$\beta = \frac{\sqrt{mk}}{\hbar}$$

The solution of this eqn may be obtained by converting it into the form of Hermite polynomial, and we get the somas

$$\psi_n(\xi) = \left(\frac{1}{2^n n!}\right)^{1/2} \left(\frac{\beta}{\pi}\right)^{1/4} H_n(\xi) e^{-\xi^2/2}$$

$$\xi = \sqrt{\beta} x$$

$$H_n(\xi) = (-1)^n e^{\xi^2} \frac{d^n}{d\xi^n} e^{-\xi^2}$$

$$n=0 \quad H_0(\xi) = 1$$

$$n=1 \quad H_1(\xi) = 2\xi$$

$$n=2 \quad H_2(\xi) = 4\xi^2 - 2$$

(ii)

we get

$$\frac{\alpha}{\beta} = 2n+1$$

$$\frac{\frac{2mE}{\hbar^2}}{\frac{\sqrt{mk}}{\hbar}} = 2n+1$$

$$\psi_n = \left(\frac{1}{2^n n!}\right)^{1/2} \left(\frac{B}{\pi}\right)^{1/4} H_n(\xi) e^{-\xi^2/2}$$

$$n=0 \quad \psi_0 = \left(\frac{1}{2^0 0!}\right)^{1/2} \left(\frac{B}{\pi}\right)^{1/4} H_0(\xi) e^{-\xi^2/2}$$

$$\psi_0 = \left(\frac{B}{\pi}\right)^{1/4} e^{-\xi^2/2}$$

$$\psi_0 = \left(\frac{B}{\pi}\right)^{1/4} e^{-Bx^2/2}$$

$$E_0 = \frac{1}{2} h\nu$$

$$n=1 \quad \psi_1 = \left(\frac{1}{2^1 1!}\right)^{1/2} \left(\frac{B}{\pi}\right)^{1/4} H_1(\xi) e^{-\xi^2/2}$$

$$= \frac{1}{\sqrt{2}} \left(\frac{B}{\pi}\right)^{1/4} 2\xi e^{-\xi^2/2}$$

$$\psi_1 = \left(\frac{B}{\pi}\right)^{1/4} \sqrt{2} \xi e^{-Bx^2/2}$$

$$E_1 = \frac{3}{2} h\nu \text{ OR } \frac{3}{2} h\omega$$

	$n=0$	$n=1$	$n=n$
	$\psi_0 = \left(\frac{B}{\pi}\right)^{1/4} e^{-Bx^2/2}$	$\psi_1 = \left(\frac{B}{\pi}\right)^{1/4} \sqrt{2} \xi e^{-Bx^2/2}$	$\psi_n(\xi) = \left(\frac{1}{2^n n!}\right)^{1/2} \left(\frac{B}{\pi}\right)^{1/4} H_n(\xi) e^{-\xi^2/2}$
$\langle x \rangle$	0	0	0
$\langle px \rangle$	0	0	0
$\langle x^2 \rangle$	$\frac{1}{2B}$	$\frac{3}{2B}$	$(n+\frac{1}{2}) \frac{1}{B}$
$\langle p^2 \rangle$	$B \frac{h^2}{2}$	$\frac{3}{2} B h^2$	$(n+\frac{1}{2}) B h^2$
$\langle K_x \rangle$	$\frac{B h^2}{4m} = \frac{1}{4} h\nu$	$\frac{3}{4} \frac{B h^2}{m} = \frac{3}{4} h\nu = \frac{3}{4} h\omega$	$(n+\frac{1}{2}) \frac{B h^2}{2m} = \frac{(n+\frac{1}{2}) h\nu}{2}$
$\langle V_x \rangle$	$\frac{1}{4} \frac{K}{B} = \frac{1}{4} h\nu = \frac{1}{4} h\omega$	$\frac{3}{4} \frac{K}{B} = \frac{3}{4} h\nu = \frac{3}{4} h\omega$	$\frac{1}{2} K (n+\frac{1}{2}) B = \frac{(n+\frac{1}{2}) h\nu}{2}$
$\langle E \rangle$	$\frac{1}{2} h\nu$	$\frac{3}{4} h\nu + \frac{3}{4} h\nu = \frac{3}{2} h\nu$	$(n+\frac{1}{2}) h\nu$

Plot of ψ & ψ^2 v/s x in Quantum mechanical SHO. -

$$\psi_0 = \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\beta x^2/2}$$

ψ_0 is maximum when

$$(\psi_0)_{\max} = \left(\frac{\beta}{\pi}\right)^{1/4}$$

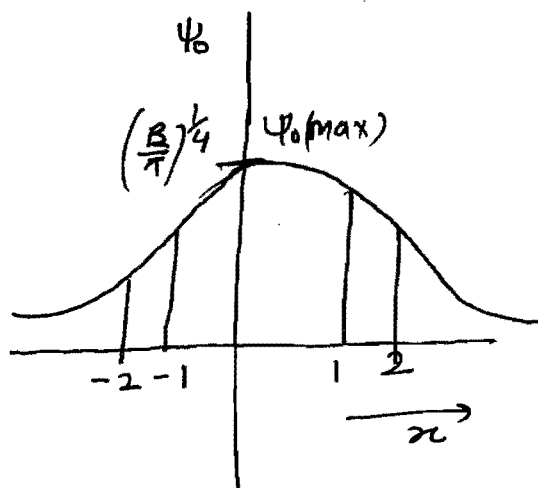
$$e^{-\beta x^2/2} = 1 = e^0$$

$$\frac{\beta x^2}{2} = 0$$

$$\boxed{x=0}$$

$$x = \pm 1 = \left(\frac{\beta}{\pi}\right)^{1/4} e^{\mp \beta/2}$$

$$x = \pm 2 = \left(\frac{\beta}{\pi}\right)^{1/4} e^{\mp 2\beta}$$



$\boxed{\text{node} = 0}$

$\boxed{\text{gaussian function}}$

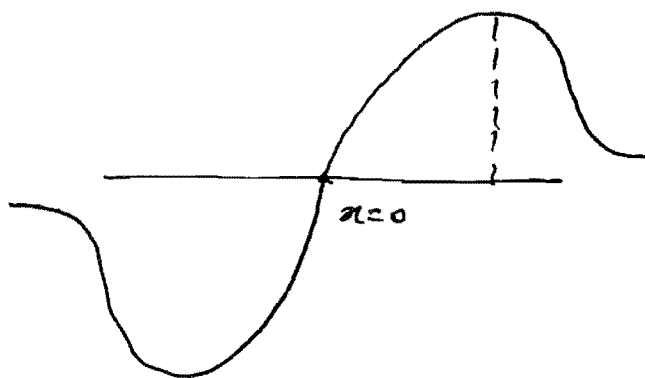
function is maximum at $x=0$ and decreases exponentially with the value of x shift from 0.

*

$$\psi_1 = \left(\frac{\beta}{\pi}\right)^{1/4} \sqrt{2\beta} x e^{-\beta x^2/2}$$

$$x=0$$

$$\psi_1 = 0$$



Function ψ_1 becomes zero at $x=0$

As the value of x shift from zero

it first increases then decreases

$$\psi_1(x) = x e^{-\beta x^2/2}$$

$$x = +1 \quad \psi_1(1) = e^{-\beta/2}$$

$$\psi_1(-1) = -e^{-\beta/2}$$

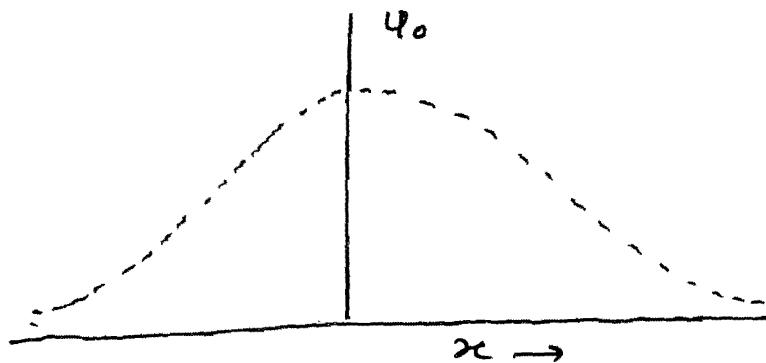
$$\psi_1(1) = -\psi_1(-1)$$

$\psi_0, \psi_2, \psi_4 \dots$ Symmetric

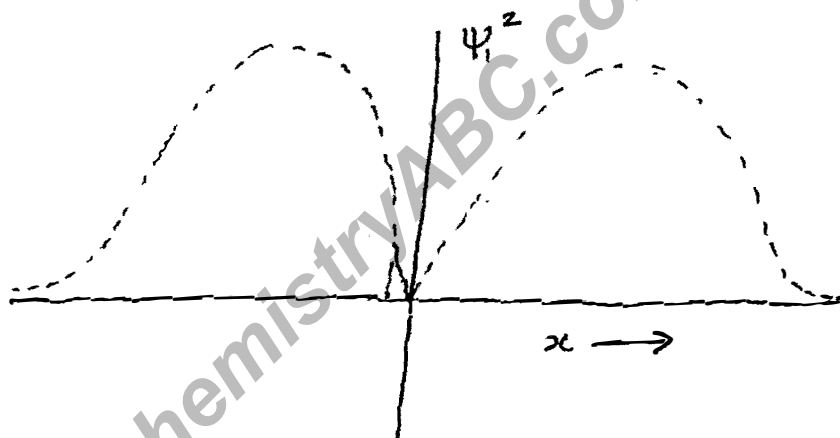
$\psi_1, \psi_3, \psi_5 \dots$ Anti-Symmetric

Plot of ψ^2 v/s x (Probability) -

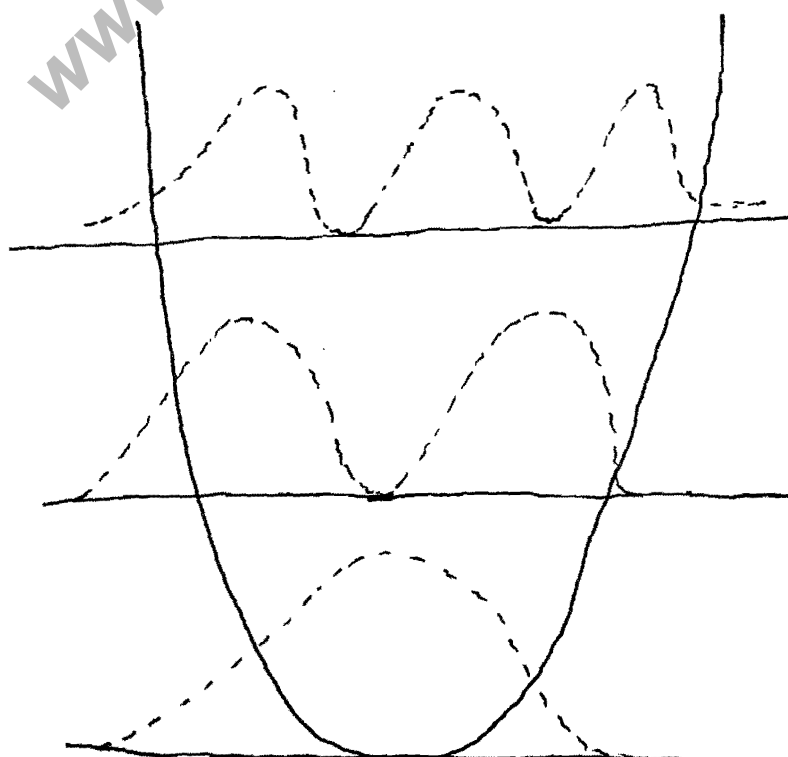
ψ_0 vs x

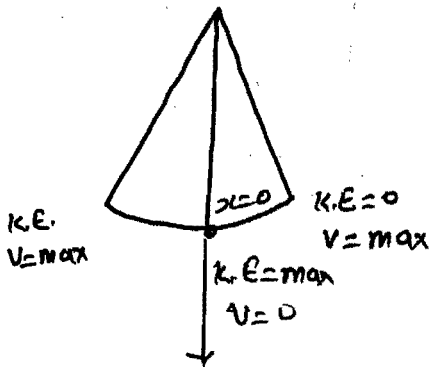


ψ_1 vs x (probability) -



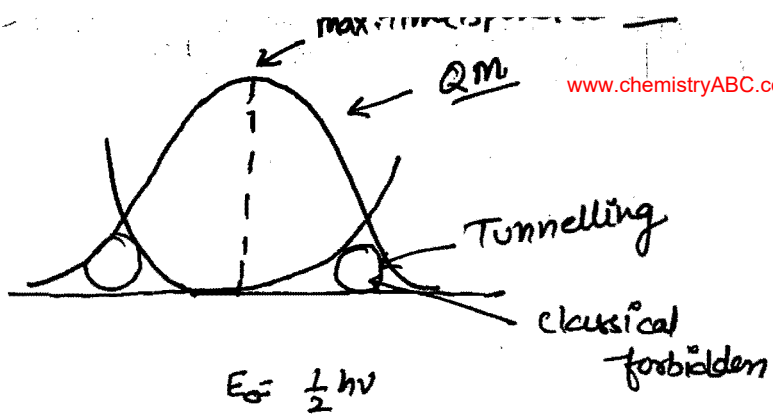
★ Comparison of Classical & quantum mechanical SHO -





at $x=0$

Spend min time at $x=0$



Features -

- From the graph of ψ & ψ^2 vs x in Q.M. SHO it is clear that particle spends maximum time at eqm position (at $x=0$) in the ground state because function is max. at $x=0$.
But in classical SHO particle spends min. time at ($x=0$) eqm position.
- In classical SHO K.E. & P.E. may be zero but in Q.M. SHO neither K.E. zero. nor P.E. zero.

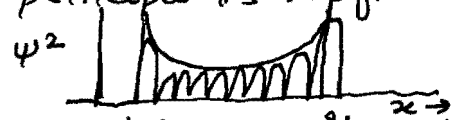
In classical SHO it is considered

$$K.E. = 0 \quad \text{at extremum of vibration}$$

$$P.E. = 0 \quad \text{at } x=0 \text{ (at eqm)}$$

- In classical SHO particle have finite amplitude of vibration but in Q.M. SHO the value of function exist b/w $-\infty$ to $+\infty$ so in Q.M. SHO there is the change of finding particle in classical forbidden region, it is called tunnelling & this tunnelling probability \uparrow es with \uparrow es in value of (n) becoz as (n) \uparrow es classical behaviour \uparrow es.

④ ~~As the value of~~ At higher value of n when we plot ψ^2 v/s x we get that ② large maxima at extremum of vibration & a no. of small maxima b/w these two large maxima means the probability of finding particle at extremum of vibration. Classical behaviour emerges & Bohr's Correspondance principle is verified.



⑤ Symmetry of the wave function is governed by Hermite polynomial as our function is containing two part

$$\psi = H_n(\xi) e^{-\xi^2/2}$$

↓
Always symmetric

$$H_0(\xi) = 1$$

$$\psi_0 = \text{Symmetric}$$

$$H_1(\xi) = 2\xi = 2\sqrt{B}x \quad \psi_1 = \text{antisymmetric}$$

$$H_2(\xi) = 4\xi^2 - 2 = 4Bx^2 - 2 \quad \psi_2 = \text{Symmetric}$$

If Hermite contain x^{even} function symmetric

" " " " x^{odd} function antisymmetric

★ 2-D SHO —

When we study harmonic oscillator for high dimensions

(for 2-D OR 3-D) we have to classify SHO in two category.

- ① Anisotropic SHO ② Isotropic SHO

$$\downarrow$$

$$V_x \neq V_y \neq V_z$$

$$B_x \neq B_y \neq B_z$$

$$\downarrow$$

$$V_x = V_y = V_z = V$$

$$B_x = B_y = B_z = B$$

So we have two different results on the basis of type of SHO.

★ 2-D anisotropic SHO —

As our hamiltonian for 2D-motion is summation of two hamiltonian operator for 1-D motion, then our resultant function

$$\Psi(x,y) = \Psi_x + \Psi_y$$

$$H(x,y) = H_x + H_y$$

$$= -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} kx^2 - \frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} + \frac{1}{2} ky^2$$

$$H_{2D} = K_{2D} + U_{2D}$$

$$\Psi(x,y) = \Psi_x \Psi_y$$

$$= \left(\frac{B_x}{\pi}\right)^{1/4} \left(\frac{1}{2^n n! m_x}\right)^{1/2} \left(H_n(x/\xi_x) e^{-\xi_x^2/2} \right)$$

$$\times \left(\frac{B_y}{\pi}\right)^{1/4} H_m(y/\xi_y) \left(\frac{1}{2^m m! m_y}\right)^{1/2} e^{-\xi_y^2/2}$$

$$E_{(x,y)} = (n_x + \frac{1}{2}) h\nu_x + (n_y + \frac{1}{2}) h\nu_y$$

★ 2D-isotropic SHO -

$$\Psi_{2D} = \left(\frac{\beta}{\pi}\right)^{1/4} \left(\frac{1}{2^{n_x} n_x!}\right)^{1/2} H_{n_x}(\xi_x) e^{-\xi_x^2/2}$$

$$\times \left(\frac{\beta}{\pi}\right)^{1/4} \left(\frac{1}{2^{n_y} n_y!}\right)^{1/2} H_{n_y}(\xi_y) e^{-\xi_y^2/2}$$

$$\Psi_{(2D) 0,0} = \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\beta x^2/2} \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\beta y^2/2}$$

$$E_{2D} = (n_x + \frac{1}{2}) h\nu + (n_y + \frac{1}{2}) h\nu$$

$$E_{2D} = (n_x + n_y + 1) h\nu$$

$$E_{2D} = (n_x + n_y + 1) \hbar\omega$$

Imp.

★ Energy levels corresponding to 2D-isotropic SHO -

$$E_{2D} = (n_x + n_y + 1) h\nu$$

<u>3,1</u>	<u>1,3</u>	<u>4,0</u>	<u>0,4</u>	<u>2,2</u>	5hν g=5
<u>2,1</u>	<u>1,2</u>	<u>3,0</u>	<u>0,3</u>	4hν g=4	
<u>(2,0)</u>	<u>(0,2)</u>	<u>(1,1)</u>	3hν g=3		
<u>(1,0)</u>	<u>(0,1)</u>	2hν g=2			
<u>(0,0)</u>	hν OR hν g=1				

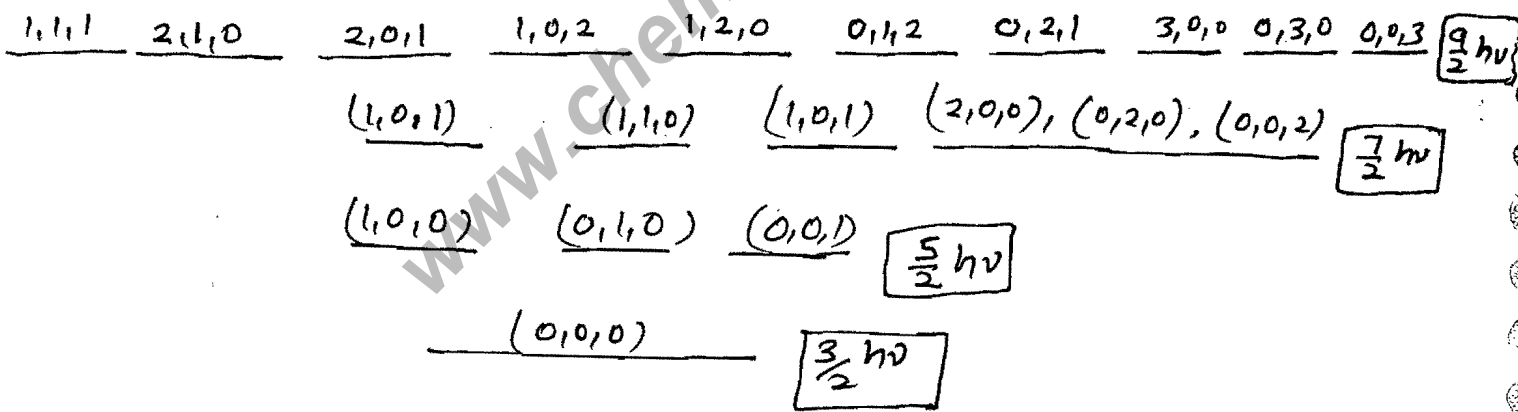
★ 3D - isotropic SHO -

$$\begin{aligned} (\psi_{3D})_{n_x=0, n_y=0, n_z=0} &= \left(\frac{B}{\pi}\right)^{1/4} e^{-Bx^2/2} \left(\frac{B}{\pi}\right)^{1/4} e^{-By^2/2} \left(\frac{B}{\pi}\right)^{1/4} e^{-Bz^2/2} \\ &= \left(\frac{B}{\pi}\right)^{3/4} e^{-B(x^2+y^2+z^2)/2} \end{aligned}$$

$$\begin{aligned} (E_{3D})_{\text{isotropic}} &= (n_x + \frac{1}{2}) h\nu + (n_y + \frac{1}{2}) h\nu + (n_z + \frac{1}{2}) h\nu \\ &= (n_x + n_y + n_z + \frac{3}{2}) h\nu \end{aligned}$$

★ Energy level diagram for 3D - isotropic SHO -

$$E_{(3D)} = n_x + n_y + n_z + \frac{3}{2} h\nu$$



$$\frac{5}{2} h\nu$$

$$\frac{5}{2} - \frac{3}{2} = 1 h\nu$$

$n=1$

$$g_n = \frac{(n+1)(n+2)}{2}$$

$$g_n = \frac{(n+1)(n+2)}{2} = \frac{(1+1)(1+2)}{2} = 3$$

DPP Quantum mechanics

1. Consider a classical harmonic oscillator with a mass m and a force constant k oscillating with a frequency ν . Which of the following statements is NOT true for this system? TIFR 2013

- A) ν increases if m decreases. **T**
 B) The oscillator is most likely to be found at its equilibrium position. **F**
 C) The acceleration is maximum at its turning points. **- T**
 D) ν does not depend on how large the amplitude of the oscillation is. **T**

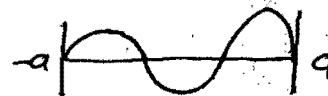
$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$$

2. For a harmonic oscillator in its ground state i.e. $v=0$ the energy is given by $0.5 h\nu$ where ν is the vibrational frequency. This is due to its TIFR 2015

- (a) its kinetic energy (b) Potential energy
 (c) sum of kinetic energy and potential energy (d) heat of formation

3. Which of the following statements is true TIFR 2015

- (i) For a harmonic oscillator potential, the spacing between adjacent energy level remains constant with increase in quantum number. **T**
 (ii) For Morse oscillator potential the spacing between adjacent energy level increases with increase in vibrational quantum number. **F**
 (iii) Harmonic oscillator are used to explain bond dissociation **F**
 (iv) Morse oscillator are used to explain the oscillation. **T**
 (a) i,ii,iii (b) i,iv (c) i,ii,iv (d) i,ii,iii,iv



4. A free particle of mass ' m ' is confined to a region of length L . The de-Broglie wave associated with the particle is sinusoidal as given in the figure (should be discussed in class). The energy of the particle is

$$\frac{9h^2}{32mL^2}$$

IIT JAM Physics

$$n=3$$

$$E_n = \frac{n^2 h^2}{32mL^2}$$

5. Consider the statements

- i) Pure substance are required for studies by Raman spectra, studies by IR spectra do not require a high degree of purity.
 ii) Water can be used as a solvent in Raman as well as in IR spectra.
 iii) for intense Raman line concentrated solution is required.

Correct statements above are a) I,iii b) ii,iii c) I,ii,iii d) none

6. The quantum mechanical virial theorem for a general potential $V(x,y,z)$ is given by $\langle x \frac{\partial V}{\partial x} + y \frac{\partial V}{\partial y} + z \frac{\partial V}{\partial z} \rangle = 2T$ where T is the kinetic energy operator and $\langle \rangle$ indicates expectation value. This leads to the following relation between the expectation value of kinetic energy and potential energy for a quantum mechanical harmonic oscillator problem with potential

$$V = \frac{1}{2} k_x x^2 + \frac{1}{2} k_y y^2 + \frac{1}{2} k_z z^2$$

Dec 2013 CSIR

- (a) $\langle T \rangle = \langle V \rangle$ (b) $\langle T \rangle = -\frac{1}{2} \langle V \rangle$ (c) $\langle T \rangle = \frac{1}{2} \langle V \rangle$ (d) $\langle T \rangle = -\langle V \rangle$

7. The most probable value of ' r ' for an electron in 1s orbital of hydrogen atom is

- (a) $a_0/2$ (b) a_0 (c) $\sqrt{2}a_0$ (d) $3a_0/2$

Dec 2013 CSIR

8. The most probable radius for an electron in 2s orbital is $(3 - \sqrt{5})a_0$... $(3 + \sqrt{5})a_0$

9 Consider the statements

- i) wave function decays more slowly as $E \rightarrow V_0$ in case of tunneling process. T
- ii) The normalization constant in case of SHO is dependent on mass T
- iii) Molecular spectra is much more complicated than atomic spectra T

Correct statements above are a) I,iii b) ii,iii c) I,ii,iii d) I,ii

10. Combining two real wave functions ϕ_1 and ϕ_2 , the following functions are constructed: $A = \phi_1 + \phi_2$, $B = \phi_1 - i\phi_2$, $C = i\phi_1 + \phi_2$, $D = i(\phi_1 + \phi_2)$. The correct statement will then be Dec 2012 CSIR

- (a) A and B represent the same state
- (b) A and C represent the same state
- (c) A and D represents the same state
- (d) B and D represents the same state

11. The energy of a harmonic oscillator in its ground state is $\frac{1}{2} \hbar \omega$. According to the virial theorem, the average kinetic (T) and potential (V) energies of the above are

- (a) $T = \frac{1}{4} \hbar \omega$; $V = \frac{1}{4} \hbar \omega$
- (b) $T = \frac{1}{8} \hbar \omega$; $V = \frac{3}{8} \hbar \omega$
- (c) $T = \hbar \omega$; $V = -\frac{1}{2} \hbar \omega$
- (d) $T = \frac{3}{8} \hbar \omega$; $V = \frac{1}{8} \hbar \omega$

12 Suppose, the ground stationary state of a harmonic oscillator with force constant 'k' is given by $\Psi_0 = \exp[-Ax^2]$ Then, A should depend on m and k as

- (a) $A \propto k^{-1/2} m^{1/2}$
- (b) $A \propto km$
- (c) $A \propto k^{1/2} m^{1/2}$
- (d) $A \propto k^{1/3} m$

13 If magnitude of transition dipole is considered same for all type of transition then the lifetime for electronic transition in the proper order is

- (a) Electronic < vibrational < rotational
- (b) vibrational < rotational < electronic
- (c) Electronic > vibrational > rotational
- (d) Electronic = vibrational < rotational

$\Delta E \propto \frac{h}{4\pi}$

14 The fundamental vibrational frequency ν of a homonuclear diatomic molecule with atomic mass m and force constant k is

- a) $\nu = (1/2\pi)(k/m)^{0.5}$
- (b) $\nu = (1/2\pi)(2k/m)^{0.5}$
- (c) $\nu = (1/2\pi)(k/2m)^{0.5}$
- (d) $\nu = (2/2\pi)(k/m)^{0.5}$

$\mu = \frac{m_1 m_2}{m_1 + m_2}$
 $m_1 = m_2$
 $\mu = \frac{m^2}{2m}$

15 At a given temperature, for a rigid rotor, the probability that a system is in the rotational state J=0 is 0.6, in state J=1 is 0.3, and 0.1 in J=2. The average energy of rotor at the given temperature is

- a) 6.0 B
- (b) 1.2 B
- c) 3.6 B
- d) 4.8 B

ψ_0, ψ_1, ψ_2 $\langle E \rangle = p_0 E_0 + p_1 E_1 + p_2 E_2$
 $E = B J(J+1)$

16 The correct statement about both the average value of position $\langle x \rangle$ and momentum $\langle p \rangle$ of a 1-d harmonic oscillator wave function is

- a) $\langle x \rangle \neq 0$ and $\langle p \rangle \neq 0$
- (b) $\langle x \rangle = 0$ but $\langle p \rangle \neq 0$
- (c) $\langle x \rangle = 0$ and $\langle p \rangle = 0$
- d) $\langle x \rangle \neq 0$ but $\langle p \rangle = 0$

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16) Fill in the Blanks

a) The degeneracy corresponding to 3D isotropic SHO with energy $4.5 h \nu$ is ... 10

b) For the particle in a box problem in $(0, l)$ the value of $\langle x^4 \rangle$ in the $n \rightarrow \infty$ limit would be,

$n \rightarrow \infty$ 0 to l

$\langle x^4 \rangle = \frac{1}{2} \left[\frac{x^{n+1}}{n+1} \right]_0^l$ $\langle x^4 \rangle = \frac{1}{2} \left[\frac{x^5}{5} \right]_0^l = \frac{l^5}{5}$

$\frac{(n+1)(n+2)}{2}$

DP
 3

$\frac{7}{2} h\nu$

$\frac{7}{2} - \frac{3}{2} = 2h\nu$

$n=2$

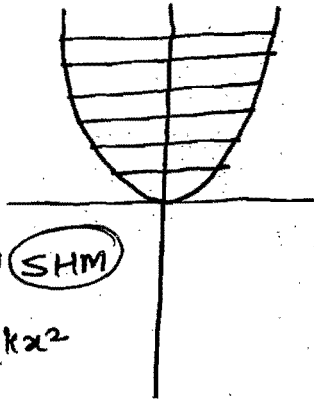
$g_n = \frac{(2+1)(2+2)}{2} = 6$

$g=6$

DPP →

③

Ideal

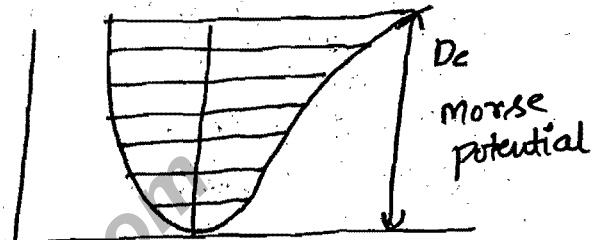


Hooker's law (SHM)

$V = \frac{1}{2} kx^2$

$E = (n + \frac{1}{2}) h\nu$

Real



$V = D_e [1 - e^{-ax}]^2$

$a \rightarrow$ morse const

$a = \sqrt{\frac{k_f}{2D_e}} \rightarrow$ force const

D_e - dissociation energy from the bottom of the pot. curve

x - displace of atom from eqm position

$D_0 \rightarrow$ True Dissociation energy
Dissociation energy from the ground state

$D_e = D_0 + E_0$

$\frac{n_2}{+M_2} = M_2$
 $1 = \frac{M_2}{2M}$

$E = (n + \frac{1}{2}) h\nu - (n + \frac{1}{2})^2 h\nu x_e$

x_e - anharmonicity const.

$x_e = \frac{h\nu}{4D_e}$

+2)

$$x \frac{dV}{dx} + y \frac{dV}{dy} + z \frac{dV}{dz} = 2T \quad \text{--- (1)}$$

$$V = \frac{1}{2} k_x x^2 + \frac{1}{2} k_y y^2 + \frac{1}{2} k_z z^2$$

$$\frac{dV}{dx} = \frac{1}{2} k_x \frac{d}{dx} x^2$$

$$= \frac{1}{2} k_x \cdot 2x = k_x x$$

$$\frac{dV}{dy} = k_y y$$

$$\frac{dV}{dz} = k_z z$$

$$x k_x x + y k_y y + z k_z z = 2T$$

$$k_x x^2 + k_y y^2 + k_z z^2 = 2T$$

$$2V = 2T$$

$$V = T$$

★ In case of hydrogen -

$$\langle T \rangle = -\frac{1}{2} \langle V \rangle$$

$$V = \frac{-e^2}{4\pi\epsilon_0 (x^2 + y^2 + z^2)^{3/2}}$$

$$r^2 = x^2 + y^2 + z^2$$

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

$$x \frac{dV}{dx} + y \frac{dV}{dy} + z \frac{dV}{dz} = 2T$$

*

$$\langle x^n \rangle = \left[\frac{x^{n+1}}{n+1} \right]_0^L$$

As $n \rightarrow \infty$

In Box problem

↓
0-L

★ Rigid Rotor (elementary idea)

atom
Acc. to Hamiltonian operator for hydrogenic

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V$$

$$= -\frac{\hbar^2}{2m} \left(\frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) - \frac{e^2}{4\pi \epsilon_0 r}$$

$$L^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]$$

To study the rotational motion of microscopic particle we introduce total angular momentum operator in Hamiltonian as

$$H = -\frac{\hbar^2}{2m r^2} \left[\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] + V$$

$$= \frac{1}{2I} \left[-\hbar^2 \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} - \hbar^2 \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \right] + V$$

$$H = \frac{1}{2I} \left[-\hbar^2 \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + L^2 \right] + V$$

$$H = -\frac{\hbar^2}{2I} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{L^2}{2I} + V$$

As Rigid rotor model is proposed to study rotational motion

$$\rightarrow \ell = \text{fixed} \Rightarrow V = \text{fixed}$$

To avoid mathematical complication $V=0$

$$H = \frac{L^2}{2I}$$

$$H\psi = \frac{L^2}{2I} \psi$$

$$= \frac{\ell(\ell+1)\hbar^2}{2I} \psi = E\psi$$

$$E = \frac{\hbar^2}{2I} \ell(\ell+1)$$

$$E = B J(J+1)$$

$$B = \frac{\hbar^2}{2I}$$

$$I = mR^2$$

The quantum no. is (borrowed) discussed during the study of microscopic particles electronic motion, now we are studying electronic motion, so we replace ℓ by J & J behaves similar to ℓ

$$J = 1$$

$$m_J = 1, 0, -1$$

$$J=1 \quad E_1 = 2B \quad g = 3$$

$$J=2 \quad E_2 = 6B \quad g = 5$$

$$J=3 \quad E_3 = 12B \quad g = 7$$

*degeneracy -

$$g_J = 2J+1$$

Qus. The value of energy corresponding to a quantum mech. rotating particle is $E = \frac{10\hbar^2}{I}$ find the degeneracy

$$\frac{10\hbar^2}{I} = \frac{\hbar^2}{2I} J(J+1)$$

$$J(J+1) = 20$$

$$J = 4, -5$$

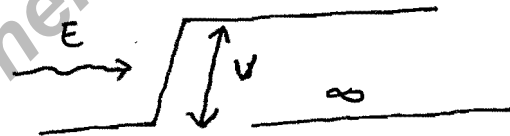
$$g_J = 2J+1$$

$$= 2 \times 4 + 1$$

$$g_J = 9$$

★ Potential Barriers problem -

① Pot Barriers Problem with infinite width -



$$\left. \begin{array}{l} \textcircled{1} \quad E < V \\ \quad \quad E = V \end{array} \right\}$$

Reflection $R=1$

Transmission $T=0$

$$R+T = 1 \text{ Always}$$

$$\textcircled{2} \quad E > V$$

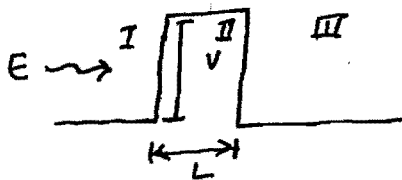
$$R = \frac{(p_1 - p_2)^2}{(p_1 + p_2)^2}$$

$$T = \frac{4 p_1 p_2}{(p_1 + p_2)^2}$$

$$p_1 = \sqrt{2mE}$$

$$p_2 = \sqrt{2m(E-V)}$$

② Potential barrier problem with finite width -



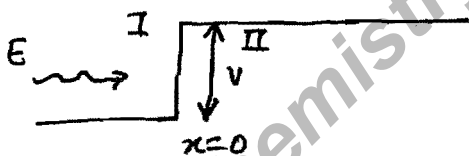
$E < V$

$$T_{\text{exact}} = \frac{4E(E-V)}{4E(V-E) + V^2 \left(\frac{e^{k_2 L} - e^{-k_2 L}}{2} \right)^2}$$

$$k_2 = \sqrt{\frac{2m(V-E)}{\hbar^2}} = \frac{p_2}{\hbar}$$

$$T_{\text{approx}} = e^{-2 \sqrt{\frac{2m(V-E)}{\hbar^2}} \cdot L}$$

★ Pot. Barrier with infinite width - Consider a free particle with energy E , mass m collides or impinges on a pot. barrier of height V and infinite width at $x=0$



Schrodinger eqn corresponding to movement of particle in Ist region

$$\frac{d^2 \psi}{dx^2} + \frac{2m}{\hbar^2} (E - V) \psi = 0$$

In Ist region $V=0$

$$\frac{d^2 \psi_I}{dx^2} + \frac{2m}{\hbar^2} E \psi_I = 0$$

$$k_1^2 = \frac{2mE}{\hbar^2}$$

$$k_1 = \sqrt{\frac{2mE}{\hbar^2}} = \frac{p_1}{\hbar}$$

$$\frac{d^2 \psi_I}{dx^2} + k_1^2 \psi_I = 0 \Rightarrow \text{Soln } \psi_I = A \sin k_1 x + B \cos k_1 x$$

$$\psi_I = A e^{ik_1 x} + B e^{-ik_1 x}$$

movement of particle along +ve x-direction in I region ↑
In -x direction

Schrodinger eqn corresponding to movement of particle in II region-

$$\frac{d^2 \psi_{II}}{dx^2} + \frac{2m}{\hbar^2} (E - V) \psi_{II} = 0$$

$$\frac{d^2 \psi_{II}}{dx^2} + k_2^2 \psi_{II} = 0$$

$$\left\{ \begin{aligned} k_2^2 &= \frac{2m}{\hbar^2} (E - V) \\ k &= \frac{\sqrt{2m(E - V)}}{\hbar} = \frac{p_2}{\hbar} \end{aligned} \right.$$

↓
Som

$$\psi_{II} = C e^{ik_2 x} + D e^{-ik_2 x}$$

$$= C e^{i p_2 x / \hbar} + D e^{-i p_2 x / \hbar}$$

∴ $\psi_{II} = C e^{ik_2 x}$
 $= C e^{i p_2 x / \hbar}$

↳ represents the movement of particle in -ve x direction in II region is neglected for a pot. barrier of infinite length because in II region movement of particle in -x direction not take place

To find the relation b/w A, B & C apply boundary condition

at $x=0$ $\psi_I = \psi_{II}$

$$\frac{d\psi_I}{dx} = \frac{d\psi_{II}}{dx}$$

① $(\psi_I)_{x=0} = (\psi_{II})_{x=0}$

$$A e^{i p_1 \cdot 0 / \hbar} + B e^{-i p_1 \cdot 0 / \hbar} = C e^{i p_2 \cdot 0 / \hbar}$$

$$\boxed{A + B = C} \quad \text{--- ①}$$

② $\left(\frac{d\psi_I}{dx}\right)_{x=0} = \left(\frac{d\psi_{II}}{dx}\right)_{x=0}$

$$\frac{d\psi_I}{dx} = i k_1 A e^{i k_1 x} - i k_1 B e^{-i k_1 x}$$

$$\frac{d\psi_{II}}{dx} = i k_2 C e^{i k_2 x}$$

$$\left(\frac{d\psi_I}{dx}\right)_{x=0} = i k_1 A - i k_1 B$$

$$= \frac{i p_1}{\hbar} A - \frac{i p_1}{\hbar} B$$

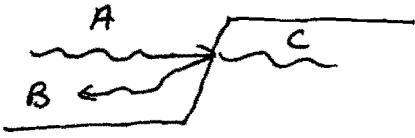
$$\left(\frac{d\psi_{II}}{dx}\right)_{x=0} = i k_2 C e^0$$

$$= \frac{i p_2}{\hbar} C$$

from schrodinger eqn
 $\frac{d^2 \psi}{dx^2} + \frac{2m}{\hbar^2} (E - V) \psi = 0$
 for $\psi \rightarrow$ finite
 $\frac{d^2 \psi}{dx^2} \rightarrow$ finite
 if $\frac{d\psi}{dx} \rightarrow$ continuous

$$\left(\frac{d\psi}{dx}\right)_{x=0} = \left(\frac{d\psi}{dx}\right)_{x=0}$$

$$\frac{i p_1 A}{\hbar} - \frac{i p_1 B}{\hbar} = \frac{i p_2 C}{\hbar} \Rightarrow \boxed{p_1 A - p_1 B = p_2 C} \quad \text{--- (2)}$$



The value of B in eqn (1) is $B = C - A$
 put in eqn (2) we have

$$p_1 A - p_1 (C - A) = p_2 C$$

$$p_1 A - p_1 C + p_1 A = p_2 C$$

$$(p_1 + p_2) C = 2 p_1 A$$

$$\boxed{C = \frac{2 p_1 A}{p_1 + p_2}}$$

Similarly

$$B = \frac{(p_1 - p_2) A}{(p_1 + p_2)}$$

Probability & current density

$$J = \frac{\hbar}{2im} [\psi^* \nabla \psi - \psi \nabla \psi^*]$$

$$= \frac{\hbar}{2im} \left[\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x} \right]$$

$$J_{\text{I}} = \frac{p_1}{m} |A|^2 - \frac{p_1}{m} |B|^2$$

← Reflected wave
→ Incident wave

$$|A|^2 = AA^*$$

$$|B|^2 = BB^*$$

$$|C|^2 = CC^*$$

$$J_{\text{T}} = \frac{p_2}{m} |C|^2 \quad \text{--- Transmitted}$$

Transmittance

$$T = \frac{\text{mag. of Transmitted wave intensity}}{\text{" " Incident " "}}$$

$$= \frac{\frac{p_2}{m} |C|^2}{\frac{p_1}{m} |A|^2} = \frac{p_2 |C|^2}{p_1 |A|^2}$$

$$= \frac{p_2 \left(\frac{2 p_1}{p_1 + p_2}\right)^2 |A|^2}{p_1 |A|^2}$$

$$\boxed{T = \frac{4 p_1 p_2}{(p_1 + p_2)^2}}$$

Reflectance: mag. of Reflected wave Int

" " Incident "

$$= \frac{p_1 |B|^2}{m}$$

$$\frac{p_1 |A|^2}{m}$$

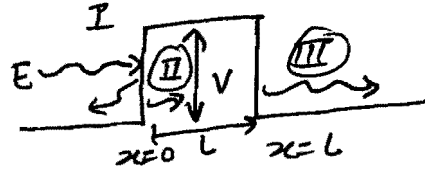
$$= \frac{\left(\frac{p_1 - p_2}{p_1 + p_2}\right)^2 |A|^2}{|A|^2}$$

$$\boxed{R = \frac{(p_1 - p_2)^2}{(p_1 + p_2)^2}}$$

② Pot. Barrier Problem with finite width -

Let us consider a free

particle of mass m , Energy E , collides with pot. barrier of height V ($0 < x < L$) as



Schrodinger eqn in Region I -

$$\frac{d^2\psi_I}{dx^2} + \frac{2m}{\hbar^2} (E-0) \psi_I = 0$$

$$\frac{d^2\psi_I}{dx^2} + \frac{2mE}{\hbar^2} \psi_I = 0$$

$$\frac{d^2\psi_I}{dx^2} + k_1^2 \psi_I = 0$$

$$\psi_I = Ae^{ik_1x} + Be^{-ik_1x}$$

$$\psi_I = Ae^{i\frac{p_1x}{\hbar}} + Be^{-i\frac{p_1x}{\hbar}}$$

$$E < V$$

We are studying Tunneling phenomenon -

Particle having energy less than the energy of barrier have the tendency to cross the barrier is known as tunneling

OR

To find the particle in classical forbidden region is tunneling

② Schrodinger eqn in II region -

$$\frac{d^2\psi_{II}}{dx^2} + \frac{2m}{\hbar^2} (E-V) \psi_{II} = 0$$

$$\frac{d^2\psi_{II}}{dx^2} + k_2^2 \psi_{II} = 0$$

$$k_2 = \frac{\sqrt{2m(E-V)}}{\hbar} = \frac{p_2}{\hbar}$$

$$\psi_{II} = Ce^{ik_2x} + De^{-ik_2x}$$

$$= Ce^{i\frac{p_2x}{\hbar}} + De^{-i\frac{p_2x}{\hbar}}$$

Schrodinger eqn in III region -

$$\frac{d^2 \psi_{III}}{dx^2} + \frac{2m}{\hbar^2} (E-0) \psi_{III} = 0$$

$$\frac{d^2 \psi_{III}}{dx^2} + \frac{2m}{\hbar^2} E \psi_{III} = 0$$

$$\frac{d^2 \psi_{III}}{dx^2} + k_1^2 \psi_{III} = 0$$

$$k_1^2 = \frac{2mE}{\hbar^2}$$

$$\Downarrow$$
$$\psi_{III} = E e^{i p_1 x / \hbar} + F e^{-i p_1 x / \hbar}$$

Applying Boundary Conditions -

Current density

$$J_I = \frac{p_1}{m} |A|^2 - \frac{p_1}{m} |B|^2$$

$$J_{III} = \frac{p_1}{m} |E|^2$$

$$\text{Reflectance} = \frac{\frac{p_1}{m} |B|^2}{\frac{p_1}{m} |A|^2} = \frac{|B|^2}{|A|^2}$$

$$\text{Transmittance} = \frac{\frac{p_1}{m} |E|^2}{\frac{p_1}{m} |A|^2} = \frac{|E|^2}{|A|^2}$$

When we put the boundary condition and solve the resultant eqn by doing lot of algebra, we get, the expression of Tunneling / T

$$T = \frac{4E(V-E)}{4E(V-E) + V^2 \sinh^2(k_2 L)}$$

$$\sinh(k_2 L) = \frac{e^{k_2 L} - e^{-k_2 L}}{2}$$

$$T = \frac{4E(V-E)}{4E(V-E) + v^2 \left(\frac{e^{k_2L} - e^{-k_2L}}{2} \right)^2}$$

$$k_2 = \frac{p_2}{\hbar} = \frac{\sqrt{2m(V-E)}}{\hbar}$$

if k_2L is large means

either V large OR L large OR both large

$$e^{k_2L} \gg e^{-k_2L}$$

Then

$$T = \frac{4E(V-E)}{4E(V-E) + v^2 \left(\frac{e^{k_2L}}{2} \right)^2}$$

$$T = \frac{16E(V-E)}{16E(V-E) + v^2 e^{2k_2L}}$$

As k_2L large

V large

v^2 very large

$$\Rightarrow v^2 e^{2k_2L} \gg 16E(V-E)$$

$$T = \frac{16E(V-E)}{v^2 e^{2k_2L}} = \frac{16E(V-E)}{v^2} e^{-2k_2L}$$

As V is large, then E

As value of v increases, $\frac{16E(V-E)}{v^2}$ tends to unity

$$\therefore T_{\text{approx}} = e^{-2k_2L} = e^{-2 \frac{\sqrt{2m(V-E)}}{\hbar} L}$$

Factors affecting

$$V \uparrow T \downarrow$$

$$m \uparrow T \downarrow$$

$$L \uparrow T \downarrow$$

$$E \uparrow T \uparrow$$

$$p_1 = \sqrt{2mE} \quad p_2 = \sqrt{2m(E-V)}$$

$$\frac{\hbar}{m} = \sqrt{2mE} \quad \frac{\hbar}{2m} = \sqrt{2m(E-V)}$$

$$\frac{\sqrt{2m(E-V)}}{\sqrt{2mE}} = \frac{\frac{\hbar}{2m}}{\frac{\hbar}{m}} = \frac{1}{2}$$

$$\frac{\sqrt{E-V}}{\sqrt{E}} = \frac{1}{2} \Rightarrow \frac{E-V}{E} = \frac{1}{4}$$

$$1 - \frac{V}{E} = \frac{1}{4}$$

$$\frac{V}{E} = 1 - \frac{1}{4}$$

$$\frac{V}{E} = \frac{3}{4}$$

②

$$\psi = A e^{ik_1 x}$$

$$k_1 = \frac{p_1}{\hbar} = \frac{\sqrt{2mE}}{\hbar}$$

$$A e^{ik_1 x} + B e^{-ik_1 x}$$

$$J_1 = \frac{p_1}{m} |A|^2 = \frac{p_1}{m} |B|^2$$

$$\frac{k_1 \hbar}{m} |A|^2$$

③

$$T = \frac{4 p_1 p_2}{(p_1 + p_2)^2}$$

$$p_1 = \sqrt{2mE}$$

$$p_2 = \sqrt{2m(E-V)}$$

$$= \frac{4 \sqrt{E} \sqrt{E-V}}{(\sqrt{E} + \sqrt{E-V})^2}$$

$$\frac{4 \sqrt{5} \sqrt{2}}{(\sqrt{5} + \sqrt{2})^2} = \frac{12.64}{13.32}$$

DPP 10

1. Consider the statements

(a) Each wavefunction is orthogonal to all of others even if the symmetry of two function is same. **T** *in SHO*(b) The particle in box function differ from the harmonic oscillator function because in PIB model tunneling phenomena does not exist but in SHO it exist. **T**(c) A particle with wavelength M strikes the potential barrier with region of $2M$ wavelength the ratio of V and E is $2/1$. **F** *infinite width*

The correct statements above are (a) i,ii (b) ii,iii (c) i,iii (d) i,ii,iii (e) none (f) all

2. The probability current density corresponding to function $\psi = Ae^{ikx}$ is(a) $hk/2\pi m$ (b) $(hk/2\pi m) A^2$ (c) $(2\pi/hkm) A^2$ (d) none3. An electron with energy 5 eV strikes a potential barrier of infinite width and with height 3 eV then the transmission coefficient is(a) 0.1 (b) 0.3 (c) 0.5 (d) 0.6 (e) none

4. When a particle with energy higher than potential barrier strikes the barrier with infinite width then the expression of transmission coefficient is

a) $T = e^{-2\sqrt{2m(V-E)}L/\hbar}$

b) $T = \sqrt{2m(V-E)} \cdot L/\hbar$

c) $T = e^{-2\sqrt{2m(V-E)}L/\hbar}$

d) $T = \{4P_1P_2/(P_1+P_2)^2\}$

5. Consider the statement

i) function ψ_0 and ψ_1 are orthogonal to each other in 1D SHO. **T**ii) The average value of kinetic energy in first excited state in case of 1D SHO is 0.75 hv . **T**iii) Maximum amplitude in SHO is a classical term that may be obtained by equating potential energy to the kinetic energy. **F** *$V = Et$*

The correct statements above are (a) i,ii (b) ii,iii (c) i,iii (d) i,ii,iii

6. Consider the statement

i) The spacing between n energy level and ground state in SHO is $nh\nu$. **F** *$nh\nu$* ii) The degeneracy concept in SHO occur when we discuss anisotropic SHO. **F** *(in isotropics)*iii) As we move towards higher vibrational quantum number tunneling probability in SHO decreases. **T**

The correct statements above are (a) i only (b) ii only (c) iii only (d) i,ii (e) i,ii,iii (f) none

7. Consider the statements

i) The spacing between the energy levels is $\hbar\omega$ and there is a zero point energy at $(1/2)\hbar\omega$. In 1900 Planck's treatment of blackbody radiation predicted the same arrangement of energy levels. **T**ii) The spacing between energy levels of an oscillator with a large force constant k is higher than spacing between energy levels of an oscillator with a small force constant k . **T** *$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}}$* iii) ψ_{2p-1} and ψ_{2p1} are eigenfunction of L_z but ψ_{2px} and ψ_{2py} are not eigenfunction of L_z . **T**

The correct statements above are (a) i,ii (b) ii,iii (c) i,iii (d) i,ii,iii (e) none

ψ_0
 ψ_{p2} } are
eigenfunction
of L_z

$\psi_{2p-1} \propto \sin\theta e^{-i\phi}$
 $\psi_{2p+1} \propto \sin\theta e^{i\phi}$

$\psi_{2px} \propto \sin\theta \cos\phi$
 $\psi_{2py} \propto \sin\theta \sin\phi$ } not L_z
function
eigen

$$E_1 - E_0 = h\nu$$

$$E_0 = \frac{h\nu}{2}$$

$$E_0 = \frac{2143}{2} = 10.71$$

$$k = 4\pi^2 c^2 \nu \mu$$

8) The strongest infrared band of $^{12}\text{C}^{16}\text{O}$ occurs at 2143 cm^{-1} the force constant of $^{12}\text{C}^{16}\text{O}$ is

- (a) 2155 N/m (b) 1855 N/m (c) 1658 N/m (d) 2056 N/m

9 fill in the blanks

i) The term degeneracy is applicable to the eigenvalue of any operator not just the Hamiltonian

ii) The function ψ_{2pz} is zero in xy plane.

iii) If the harmonic oscillator wavefunction ψ_n is an even function than ψ_{n+1} is an odd function.

iv) The $n=10$ harmonic oscillator has 10 nodes

v) For $n=1$ harmonic oscillator the most likely position of particle is at.....

vi) The IR spectrum of $^1\text{H}^{35}\text{Cl}$ has its strongest band at $8.65 \times 10^{13} \text{ Hz}$ the approximate zero point vibrational energy for $^1\text{H}^{35}\text{Cl}$ is $\frac{1}{2} h\nu = \frac{1}{2} \times 6.6 \times 10^{-34} \times 8.65 \times 10^{13}$

10 Out of p_x, p_y and p_z orbital of hydrogen atom which of the following is an eigenfunction of L_z

- (a) only p_z is the eigenfunction (b) only p_x (c) p_x and p_y (d) all

11 Consider the statements

$$E = \frac{h^2}{8\pi^2 I} J(J+1)$$

i) The energy of a rotating particle is $28h^2/I$ the degeneracy corresponding to this energy level is 15. T

ii) The probability corresponding to $J=0$ state is 0.1, probability corresponding to $J=1$ state is 0.6 and probability corresponding to $J=2$ state is 0.3 then average value of energy is 3 B. T

iii) The value of magnetic quantum number of p_x orbital is +1. F

Correct statement above are (a) i,ii (b) i,ii,iii (c) ii,iii (d) i,iii (e) none

12. Consider the statement

i) The wavefunctions corresponding to hydrogenic atom are real function when $m=0$, and complex function otherwise. T

ii) The probability of finding the electron in $1s$ state outside a sphere of radius $3a_0$ is 0.062. T

$$P = 1 - e^{-2D} (2D^2 + 2D)$$

$$D = 3$$

iii) In rigid rotor potential energy is taken is zero because no hindrance in rotation. T

The correct statement above are

- (a) i,ii (b) ii,iii (c) i,iii (d) i,ii,iii (e) none

13. Suppose that the wavefunction for a system can be written as

$$\Psi = (1/2)\Phi_1(x) + (1/4)\Phi_2(x) + \frac{(3+\sqrt{2}i)}{4}\Phi_3(x)$$

(i) The function ψ is not normalised because imaginary part is present. F

(ii) Function ψ is not normalized but can be normalize. F

(iii) Function ψ is normalized. If the energy corresponding to state $\Phi_1(x), \Phi_2(x)$ and $\Phi_3(x)$ is $E_1, 3E_1$ and $7E_1$ then the energy corresponding to state $\Phi_3(x)$ is $7E_1/16$.

True statement above are (a) i,ii (b) ii,iii (c) i,iii (d) i,ii,iii (e) none (f) ii only

14. A hydrogenic $3p$ orbital has the following form of the radial wave function ($\alpha_i = \text{constant}$)

- (a) $(\alpha_1 - r)e^{-\alpha_2 r}$ (b) $r^2 e^{-\alpha_3 r}$ (c) $r(\alpha_4 - r)(\alpha_5 - r)e^{-\alpha_6 r}$ (d) $r^3 e^{-\alpha_7 r}$

15. Consider the statements

i) There are exactly $2l+1$ different wavefunction $\psi_{n,l,m}$ for each $E_{n,l,m}$.

ii) There are exactly $l(l+1)$ different wavefunction $\psi_{n,l,m}$ for each $E_{n,l,m}$

iii) $E_{n,l,m}$ does not depend on l and m for the Coulomb potential.

The correct statement above are, (a) i, ii (b) ii, iii (c) i, ii, iii (d) i, iii (e) none (f) iii only (g) ii only

- Approximation method in QM -

Most problem encountered in QM can not be solved exactly.

Exact soln of Schrodinger eqn is exist for a few idealise system

So a no. of problem don't have exact soln, for those problem we have to focus on approximate soln. A no. of method have been develop for this purpose we consider approximation method

that deal with stationary state corresponding to

Time independent Hamiltonian. To study problem of stationary state we focused on (3) method

- (i) Perturbation
- (ii) Variation
- (iii) WKB method

Perturbation method-

Perturbation theory is used when the deviation b/w two problems (ideal & exact) is small & it based on the assumption that the problem we want to solve is slightly different from a problem that can be solved exactly. It is suitable for calculating the contribution associated with this deviation. This contribution is add as a correction to energy & wave function of exactly solvable Hamiltonian. Perturbation theory use exact soln to obtain approximate soln.

$$H^0 \psi_n^0 = E_n^0 \psi_n^0 \rightarrow \begin{array}{l} \text{Zero order} \\ \text{perturbation} \\ \text{OR} \\ \text{exact} \end{array}$$

nth state

$$E_n^{(1)} \leftarrow \begin{array}{l} \text{order of perturbation} \\ \text{state.} \end{array}$$

$$H^0 \psi_n^0 = E_n^0 \psi_n^0$$

If original Hamiltonian H^0 , original function ψ_n^0 (unperturbed)

E_n^0 - exact form of Schrodinger's energy

Then $H^0 \psi_n^0 = E_n^0 \psi_n^0$

If Hamiltonian is slightly perturbed by ΔH & corresponding change in energy is ΔE

$$\Delta E_n^{(1)} = \int \psi_n^0 \Delta H \psi_n^0 d\tau$$

First order correction to n th state of energy, is not else but may be considered as expectation value corresponding to perturbed part of Hamiltonian. When we take unperturbed part in consideration

$$\Delta E_n^{(1)} = \int \underbrace{\psi_n^0}_{\text{Unperturbed}} \underbrace{\Delta H}_{\text{Perturbed}} \underbrace{\psi_n^{(0)}}_{\text{Unperturbed}} d\tau$$

$$H_0 \psi_n^0 = E_n^0 \psi_n^0$$

$$(H_0 + \Delta H)(\psi_n^0 + \Delta \psi) = (E_n^0 + \Delta E)(\psi_n^0 + \Delta \psi)$$

$$E_n^{(1)} = E_n^{(0)} + \Delta E_n^{(1)} \text{ --- Corrected energy}$$

\swarrow
 Total energy of n th
 state after the 1st order
 perturbation.

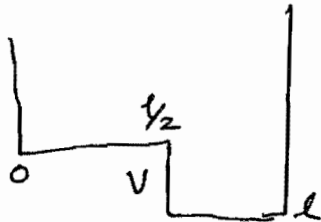
Feature of 1st order perturbation -

① If exactly solvable system is perturbed by constt. variable then value of energy correction below of perturbation may be obtained by result of probability.

eg. If particle is confined to box of l



& a perturbation is introduced as



$$\begin{aligned}
 0 < x < \frac{l}{2} & \quad H^1 = V \\
 \frac{l}{2} < x < l & \quad V = 0
 \end{aligned}$$

Then energy correction to the n th state because of 1st order perturbation

$$\Delta H = V$$

↙
0 to $\frac{L}{2}$

$$\Delta E_n^{(1)} = \int_0^{L/2} \psi_n^0 \Delta H \psi_n^0 d\tau$$

$$= \int_0^{L/2} \psi_n^0 V \psi_n^0 d\tau$$

$$= V \int_0^{L/2} \psi_n^0 \psi_n^0 d\tau$$

$$= V \left[\frac{1}{2} \right]$$

$$\left[\because \int_0^{L/2} \psi_n^0 \psi_n^0 d\tau = \frac{1}{2} \right]$$

$$= \frac{V}{2}$$

② If perturbation is introduced in SHO by ~~even~~ odd powers of x , then first order correction ~~is~~ to energy is zero.

eg. In 1-D SHO ut H' OR $\Delta H = x^3$ is introduced as the perturbation

$$\Delta E_n^{(1)} = \int \psi_n^{(0)} H' \psi_n^0 d\tau$$

$$= \int \psi_n^{(0)} x^3 \psi_n^0 d\tau$$

$$\boxed{\Delta E_n^{(1)} = 0}$$

$$\left[\because \int \psi_n^0 x^3 \psi_n^0 d\tau = 0 \right]$$

OR

$$H' = Ax$$

$$\Delta E_n^{(1)} = 0$$

③ If perturbed part of Hamiltonian is containing of position or any power of position only then the energy correction may be obtained by using the average value.

e.g. - If we introduce perturbed part of Hamiltonian in 1-D box of 0 to L, then first order energy correction to the nth state as

$$\Delta H = H' = \lambda x$$

$$\Delta E_n^{(1)} = \int \psi_n^0 \lambda x \psi_n^0 dx$$

$$= \lambda \int \psi_n^0 x \psi_n^0 dx$$

$$= \lambda \langle x \rangle$$

$$= \lambda \frac{L}{2}$$

④ If perturbed part of Hamiltonian of Dirac delta function then the energy correction because of perturbed part of Hamiltonian is obtained by mathematical operation of Dirac delta function.

The delta function can be defined by

$$\int_{-\infty}^{\infty} f(x) \delta(x) dx = f(0)$$

\downarrow
 $\delta(x-0)$
 $x=0$

$$\int_{-\infty}^{\infty} f(x) \delta(x-a) f(x) dx = f(a)$$

$$\downarrow$$

$$x=a$$

Most useful property of delta function is

$$\# \int_a^b f(x) \delta(x-m) dx = I$$

$$\text{If } a < m < b$$

$$I = f(m)$$

Other wise

$$I = 0$$

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20

$$H' \text{ OR } \Delta H = \delta(x - \frac{l}{2})$$

First order correction to ground state energy

$$\Delta E_1^{(1)} = \int \psi_1^0 \Delta H \psi_1^0 dx$$

$$= \int_0^l \sqrt{\frac{2}{L}} \sin \frac{\pi x}{L} \delta(x - \frac{l}{2}) \sqrt{\frac{2}{L}} \sin \frac{\pi x}{L} dx$$

$$= \frac{2}{L} \int_0^l \sin \frac{\pi x}{L} \delta(x - \frac{l}{2}) \sin \frac{\pi x}{L} dx$$

↓

Dirac δ under value of $x = \frac{l}{2}$

$$0 < x < \frac{l}{2}$$

$$\Rightarrow f(\frac{l}{2})$$

$$= \frac{2}{L} \sin \frac{\pi}{L} \frac{L}{2} \sin \frac{\pi}{L} \frac{L}{2}$$

$$= \frac{2}{L} \sin \frac{\pi}{2} \sin \frac{\pi}{2}$$

$$\Delta E_1^{(1)} = \frac{2}{L}$$

$$H_n^0 \psi_n^0 = E_n^0 \psi_n^0$$

The solution corresponding to exact soln of schrodinger

If we perturb the Hamiltonian by ΔH

The new Hamiltonian is

$$H_n = H_n^0 + \Delta H$$

New function is

$$\psi_n = \psi_n^0 + \Delta \psi$$

New energy value is

$$E_n = E_n^0 + \Delta E$$

Because the deviation from ideality is small (when we study perturbation)

So new Hamiltonian, new function and new energy must also follow schrodinger, means

$$H_n \psi_n = E_n \psi_n$$

$$(H_n^0 + \Delta H)(\psi_n^0 + \Delta \psi) = (E_n^0 + \Delta E)(\psi_n^0 + \Delta \psi)$$

$$\underline{H_n^0 \psi_n^0} + H_n^0 \Delta\psi + \Delta H \psi_n^0 + \Delta H \Delta\psi$$

$$= \underline{E_n^0 \psi_n^0} + E_n^0 \Delta\psi + \Delta E_n \psi_n^0 + \Delta E_n \Delta\psi$$

$$[\because H_n^0 \psi_n^0 = E_n^0 \psi_n^0] \text{---(1)}$$

$$H_n^0 \Delta\psi + \Delta H \psi_n^0 + \Delta H \Delta\psi = E_n^0 \Delta\psi + \Delta E_n \psi_n^0 + \Delta E_n \Delta\psi$$

First Term and last term are neglected because

ΔH is small

$\Delta\psi$ is small

$\Delta H \Delta\psi \rightarrow$ further small \Rightarrow neglected.

$\Delta E_n \Delta\psi \rightarrow$ neglected

$$\boxed{H_n^0 \Delta\psi + \Delta H \psi_n^0 = E_n^0 \Delta\psi + \Delta E_n \psi_n^0} \text{---(2)}$$

each term in eqn (2) is the multiplication of one unperturbed term & one of perturbed, so this eqn represents the first-order perturbation.

$$H_n^0 \Delta\psi + \Delta H \psi_n^0 = E_n^0 \Delta\psi + \Delta E_n \psi_n^0$$

To determine the value of ΔE_n multiply by ψ_n^{0*} from the left side & integrated w.r.t $d\tau$ as

$$\begin{aligned} \int \psi_n^{0*} H_n^0 \Delta\psi d\tau + \int \psi_n^{0*} \Delta H \psi_n^0 d\tau \\ = \int \psi_n^{0*} E_n^0 \Delta\psi d\tau + \int \psi_n^{0*} \Delta E_n \psi_n^0 d\tau \end{aligned}$$

$$\int \psi_n^{0*} H_n^0 \Delta \psi d\tau - \int \psi_n^{0*} E_n^0 \Delta \psi d\tau + \int \psi_n^{0*} \Delta H \psi_n^0 d\tau = \Delta E_n \int \psi_n^{0*} \psi_n^0 d\tau$$

$$\int \psi_n^{0*} (H_n^0 - E_n^0) \Delta \psi d\tau + \int \psi_n^{0*} \Delta H \psi_n^0 d\tau = \Delta E_n$$

$$\int \psi_n^{0*} (H_n^0 - E_n^0) \Delta \psi d\tau$$

This term is zero if $H_n^0 - E_n^0$ is Hermitian, as

$$\int \Delta \psi (H_n^0 - E_n^0)^* \psi_n^{0*} d\tau$$

$$\int \Delta \psi (H_n^0 \psi_n^{0*} - E_n^0 \psi_n^{0*}) d\tau$$

$$= 0 \quad \left[\because H_n^0 \psi_n^{0*} = E_n^0 \psi_n^{0*} \right]$$

$$\therefore \Delta E_n = \int \psi_n^{0*} \Delta H \psi_n^0 d\tau$$

DPP-11

(2)

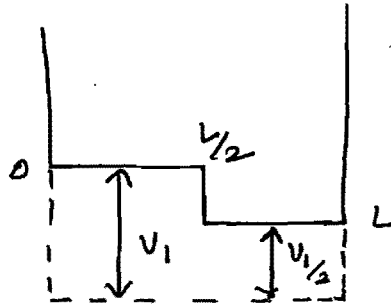
$$\Delta E_0^{(1)} = \int \psi_0 \Delta H \psi_0 dx$$

$$= \int \psi_0 \lambda x \psi_0 dx$$

$$= \lambda \int \psi_0 x \psi_0 dx$$

$$= 0$$

③



$$n=1 = \Delta E_1^{(1)} = ?$$

$$\begin{aligned} & \int_0^{L/2} \psi_1^0 V_1 \psi_1^0 dx + \int_{L/2}^L \psi_1^0 \frac{V_1}{2} \psi_1^0 dx \\ &= V_1 \int_0^{L/2} \psi_1^0 \psi_1^0 dx + \frac{V_1}{2} \int_{L/2}^L \psi_1^0 \psi_1^0 dx \\ &= V_1 \frac{L}{2} + \frac{V_1}{2} \frac{L}{2} \\ &= \frac{V_1}{2} + \frac{V_1}{4} \\ &= \frac{3V_1}{4} \end{aligned}$$

④

$$\psi = \sqrt{\frac{2}{L}} \sin \frac{n_x \pi}{L} x \sqrt{\frac{2}{L}} \sin \frac{n_y \pi}{L} y \sqrt{\frac{2}{L}} \sin \frac{n_z \pi}{L} z$$

$$E = \frac{(n_x^2 + n_y^2 + n_z^2) \hbar^2}{8mL^2}$$

$$\begin{aligned} \Delta E_{1,1,1}^{(1)} &= \int \psi_{1,1,1} \Delta \psi_{1,1,1} d\tau \\ &= \int_0^L \int_0^L \int_0^L \sqrt{\frac{2}{L}} \sin \frac{\pi x}{L} \sqrt{\frac{2}{L}} \sin \frac{\pi y}{L} \sqrt{\frac{2}{L}} \sin \frac{\pi z}{L} V_0 L^3 \delta(x-0.25L) \delta(y-0.75L) \\ &\quad \delta(z-0.25L) \sqrt{\frac{2}{L}} \sin \frac{\pi x}{L} \sqrt{\frac{2}{L}} \sin \frac{\pi y}{L} \sqrt{\frac{2}{L}} \sin \frac{\pi z}{L} \end{aligned}$$

$$\left(\frac{\sqrt{2}}{L}\right)^6 V_0 L^3 \int_0^L \sin \frac{\pi x}{L} \delta(x-0.25L) dx \int_0^L \sin \frac{\pi x}{L} \delta(x-0.75L) \sin \frac{\pi y}{L} dy$$

$$\int_0^L \sin \frac{\pi z}{L} \delta(x-0.25)L \sin \frac{\pi z}{L} dz$$

$$= \left(\frac{2}{L}\right)^3 V_0 L^3 \sin \frac{\pi}{L} \cdot \frac{L}{4} \sin \frac{\pi}{L} \cdot \frac{L}{4} \cdot \sin \frac{\pi}{L} \frac{3L}{4} \sin \frac{\pi}{L} \cdot \frac{3L}{4}$$

$$\cdot \sin \frac{\pi}{L} \frac{L}{4} \sin \frac{\pi}{L} \cdot \frac{L}{4}$$

$$= 8V_0 \sin \frac{\pi}{4} \sin \frac{\pi}{4} \sin \frac{3\pi}{4} \sin \frac{3\pi}{4} \sin \frac{\pi}{4} \sin \frac{\pi}{4}$$

$$= 8V_0 \times \frac{1}{8}$$

$$= V_0$$

→ Total energy of ground state —

$$E_{1,1,1}^{(1)} = E_{1,1,1}^{(0)} + \Delta E_{1,1,1}^{(1)}$$

$$= \frac{3h^2}{8mL^2} + V_0$$

odd $\Rightarrow 0$

(5)

$$V = \frac{k}{2} x^2 + \underbrace{\frac{r}{6} x^3 + \frac{b}{24} x^4}_{\Delta H}$$

$$\Delta E_0^{(1)} = \int \psi_0 \Delta H \psi_0 d\tau$$

$$= \int \left(\frac{B}{\pi}\right)^{1/4} e^{-Bx^2/2} \frac{b}{24} x^4 \left(\frac{B}{\pi}\right)^{1/4} e^{-Bx^2/2} dx$$

$$= \left(\frac{B}{\pi}\right)^{1/2} \cdot \frac{b}{24} \int_{-\infty}^{\infty} e^{-\frac{Bx^2}{2}} x^4 e^{-\frac{Bx^2}{2}} dx$$

$$= \left(\frac{B}{\pi}\right)^{1/2} \cdot \frac{b}{24} \int_{-\infty}^{\infty} x^4 e^{-Bx^2} dx$$

$$= \left(\frac{B}{\pi}\right)^{1/2} \cdot \frac{b}{24} \cdot \frac{\frac{3}{2} \cdot \frac{1}{2} \sqrt{\pi}}{\beta^{5/2}}$$

$$= \frac{b}{32 \beta^2}$$

⑥

$$H = \underbrace{-\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r}}_{\text{exact}} + \underbrace{eE \cos\theta}_{\text{Corrected}}$$

$$H' = H_0 + \Delta H$$

$$\Delta H = eE \cos\theta \quad (\text{electric field applied from } z \text{ direction})$$

$$\Delta E_{1s}^{(1)} = \int \psi_{1s} \Delta H \psi_{1s} d\tau$$

$$= eE \int_0^a \int_0^{2\pi} \int_0^\pi r^2 e^{-2r/a_0} \cos\theta \sin\theta d\theta \int_0^{2\pi} d\phi$$

$$= 0$$

⑧

$$\int \psi_m(\phi) P \sin\phi \psi_m^*(\phi) d\phi$$

$$= \int \frac{1}{\sqrt{2\pi}} e^{im\phi} P \sin\phi e^{-im\phi} d\phi$$

$$= \frac{P}{2\pi} \int_0^{2\pi} \sin\phi d\phi$$

$$= \frac{P}{2\pi} [\cos 2\pi - \cos 0] = 0$$

$$\Delta E_i^{(1)} = \int \psi_i \Delta H \psi_i dx$$

$$= \int_{-a}^a \psi_i (ba - bx) \psi_i dx$$

$$= \int_{-a}^a \psi_i ba \psi_i dx - \int_{-a}^a \psi_i bx \psi_i dx$$

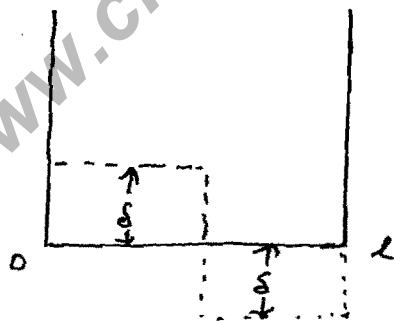
$$= ba \int_{-a}^a \psi_i \psi_i dx - b \int_{-a}^a \psi_i x \psi_i dx$$

$$= ba - 0$$

$$= ba$$

(11)
Note:-

In general when a system disturb or correction is made in exactly solvable system then it is true because there is addition of Hamiltonian part in the exactly solvable Hamiltonian. (In hypothetical case the value of ΔH may be taken -ve)



$$\int_0^L \psi_n \Delta H \psi_n dx$$

$$= \int_0^{\delta/2} \psi_n \delta \psi_n dx + \int_{\delta/2}^L \psi_n (-\delta) \psi_n dx$$

$$= \delta \frac{L}{2} - \delta \frac{L}{2}$$

$$= 0$$

(13)

$$\begin{aligned} \Delta E_n^{(1)} &= \int_0^{2L} \frac{1}{\sqrt{L}} \sin \frac{n\pi x}{2L} dV_0 \delta(x-L) \frac{1}{\sqrt{L}} \sin \frac{n\pi x}{2L} dx \\ &= \frac{dV_0}{L} \int_0^{2L} \sin \frac{n\pi x}{2L} \delta(x-L) \sin \frac{n\pi x}{2L} dx \\ &= \frac{dV_0}{L} \sin \frac{n\pi}{2L} \cdot L \sin \frac{n\pi}{2L} \cdot L \end{aligned}$$

$$\Delta E_n^{(1)} = \frac{dV_0}{L} \sin^2 \frac{n\pi}{2L}$$

$$E = E_n^{(0)} + \Delta E_n^{(1)}$$

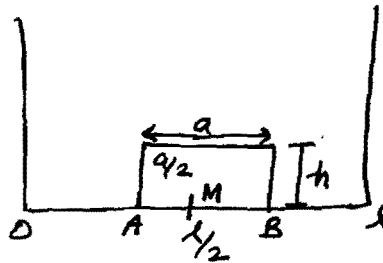
$$= \frac{n^2 h^2}{32mL^2} + \frac{dV_0}{L} \sin^2 \frac{n\pi}{2L}$$

$$E = \frac{n^2 h^2}{32mL^2} + 0 \text{ when } n = \text{even}$$

$$\frac{dV_0}{L} \text{ " } n = \text{odd}$$

(14)

OA to OB
 ↓ ↓
 OM-AM OM+MB
 $\frac{l}{2} - \frac{a}{2}$ $\frac{l}{2} + \frac{a}{2}$
 $\frac{l-a}{2}$ $\frac{l+a}{2}$



$$\int_{\frac{l-a}{2}}^{\frac{l+a}{2}} \psi_1^* \Delta H \psi_1 dx$$

$$= \frac{2}{L} \int_{\frac{l-a}{2}}^{\frac{l+a}{2}} \sin \frac{\pi x}{L} h \sin \frac{\pi x}{L} dx$$

$$= \frac{2h}{L} \int_{\frac{l-a}{2}}^{\frac{l+a}{2}} \sin^2 \frac{\pi x}{L} dx$$

$$= \frac{1}{2} [x] - \frac{1}{4b} [\sin 2bx]$$

DPP 11 Quantum Chemistry

1. The first-order correction to energy for the ground state of a particle-in-a-box (0 to L) due to a perturbation λx would be (a) $\lambda L/2$ (b) λL (c) $2\lambda L$ (d) 2 **CSIR MODEL PAPER**

2. A particle in a one dimensional harmonic oscillator in x-direction is perturbed by a potential λx (λ is a number). The first-order correction to the energy of the ground state (a) is zero (b) is negative (c) is positive (d) may be negative or positive but NOT zero. **CSIR June**

3. A particle is confined to move in a 1D box of length L, the left half of the box is perturbed by V_1 and right half of the box is perturbed by $V_1/2$, First order correction to the ground state energy because of perturbation is **PHYSICS**

(a) $V_1/4$ (b) $3V_1/4$ (c) $5V_1/4$ (d) $3V_1/2$ (e) none

4. Find the exact energies and wave functions of the ground and first excited states and specify their degeneracies for the infinite cubic potential well $V=0$ [$0 < x < L$, $0 < y < L$, $0 < z < L$]. Now add the following perturbation to the infinite cubic well $H_p = V_0 L^3 \delta(x-0.25L) \delta(y-0.75L) \delta(z-0.25L)$. Using first order perturbation theory calculate the energy of the ground state.

5. An oscillator is governed by the potential $V = (k/2)x^2 + (\gamma/6)x^3 + (b/24)x^4$ using a harmonic oscillator as an unperturbed problem, calculate the first order correction to the energy of the ground state in simple harmonic oscillator is..... **from z direction**

6. A hydrogen atom is in an electric field of strength E . The Hamiltonian operator for this system is as given $H = -(\hbar^2/2m_e) \Delta^2 - (e^2/4\pi\epsilon_0 r) + eE \cos \theta$, The first order correction to ground state energy of hydrogen atom is (a) $E\pi$ (b) $E\pi/2$ (c) E (d) 0 E none **$E \propto \cos \theta$**

7. Consider the statements **$V = \frac{1}{2} E z$**

(a) First order correction to the ground state energy is the expectation value corresponding to perturbed part of Hamiltonian when we take perturbed part of function into consideration. **F**

(b) When the value of first order energy correction because of perturbation becomes zero then we apply second order or higher order perturbation. **T**

(c) perturbation method generally apply when the deviation of the real system from ideality is large. **F**

Correct statements above are

i) a,b (ii) b,c (iii) a,b,c (iv) b only (v) a only (vi) none

8. When we operate perturbed part of Hamiltonian $H_1 = P \sin \Phi$ on rotating particle. Then first order correction to the energy is

(a) P (b) $P/2\pi$ (c) $P^2/4\pi^2$ (d) 0

9. When we perturb Simple harmonic oscillator by odd power of x then first order and second order energy correction becomes equal to **Zero**

(a) Constant (b) zero (c) nonzero (d) can not calculate

10. Particle is confined to move in a 1D box of length $-L$ to $+L$, the system is perturbed by $b(a-x)$ then first order correction to the ground state energy is **..0... Gate phys**

11. A one-dimensional box potential is perturbed so that it is raised by a constant amount, δ , in the left half of the box, and lowered by δ in the right half then first order correction in energy (a) Zero in ground state because it is symmetric but non zero in first excited state because it is antisymmetric

(b) Non zero in ground state because it is symmetric but zero in first excited state because it is antisymmetric (c) Zero in both ground and first excited state

(d) non-zero in both ground and first excited state

(15)

Q12. Consider the statement

(a) first-order correction to the energy is the expectation value for the perturbation operator calculated using the wavefunction of the perturbed system. **F**

(b) Particle is confined to move in 1D box of length L box is perturbed by amount λx^2 first order correction to the energy is $\lambda L^2/3$. **F**

(c) When perturbative correction is applied on the ground state, the second order correction to energy is always positive

The correct statements above are (a) 1,2 (b) 2,3 (c) 1,3 (d) all (e) none

Q13 Using first-order perturbation theory, calculate the energy of the n th excited state for a spinless

particle of mass m moving in an infinite potential well of length $2L$, with walls at $x = 0$ and $x = 2L$: $V=0$ inside the box and V is infinite elsewhere which is modified at the bottom by the following perturbation $V_p = \lambda V_0 \delta(x-L)$.

Q14. Determine the first order correction to the energy in ground state from the following figure (discussed in the class)

Q15. Calculate the first order correction to energy for a particle in a 1-D box of length a with the potential $V = x/a$ inside the box and $V = \infty$ outside.

Q16. Consider the one-particle, 1D system with potential energy $V = \hbar^2/ml^2$ for $l/4 < x < 3l/4$, $V=0$ for $0 < x < l/4$ and $x > 3l/4$ What result do you expect (to first order) if the potential \hbar^2/ml^2 is treated as a perturbation.

Q17. A particle is confined to move in 1-D box of length L . $V=0$ is inside half of the wavelength, $V=0.1 E_1^0$ in the other half and V is infinite other wise. Where E_1^0 is the ground state energy.

Q18. A particle is confined to move in 1 D box of length $2a$ ($-a < x < a$) if the system is perturbed by $V = \delta\{x-(a/2)\}$ then first order energy correction to first excited state is $\dots \frac{1}{a} \dots$ Gate Chem $n=2$

Q19. When we operate perturbed part of Hamiltonian $H_1 = P \cos \Phi$ on rotating particle. Then first order correction to the m th state of energy is \dots (if $\psi = (2\pi)^{-1/2} e^{im\phi}$ for rotating particle in m state) Gate Chem

Q20. A particle is confined to move in 1 D box of length l , if system is perturbed by $\delta\{x-(l/2)\}$ Then first order energy correction to the ground state is $\Delta E_1^{(1)} = \dots \frac{2}{l} \dots$ CSIR CHEM $\Delta E_1^{(1)} = \frac{2}{l}$

Q21. A particle in a 1D harmonic oscillator in x direction is perturbed by a potential λx (λ is a number). The first order correction to the energy of the ground state is CSIR CHEM

a) is zero

b) is negative

c) is positive

d) may be negative, positive but not zero

22. Consider an infinite, one-dimensional potential well of length L , with walls at $x = 0$ and $x = L$, that is modified at the bottom by a perturbation $V_p(x)$:

$$V(x) = \begin{cases} 0, & 0 < x < L, \\ \infty, & \text{elsewhere,} \end{cases} \quad V_p(x) = \begin{cases} V_0, & 0 \leq x \leq L/2, \\ 0, & \text{elsewhere,} \end{cases} \quad \frac{V_0}{2}$$

Using first order perturbation theory Find the value of E_n .

23. First order perturbation correction $\Delta E_n^{(1)}$ to the energy level E_n of a simple harmonic oscillator due to anharmonicity perturbation γx^3 is given by Gate Chem

a) $\Delta E_n^{(1)} = \gamma$ b) $\Delta E_n^{(1)} = \gamma^2$ c) $\Delta E_n^{(1)} = \gamma^{-1}$ d) $\Delta E_n^{(1)} = 0$

(16)

(18)

(15)

$$V = \frac{x}{a}$$

$$\begin{aligned} \Delta E_p^{(1)} &= \int_0^a \psi_n V \psi_n dx \\ &= \int_0^a \psi_n \frac{x}{a} \psi_n dx \\ &= \frac{1}{a} \times \frac{a}{2} \end{aligned}$$

$$= \frac{1}{2}$$

(16)

$$\int_{1/4}^{3/4} \psi_1(x) \frac{\hbar^2}{m\lambda^2} \psi_1 dx$$

$$= \frac{\pi \hbar^2}{m\lambda^2} (827.)$$

(18)

$$n=2$$

$$\left(\frac{1}{4}\right)$$

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★ Second order perturbation Theory -

First order correction to energy of nth state

$$\Delta E_n^{(1)} = \int \psi_n^* \Delta H \psi_n d\tau = \langle \psi_n | \Delta H | \psi_n \rangle$$

Second order correction to energy of nth state -

$$\Delta E_n^{(2)} = \sum_{m \neq n} \frac{\left(\int \psi_m^* \Delta H \psi_n d\tau \right)^2}{E_n - E_m} = \sum_{m \neq n} \frac{\langle \psi_m^* | \Delta H | \psi_n \rangle^2}{E_n - E_m}$$

$$= \sum_{m \neq n} \frac{\Delta H_{mn}^2}{E_n - E_m}$$

→ 2nd order correction in ground state energy of SHO -

$$\downarrow$$

n=0

$$\Delta E_0^{(2)} = \frac{\left(\int \psi_1 \Delta H \psi_0 d\tau \right)^2}{E_0 - E_1} + \frac{\left(\int \psi_2 \Delta H \psi_0 d\tau \right)^2}{E_0 - E_2} + \frac{\left(\int \psi_3 \Delta H \psi_0 d\tau \right)^2}{E_0 - E_3} + \dots$$

$$= \frac{\Delta H_{10}^2}{E_0 - E_1} + \frac{\Delta H_{20}^2}{E_0 - E_2} + \frac{\Delta H_{30}^2}{E_0 - E_3} + \dots$$

→ 2nd order correction in energy in first excited state of 1-D Box -

$$n=2$$

$$\Delta E_2^{(2)} = \frac{\left(\int \psi_1 \Delta H \psi_2 d\tau \right)^2}{E_2 - E_1} + \frac{\left(\int \psi_3 \Delta H \psi_2 d\tau \right)^2}{E_2 - E_3} + \frac{\left(\int \psi_4 \Delta H \psi_2 d\tau \right)^2}{E_2 - E_4} + \dots$$

$$= \frac{\Delta H_{12}^2}{E_2 - E_1} + \frac{\Delta H_{32}^2}{E_2 - E_3} + \frac{\Delta H_{42}^2}{E_2 - E_4} + \dots$$

DPP 12 Quantum Mechanics

Q1) An unperturbed 2 level system has energy eigen value E_1 and E_2 and has energy eigenfunction $\begin{bmatrix} 1 \\ 0 \end{bmatrix}$ and $\begin{bmatrix} 0 \\ 1 \end{bmatrix}$ when perturbed its Hamiltonian is represented by $\begin{matrix} E_1 & A \\ A^* & E_2 \end{matrix}$

- i) The first order correction to E_1 is (a) $4A$ (b) $2A$ (c) A (d) 0
 ii) The second order correction to energy E_1 is (a) 0 (b) A (c) A^2/E_2-E_1 (d) A^2/E_2-E_1
 iii) The first order correction to the wavefunction is

(a) $\begin{bmatrix} 0 \\ A^*/E_2 - E_1 \end{bmatrix}$ (b) $\begin{bmatrix} A^*/E_2 - E_1 \\ 0 \end{bmatrix}$ (c) $\begin{bmatrix} 0 \\ 1 \end{bmatrix}$ (d) $\begin{bmatrix} 1 \\ 1 \end{bmatrix}$

Q2. Consider a particle in a one dimensional box of length 'a' with the following potential

$$V(x) = \infty \quad x < 0$$

Dec CSIR

$$V(x) = \infty \quad x > a, \quad V(x) = 0 \quad ; \quad 0 \leq x \leq a/2 \quad V(x) = V_1 \quad a/2 \leq x \leq a$$

Starting with the standard particle in a box Hamiltonian as the zeroth order Hamiltonian and the potential of V_1 from 'a/2' to 'a' as a perturbation, the first-order energy correction to the ground state is

- (a) V_1 (b) $V_1/4$ (c) $-V_1$ (d) $V_1/2$

Q3. The unperturbed energy levels of a system are $\epsilon_0 = 0$, $\epsilon_1 = 2$ and $\epsilon_2 = 4$. The second order correction to energy for the ground state in presence of the perturbation V for which $V_{10} = 2$, $V_{20} = 4$ and $V_{12} = 6$ has been found to be

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- (a) -6 (b) 0 (c) $+6$ (d) -8

Q4. For non-degenerate perturbation theory for ground state, with $E_o^{(0)}$ as zeroth order energy,

$E_o^{(1)}$ as the first-order perturbation correction and E_o as the exact energy, which of the following is true?

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- (a) $(E_o^{(0)} + E_o^{(1)})$ is always equal to E_o (b) $(E_o^{(0)} + E_o^{(1)}) \leq E_o$
 (c) $(E_o^{(0)} + E_o^{(1)}) \geq E_o$ (d) $E_o^{(0)} \leq (E_o \leq E_o^{(1)})$

Q5. The following are the three statements about perturbation theory

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- (A) Second order perturbation correction to the ground state energy is ALWAYS negative. \bar{T}
 (B) Sum of the zeroth order and the first order corrections to the ground state energy is ALWAYS greater than the exact ground state energy. \bar{T}
 (C) Sum of the zeroth order and first order correction to the ground state energy is less than the exact state energy. \bar{F}

From the following which one is correct?

- (a) Only A is true ~~(b) Both A and B are true~~
 (c) Only C is true (d) Both B and C are true

Q6 A particle in a 1-dimensional box of length L is perturbed by a delta function potential, $\delta(x - L/4)$, in the middle of the box. The first order energy correction to the ground state will be

[Hint: $\int_{-\infty}^{\infty} f(x)\delta(x-a)dx = f(a)$]

- (a) 0 ~~(b) $1/L$~~ (c) $L/2$ (d) $2/L$

Q7 An eigenstate of energy satisfies $H\psi_n = E_n\psi_n$. In the presence of an extra constant potential V_0 . June CSIR

a) Both E_n and ψ_n will change. b) Both E_n and the average kinetic energy will change.

~~c) Only E_n will, but not ψ_n~~ d) Only ψ_n will change, but not E_n .

Q8 A particle is in a one-dimensional box with a potential $V=0$ inside the box and infinite outside. An energy state corresponding to $n = 0$ (n : quantum number) is not allowed because CSIR

a) The total energy becomes zero b) The average momentum becomes zero

~~c) The wave function becomes zero everywhere~~ d) The potential $V_0 = 0$

Q9 A hydrogen atom is in an electric field of strength E . The Hamiltonian operator for this system is as given $H = -(\hbar^2/2m_e)\Delta^2 - (e^2/4\pi\epsilon_0 r) + eE r \cos \theta$. The second order correction to ground state energy of hydrogen atom (till 4 term) is

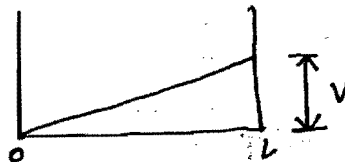
Q10 A particle is confined to move in 1 D box of length L . $V=0$ is inside half of the wavelength, $V=0.1 E_1^0$ in the other half and $V = \infty$ otherwise. Where E_1^0 is the ground state energy. Find the first order and second order energy correction (till 2 term) in perturbation theory. And write also the wavefunction corresponding to second order perturbation

Q11 A particle in a 1-dimensional box of length L is perturbed as given in figure the first order correction in ground state energy is

(figure should be given in the class)

- a) V b) V/L c) $V/2L$ d) None

(c)



Q12 Consider the statements

- i) Variational method does not require the knowledge of simpler Hamiltonian which solution is known exactly.
- ii) Trial wavefunction in variational principle should taken into account all the physical property of that states for which function is taken as trial wave function.
- iii) Variational parameter are adjustable in nature, that is used to minimize the energy that is calculated by trial wave function.

$$\begin{aligned} \epsilon_0 &= 0 & V_{10} &= 2 \\ \epsilon_1 &= 2 & V_{20} &= 4 \\ \epsilon_2 &= 4 & V_{12} &= 6 \end{aligned}$$

$$\Delta E_0^{(2)} = \frac{\left(\int \psi_1 \Delta H \psi_0^* d\tau \right)^2}{\epsilon_0 - \epsilon_1} + \frac{\left(\int \psi_2 \Delta H \psi_0^* d\tau \right)^2}{\epsilon_0 - \epsilon_2} + \dots$$

$$= \frac{\Delta H_{10}^2}{\epsilon_0 - \epsilon_1} + \frac{\Delta H_{20}^2}{\epsilon_0 - \epsilon_2} + \frac{\Delta H_{30}^2}{\epsilon_0 - \epsilon_3}$$

$$= \frac{V_{10}^2}{\epsilon_0 - \epsilon_1} + \frac{V_{20}^2}{\epsilon_0 - \epsilon_2} + \dots$$

$$= \frac{(2)^2}{0-2} + \frac{(4)^2}{0-4}$$

$$= -\frac{4}{2} - \frac{16}{4}$$

$$= \textcircled{-6}$$

$$\Delta E_n^{(2)} = \frac{\langle \psi_m^* \Delta H \psi_n^* \rangle \langle \psi_m^* \Delta H \psi_n^* \rangle}{\epsilon_n - \epsilon_m}$$

$$\Delta E_{1s}^{(1)} = 0$$

$$\Delta E_{1s}^{(2)} = \frac{\left(\int \psi_{2s} \Delta H \psi_{1s} d\tau \right)^2}{\epsilon_{1s} - \epsilon_{2s}} + \frac{\left(\int \psi_{2px} \Delta H \psi_{1s} d\tau \right)^2}{\epsilon_{1s} - \epsilon_{2px}}$$

$$+ \frac{\left(\int \psi_{2py} \Delta H \psi_{1s} d\tau \right)^2}{\epsilon_{1s} - \epsilon_{2py}} + \frac{\left(\int \psi_{2pz} \Delta H \psi_{1s} d\tau \right)^2}{\epsilon_{1s} - \epsilon_{2pz}}$$

$$\int \psi_{2s} \Delta H \psi_{1s} d\tau = 0$$

$$\downarrow \quad \downarrow$$

$$\cos\theta \quad \sin\theta d\theta = 0$$

$$\int \psi_{2p_x} \Delta H \psi_{1s} d\tau$$

$$\downarrow \quad \searrow \quad \downarrow$$

$$\sin\theta \cos\phi \quad \cos\theta \sin\theta \quad \cos\phi = 0$$

$$\int \psi_{2p_y} \Delta H \psi_{1s} d\tau$$

$$\downarrow \quad \rightarrow \int_0^{2\pi} \sin\theta \sin\phi d\phi = 0$$

$$\int \psi_{2p_z} \Delta H \psi_{1s} d\tau \neq 0$$

$$\downarrow \quad \downarrow \quad \downarrow$$

$$\cos\theta \quad \cos\theta \quad \sin\theta d\theta d\phi$$

$$\int_0^{2\pi} \int_0^\pi \cos^2\theta \sin\theta d\theta = \frac{2}{3} \int_0^{2\pi} d\phi = 2\pi$$

★ 2nd order perturbation correction to the ground state energy is always -ve

$$\Delta E_0^{(2)} = \frac{\left(\int \psi_m \Delta H \psi_0 d\tau \right)^2}{E_0 - E_m}$$

$$E_0 > E_m \quad (\text{always})$$

$$E_0 - E_m = -ve$$

$$\therefore \boxed{\Delta E_0^{(2)} = -ve}$$

★ First order perturbation correction to the function of n th state -

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$$\psi_n^{(1)} = \sum_{m \neq n} \frac{|\psi_m^0\rangle \langle \psi_m^0 | \Delta H | \psi_n^0\rangle}{E_n^0 - E_m^0}$$

eg. 1st order correction to function for $\Delta H = V$

$$\psi_1^{(1)} = \frac{\psi_2 \Delta H \psi_1 d\tau}{E_1 - E_2} \psi_2 + \frac{\psi_3 \Delta H \psi_1 d\tau}{E_1 - E_3} \psi_3 + \dots$$

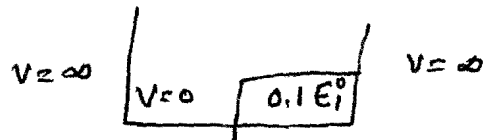
$$\psi_1^{(1)} = \left(\frac{\sqrt{2/L} \sin \frac{2\pi x}{L} \psi_2 \sin \frac{\pi x}{L}}{\frac{h^2}{8mL^2} - \frac{4h^2}{8mL^2}} \sqrt{\frac{2}{L}} \sin \frac{2\pi x}{L} x + \frac{\sqrt{2/L} \sin \frac{3\pi x}{L} \psi_3 \sin \frac{\pi x}{L}}{\frac{h^2}{8mL^2} - \frac{9h^2}{8mL^2}} \sqrt{\frac{2}{L}} \sin \frac{3\pi x}{L} x + \dots \right)$$

$$E_n^{(2)} = \int \psi_n^{(1)} \Delta H \psi_n^{(1)} d\tau$$

$$= \frac{\langle \psi_m^0 | \Delta H | \psi_n^0 \rangle \langle \psi_n^0 | \Delta H | \psi_m^0 \rangle}{E_n - E_m}$$

DPP-12

(10)



$$\Delta H = 0.1 E_1^0 = \frac{0.1 h^2}{8mL^2} \quad \left(\frac{L}{2} < x < L \right)$$

$$\Delta E_n^{(1)} = \int_{L/2}^L \psi_n \Delta H \psi_n d\tau = \frac{0.1 h^2}{8mL^2} \times \frac{1}{2} = \frac{0.1 h^2}{16mL^2}$$

$$= 0.05 \frac{h^2}{8mL^2}$$

$$E_1^{(1)} = E_n^0 + E_n^1$$

$$= \frac{h^2}{8mL^2} + \frac{0.05 h^2}{8mL^2} = \frac{1.05 h^2}{8mL^2}$$

$$\Delta E_1^{(2)} = \frac{\left(\int_{L/2}^L \psi_2 \Delta H \psi_1 d\tau \right)^2}{E_1 - E_2} + \frac{\left(\int_{L/2}^L \psi_3 \Delta H \psi_1 d\tau \right)^2}{E_1 - E_3}$$

$$\Delta H = \frac{0.1 h^2}{8mL^2}$$

$$E_1 = \frac{h^2}{8mL^2}$$

$$\psi_1 = \sqrt{\frac{2}{L}} \sin \frac{\pi x}{L}$$

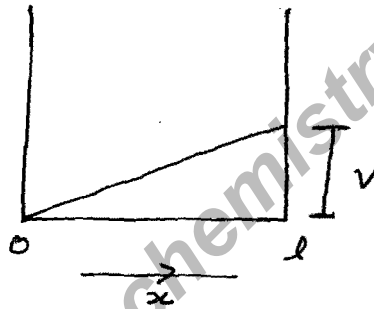
$$E_2 = \frac{4h^2}{8mL^2}$$

$$\psi_2 = \sqrt{\frac{2}{L}} \sin \frac{2\pi x}{L}$$

$$E_3 = \frac{9h^2}{8mL^2}$$

$$\psi_3 = \sqrt{\frac{2}{L}} \sin \frac{3\pi x}{L}$$

(11)



$$\Delta H = \frac{Vx}{L}$$

$$y = mx$$

$$x=0 \quad V=0$$

$$x=\frac{L}{2} \quad V=\frac{V}{2}$$

$$x=L \quad V=V$$

$$\int_0^L \psi_1 \frac{Vx}{L} \psi_1 dx$$

$$\frac{V}{L} \int_0^L \psi_1 x \psi_1 dx$$

$$= \frac{V}{L} \times \frac{L}{2} = \frac{V}{2}$$

①

$$\psi_1 = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \quad \psi_2 = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

$$H_T = \begin{bmatrix} E_1 & A \\ A^* & E_2 \end{bmatrix}$$

$$H \begin{bmatrix} 1 \\ 0 \end{bmatrix} = E_1 \begin{bmatrix} 1 \\ 0 \end{bmatrix}$$

$$H \begin{bmatrix} 0 \\ 1 \end{bmatrix} = E_2 \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

$$= \begin{bmatrix} E_1 & 0 \\ 0 & E_2 \end{bmatrix} + \begin{bmatrix} 0 & A \\ A^* & 0 \end{bmatrix}$$

$$\downarrow$$

H

$$\downarrow$$

 ΔH

$$\begin{bmatrix} E_1 & 0 \\ 0 & E_2 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \begin{bmatrix} E_1 \times 1 + 0 \times 0 \\ 0 \times 1 + E_2 \times 0 \end{bmatrix} = \begin{bmatrix} E_1 \\ 0 \end{bmatrix}$$

$$\begin{bmatrix} E_1 & 0 \\ 0 & E_2 \end{bmatrix} \begin{bmatrix} 0 \\ 1 \end{bmatrix} = \begin{bmatrix} E_1 \times 0 + 0 \times 1 \\ 0 \times 0 + E_2 \times 1 \end{bmatrix} = \begin{bmatrix} 0 \\ E_2 \end{bmatrix}$$

(v)

$$\Delta E_1^{(1)} = \langle \psi_1^* \Delta H \psi_1 \rangle$$

$$\langle \begin{bmatrix} 1 \\ 0 \end{bmatrix}^* \begin{bmatrix} 0 & A \\ A^* & 0 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} \rangle$$

$$\langle \begin{bmatrix} 1 & 0 \end{bmatrix} \begin{bmatrix} 0 & A \\ A^* & 0 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} \rangle$$

$$\langle \begin{bmatrix} 1 & 0 \end{bmatrix} \begin{bmatrix} 0 \\ A^* \end{bmatrix} \rangle$$

$$1 \times 0 + 0 \times A^*$$

$$= 0$$

(ii)

$$\Delta E_2^{(1)} = \frac{\langle \psi_2^* \Delta H \psi_1 \rangle^2}{E_1 - E_2}$$

$$\frac{\langle \begin{bmatrix} 0 \\ 1 \end{bmatrix} \begin{bmatrix} 0 & A \\ A^* & 0 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \end{bmatrix} \rangle^2}{E_1 - E_2} = \frac{\langle \begin{bmatrix} 0 & 1 \end{bmatrix} \begin{bmatrix} 0 \\ A^* \end{bmatrix} \rangle^2}{E_1 - E_2}$$

$$= \frac{A^{*2}}{E_1 - E_2}$$

(iii)

$$\psi_1 = \frac{A^*}{E_1 - E_2}$$

* Variation Principle Method -

Deviation from Ideality is large. www.chemistryABC.com

There exists many system in QM which hamiltonian is known but they can't be solved exactly or by perturbative treatment i.e. there is no closely related Hamiltonian that can be solved exactly or approximately by perturbation theory. One of the approximation method that is suitable for solving these problems is variation method. This method does not require knowledge of simpler Hamiltonian that can be solved exactly so it is considered as alternate to schrodinger eqn.

It is a hit & trial method in which we take a trial wave function to determine the average value of energy and the value of energy by trial method must be greater than energy of exact soln. To calculate the minimum energy, we consider the following (4) steps.

① Guess of the trial wave function -

Based on the physical

intention make an educated guess of a wavefunction that takes into account all the physical parameters of the state (Symmetry, node, behaviour at infinity). We also include some adjustable parameters or any possibility of unknown property and to minimize the energy.

CSID

Qus-1 A trial wave function $\psi = x(l-x)$ is proposed for a particle in one-D box. The value of energy for this wavefunction is

(1) $E = \frac{h^2}{8ml^2}$

(2) $E_{\psi} > \frac{h^2}{8ml^2}$

Soln-

Let us check the state corresponding to which trial wave function is proposed.

$\psi = x(l-x)$

0 to l

To check Node put $\psi = 0$

No. node $\Rightarrow n=1$

$x=0$ } \rightarrow boundary

$\psi=0$ }

$x=l$ } \rightarrow Boundary

$\psi=0$ }

$n=1 = E = \frac{1h^2}{8ml^2} = \frac{h^2}{8ml^2}$

$E_{\psi} > \frac{h^2}{8ml^2}$

energy of trial wave function will be greater than energy of exact wavefunction energy value.

Qus-2 A trial wave function $\psi(x) = x(\frac{l}{2}-x)(l-x)$ is proposed for particle in 1-D box. The value of energy for this wave function.

Soln \rightarrow

$\psi(x) = x(\frac{l}{2}-x)(l-x)$

To check the node - $\psi = 0$

$x(\frac{l}{2}-x)(l-x) = 0$

$x=0$

$x=0$ boundary

$\frac{l}{2}-x=0$

$x=\frac{l}{2} \rightarrow$ node

\rightarrow (n-1) \Rightarrow State $n=2$

$l-x=0$

$x=l$ boundary

$$n=2$$

$$E = \frac{4h^2}{8mL^2}$$

$$E_{\psi} > \frac{4h^2}{8mL^2}$$

Qus-3 A trial wave function that is proposed for an electronic Hydrogenic atom is $N(3-\sigma)e^{-B\sigma}$ and the energy corresponding to this wave function \bar{E} . The exact ground state wavefunction corresponding to the hydrogenic atom is $N_1e^{-\sigma}$ with energy E_1 . The first excited state wave function corresponding to hydrogenic atom is $N_2(2-\sigma)e^{-\alpha\sigma}$ with energy E_2 .

Which one of relations is correct

(a) $\bar{E} > E_2 > E_1$

(b) $E_2 > \bar{E} > E_1$

(c) $E_2 = \bar{E} > E_1$

(d) $\bar{E} > E_2$

$$\psi = N(3-\sigma)e^{-B\sigma}$$

$$\psi=0 \quad N(3-\sigma)e^{-B\sigma}$$

$(3-\sigma)$ node

$$e^{-B\sigma} = 0$$

$(\sigma < \infty)$ boundary

$$\bar{E} > E_2$$

→ Energy of trial wave function will be compared to energy of exact function of same state

② Calculate the energy by using postulate of QM -

$$E_{\phi} = \frac{\int \phi H \phi d\tau}{\int \phi \phi d\tau}$$

We get the value of E in terms of α, β

③ To minimize the value of energy differentiate the value of energy w.r.t. adjustable parameter (α, β) & get the value of adjustable parameters.

$$\frac{dE}{d\alpha} = 0$$

$$\frac{dE}{d\beta} = 0$$

④ By putting value of α, β etc. in process 3rd, we get value of energy in process ② we get E_{min}

DPP-13

$$\psi = e^{-cx^2}$$

$$E = \frac{\hbar^2}{2m} C + \frac{m\omega^2}{8C}$$

① find the value of variational parameter

$$\frac{dE}{dC} = 0 \Rightarrow \frac{\hbar^2}{2m} - \frac{m\omega^2}{8C^2} = 0$$

$$\frac{m\omega^2}{8C^2} = \frac{\hbar^2}{2m}$$

$$C^2 = \frac{2m^2\omega^2}{8\hbar^2} = C = \frac{m\omega}{2\hbar}$$

$$E = \frac{\hbar^2}{2m} \frac{m\omega}{2\hbar} + \frac{m\omega^2}{8} \frac{2\hbar}{m\omega}$$

$$= \frac{\omega\hbar}{4} + \frac{2\omega\hbar}{4} = \frac{\omega\hbar}{2}$$

(20)

$$E = \frac{3\hbar^2}{2m} \beta + \frac{3m\omega^2}{8\beta^2}$$

$$\frac{\partial E}{\partial \beta} = \frac{3}{2} \frac{\hbar^2}{m} - \frac{3m\omega^2}{8\beta^2} = 0$$

$$\frac{3}{2} \frac{\hbar^2}{m} = \frac{3m\omega^2}{8\beta^2}$$

$$24\hbar^2\beta^2 = 6m^2\omega^2$$

$$\beta^2 = \frac{6m^2\omega^2}{24\hbar^2}$$

$$\frac{6m^2\omega^2}{24\hbar^2} = \frac{m^2\omega^2}{4\hbar^2}$$

$$\beta = \frac{m\omega}{2\hbar^{3/2}}$$

(16)

$$E = \frac{e^2}{a_0} \left[Z_{\text{eff}} - \left(\frac{27}{8}\right) Z_{\text{eff}}^2 \right]$$

$$\frac{\partial E}{\partial Z_{\text{eff}}} = 0 \quad \frac{e^2}{a_0} - \frac{27}{8} \frac{e^2}{a_0} Z_{\text{eff}} = 0$$

(17)

$$E = \frac{\pi\hbar^2}{2me\alpha} - \frac{e^2}{4\epsilon_0\alpha^2}$$

$$\frac{\partial E}{\partial \alpha} = 0 \quad -\frac{\pi\hbar^2}{2me\alpha^2} + \frac{2e^2}{4\epsilon_0\alpha^3} = 0$$

$$\frac{2e^2}{4\epsilon_0\alpha^3} = \frac{\pi\hbar^2}{2me\alpha^2}$$

$$\frac{2e^2}{4\epsilon_0\alpha} = \frac{\pi\hbar^2}{2me}$$

$$\alpha = \frac{4me^2}{4\epsilon_0\pi\hbar^2}$$

$$\Delta H = E_0 \left(\frac{\alpha^2}{104} \right) \quad \psi_0 = \left(\frac{\alpha}{\pi} \right)^{1/4} e^{-\alpha^2 x^2/2}$$

$$E_0^{(1)} = \int \psi_0 \Delta H \psi_0 d\tau = \int \left(\frac{\alpha^2}{\pi} \right)^{1/4} e^{-\alpha^2 x^2/2} E_0 \left(\frac{\alpha^2}{104} \right) \left(\frac{\alpha^2}{\pi} \right)^{1/4} e^{-\alpha^2 x^2/2} dx$$

$$= \left(\frac{\alpha^2}{\pi} \right)^{1/2} E_0 \frac{\alpha^4}{104} \int_{-\infty}^{\infty} x^4 e^{-\alpha^2 x^2/2} dx$$

DPP 13 QUANTUM CHEMISTRY

1. The first order correction in the function in perturbation theory for nth state is $\sum_{m \neq n} \langle \psi_m^0 | \Delta H | \psi_n^0 \rangle \frac{\psi_m^0}{E_n^0 - E_m^0}$

2. The wave function for a 1D SHO is $\psi_0 = (\alpha^2/\pi)^{1/4} e^{-\alpha^2 x^2/2}$ for the ground state, perturbed by $E_0 (\alpha x/10)^4$. the first order change in ground state energy is

(a) $(E_0/2)10^{-4}$ (b) $(3E_0/4)10^{-4}$ (c) $(3E_0)10^{-4}$ (d) $(E_0)10^{-4}$

3. A certain 2-level system has stationary state energies E_1 and E_2 ($E_1 < E_2$) and with normalized wave functions ϕ_1 and ϕ_2 respectively. In the presence of a perturbation, the second-order correction to the energy for the first state will be

1. $\frac{\langle \phi_2 | V | \phi_2 \rangle}{E_1 - E_2}$ 2. $\frac{\langle \phi_2 | V | \phi_2 \rangle}{E_2 - E_1}$
 3. $\frac{|\langle \phi_2 | V | \phi_1 \rangle|^2}{E_1 - E_2}$ 4. $\frac{|\langle \phi_2 | V | \phi_1 \rangle|^2}{(E_1 - E_2)^2}$

4. Calculate the variational energy of a particle in a hard one-dimensional box of length a , using the variation function $\phi(x) = Ax(a-x)$. % error in energy

5. Consider the statement

i) Variational principle is valid for ground state only. F

ii) If the variational function is orthogonal to exact solutions to the Schrödinger equation that correspond to all the states of lower energy than the state we are interested in, the variational principle is still valid. \rightarrow Condition that variation principle applied to other states.

iii) The Ritz method represents a special kind of variational method. The trial function Φ is represented as a linear combination of the known basis functions $\{\psi_i\}$ with the (for the moment) unknown variational coefficients. T

The correct statements above are

a) i,ii b) ii,iii c) i,ii,iii d) i,iii e) i only

6. A trial function used in the variational method for the hydrogen atom had the form: $\psi = \exp(-c_1 r) + c_2 \exp(-r/2)$. From a variational procedure we obtained:

a) $c_1 = c_2 = 0$; b) $c_1 = 1, c_2 = 0$; c) $c_1 = 0, c_2 = 1$; d) $c_1 = 1, c_2 = 1$.

7. In the Ritz method (M terms) we obtain approximate wave functions only for:

a) the ground state; b) the ground state and M excited states; c) M states; d) one electron systems.

8. In a variational method, four classes of trial functions have been applied and the total energy computed. The exact value of the energy is equal to -50.2 eV. Choose the best approximation to this value obtained in correct calculations:

a) -48.2 eV; b) -50.5 eV; c) -45.3 eV; d) -43.0 eV.

9. In the Ritz method (Φ stands for the trial function, \hat{H} the Hamiltonian, E_0 the exact ground-state energy, ψ_0 the exact ground-state wave function, $\epsilon = \Phi | \hat{H} \Phi / \Phi | \Phi$) the trial function Φ is always a linear combination of:

a) orthonormal functions; b) unknown functions to be found in the procedure; c) eigenfunctions of \hat{H} ; d) known functions

10. Variational method Φ stands for the trial function, \hat{H} the Hamiltonian, E_0 the exact ground-state energy, and ψ_0 the exact ground-state wave function, $\epsilon = \Phi | \hat{H} \Phi / \Phi | \Phi$. If $\epsilon = E_0$, this means that:

a) $\psi_0 = \Phi$; b) $|\Phi|^2 = 1$; c) $\psi_0 = \Phi$; d) $\psi_0 = E_0$

11. A trial wavefunction used in SHO e^{-cx^2} was used and energy value was obtained as

$(\hbar^2 C/2m) + (m\omega^2/8C)$ The minimum value of energy that was obtained by variational principle is

$$\frac{\sqrt{n+1}}{2} \beta^{n+1/2}$$

$$= \frac{\sqrt{5/2}}{(\alpha^2)^{5/2}}$$

$$= \frac{3}{4} \sqrt{\pi} \alpha^5$$

fact

Imp

(a) $\hbar\omega/2$ (b) $\hbar\omega$ (c) $\hbar\omega/4$ (d) $2\hbar\omega$

12. Which of the variational function have acceptability for a particle confined to move in 1D box of length L is (a) x (b) x^2 (c) $x^2(a-x)^2$ (d) all are acceptable

13. A trial wave function for SHO was proposed i.e. $\psi = (\beta x^2 - 1)e^{-\beta x^2}$ if the energy calculated by this function is E than which of the below is correct

(a) $E > 0.5 \hbar\omega$ (b) $E > 2.5 \hbar\omega$ (c) $E > 3.5 \hbar\omega$ (d) $E > 4.5 \hbar\omega$

14. Assume that for a real system a real function is a linear combination of two orthonormal set of wavefunction Where the energy integrals are $H_{11} = -15$, $H_{12} = H_{21} = -1$, Evaluate the approximate value of energy of real system and determine the coefficient of the expansion $\psi = C_1 \Phi_1 + C_2 \Phi_2$

15. Consider the statement

$$H_{22} = -3$$

i) energy calculated by perturbation theory may be higher or lower than exact value of energy.

ii) Huckel method is an assumption, in which π, σ part of the bonding in molecule can be separated.

iii) In huckel approximation all the overlap in adjacent atom is considered as Zero. T

Correct statements above are (a) ii, iii (b) i, iii (c) i, ii (d) all (e) none

16. A normalized slater orbital for 1S orbital in Helium atom is $\psi_{1s} = (1/\pi)^{0.5} (Z_{\text{eff}}/a_0)^{1.5} e^{-Z_{\text{eff}}/a_0}$ Its leads to following energy $E = e^2/a_0 [Z_{\text{eff}} - (27/8)Z_{\text{eff}}]$ Treat Z_{eff} as a variational parameter calculate the min energy.

17. By using trial wave function $e^{-\alpha r}$ the energy calculated by variational principle is $(\pi\hbar^2/2m_e\alpha) - (e^2/4C_0\alpha^2)$, the value of variational parameter α is And the minimum value of energy obtained from variational principle is

18. The energy calculated for a multielectron atom using variational function is $E = (\alpha\hbar^2/m) - \alpha^2\hbar$ The value of variational parameter α is

(a) \hbar/m (b) $\hbar/2m$ (c) $2\hbar/m$ (d) $\hbar m$ (e) none

19. The ionization potential of hydrogen atom is 13.6 eV. The first ionization potential of a sodium atom assuming that energy of its outer electron can be represented by H-atom like model with effective nuclear charge 1.84 is

Gate 2007 Chemistry

(a) 46.0 eV (b) 11.5 eV (c) 5.1 eV (d) 2.9 eV

20. A trial wavefunction used in SHO $\beta x e^{-\beta x^2}$ was used and energy value was obtained as

$(3\pi^2\beta/2m) + (3m\omega^2/8\beta)$ The minimum value of β is

(a) $(m\omega/2\hbar)$ (b) $(m\omega/\hbar)$ (c) $2m\omega/\hbar$ (d) none of these

21. Consider the statements

i) A trial wavefunction $(2-r)e^{-\alpha r}$ is suitable for an electron in 2p orbital. F

ii) The expectation value of the energy calculated with any function ϕ obeying the same boundary conditions as the correct system wave functions cannot be lower than E_g . T

iii) Trial wave function with more than one parameter can produce impressive result but price we have to pay for that is lengthy calculation. T

Correct statements above are a) i, ii, iii b) ii, iii c) i, ii d) i, iii

22. The radial part of a hydrogenic wave function is given $asr(\alpha-r)^{\beta r}$ (α and β are constants). This function is then identifiable as

a) 2s b) 3p c) 4d d) 5f

⑬

$$\psi = (\beta x^2 - 1) e^{-\beta x}$$

To check no. of nodes -

$$x = \pm \frac{1}{\sqrt{\beta}} \quad \beta = \infty \text{ Boundary}$$

nodes = 2

State $n=2$

⑫

To check the acceptability of wave function
 First of all determine the value of energy
 and then calculate % change in energy if it is +ve
 function is valid.

$$\psi(x) = x \quad (0 < x < L)$$

$$E\psi(x) = \frac{\int x \left(\frac{h^2}{2m} \frac{d^2}{dx^2} \right) x dx}{\int x x dx} = 0$$

$$E\phi = 0$$

$$\frac{E\phi - E_1}{E_1} \times 100 = (-100\%) \quad \text{Not valid}$$

$$\phi(x) = x^2 \quad (0 < x < L)$$

$$\frac{\int x^2 \left(-\frac{h^2}{2m} \frac{d^2}{dx^2} \right) x^2 dx}{\int x^2 x^2 dx}$$

$$\frac{\int x^2 \left(-\frac{h^2}{2m} 2 \right) dx}{\int x^4 dx}$$

$$\frac{-\frac{h^2}{2m} \int x^2 dx}{\int x^4 dx}$$

Linear Variational Principle-

A special type of variation

widely used in study of molecule is so called linear variational function, a linear combination of n independent function f_1, f_2, \dots, f_n (often atomic orbital) that satisfy the boundary condition of problem.

Function may be written as

$$\psi = \sum c_i f_i$$

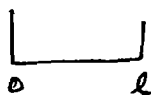
The coefficient c_i are the parameter can be determined by minimising the energy.

In linear variational principle, the trial wave function linearly dependent on the parameters.

Application-

widely applicable in studying MOT, VBT, HMOT but may be apply to simple system also.

If we take the wave function for a simpler system of PIB As



$$(i) \psi = c_1 x(l-x)$$

$$(ii) \psi = c_1 x(l-x) + c_2 x^2(l-x)^2$$

$$(iii) \psi = c_1 x(l-x) + c_2 x^2(l-x)^2 + c_3 x^3(l-x)^3$$

It was found that as the no. of variational parameters n increases the accuracy of result increases means longer the chain of a total wavefunction, closer its energy to the exact energy

$$E_1 > E_2 > E_3 > E_{\text{exact}}$$

But price we have to pay is lengthy mathematical calculation, so generally we use computer programming for this purpose.

Qus- Two trial wave functions

$$c_1 x(a-x) = \psi_1$$

$$c_1 x(a-x) + c_2 x^2(a-x)^2 = \psi_2$$

give ground state energy E_1 & E_2 for a microscopic particle in 1-D Box. By using variation method, if exact ground state energy is E_0 what is the relation?

$$E_0 < E_2 < E_1$$

Qus A particle in 1-D Box has ground state energy $E_0 = \frac{0.125 h^2}{ma^2}$

the expectation value of the above Hamiltonian with function

$$\psi(x) = x(x-a) \text{ yield } E_1$$

using a linear combination of two even function $x(x-a)$ & $x^2(x-a)^2$ we obtain the min energy E_2 .

$$\psi_1 = c_1 x(x-a) \text{ --- } E_1$$

$$\psi_2 = c_1 x(x-a) + c_2 x^2(x-a)^2 \text{ --- } E_2$$

$$E_0 < E_2 < E_1$$

★ The sum of linear variational function leads to Secular Determinate-

let us consider ψ is a linear variation-function that is summation of two wave function ϕ_1 & ϕ_2 as

$$\psi = c_1 \phi_1 + c_2 \phi_2$$

To find the energy, we use 3rd postulate (Av. value energy)

$$E = \frac{\int \psi H \psi d\tau}{\int \psi \psi d\tau}$$

$$E_{\psi} = \frac{\int (C_1 \phi_1 + C_2 \phi_2) H (C_1 \phi_1 + C_2 \phi_2) d\tau}{\int (C_1 \phi_1 + C_2 \phi_2) (C_1 \phi_1 + C_2 \phi_2) d\tau}$$

$$= \frac{\int C_1 \phi_1 H C_1 \phi_1 d\tau + \int C_2 \phi_2 H C_2 \phi_2 d\tau + \int C_1 \phi_1 H C_2 \phi_2 d\tau + \int C_2 \phi_2 H C_1 \phi_1 d\tau}{\int C_1 \phi_1 C_1 \phi_1 d\tau + \int C_2 \phi_2 C_2 \phi_2 d\tau + \int C_1 \phi_1 C_2 \phi_2 d\tau + \int C_2 \phi_2 C_1 \phi_1 d\tau}$$

$$E_{\psi} = \frac{C_1^2 \int \phi_1 H \phi_1 d\tau + C_1 C_2 \int \phi_1 H \phi_2 d\tau + C_2 C_1 \int \phi_2 H \phi_1 d\tau + C_2^2 \int \phi_2 H \phi_2 d\tau}{C_1^2 \int \phi_1 \phi_1 d\tau + C_1 C_2 \int \phi_1 \phi_2 d\tau + C_2 C_1 \int \phi_2 \phi_1 d\tau + C_2^2 \int \phi_2 \phi_2 d\tau}$$

★ Hamiltonian matrix element (Coulomb Integral)

$$\int \phi_i H \phi_i d\tau = H_{ii} \quad (\text{Coulomb integral}) \quad \int \phi_i H \phi_i d\tau = \langle \phi_i | H | \phi_i \rangle$$

$$\int \phi_i H \phi_j d\tau = H_{ij} \quad (\text{Resonance or exchange integral}) \quad (\beta)$$

$$\int \phi_1 H \phi_2 d\tau = H_{12} = \langle \phi_1 | H | \phi_2 \rangle$$

$$\int \phi_2 H \phi_1 d\tau = H_{21} = \langle \phi_2 | H | \phi_1 \rangle$$

$$\left. \begin{aligned} \int \phi_i \phi_i d\tau = S_{ii} \\ \int \phi_i \phi_j d\tau = S_{ij} \end{aligned} \right\} \text{overlap matrix element / overlap integral}$$

$$E = \frac{C_1^2 H_{11} + C_1 C_2 H_{12} + C_2 C_1 H_{21} + C_2^2 H_{22}}{C_1^2 S_{11} + C_1 C_2 S_{12} + C_2 C_1 S_{21} + C_2^2 S_{22}}$$

To minimize the value of energy put $\frac{\partial E}{\partial C_1} = 0$

$$\frac{\partial E}{\partial C_2} = 0$$

We get,

$$(H_{11} - ES_{11})C_1 + (H_{12} - ES_{12})C_2 = 0$$

$$(H_{21} - ES_{21})C_1 + (H_{22} - ES_{22})C_2 = 0$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} \begin{vmatrix} C_1 \\ C_2 \end{vmatrix} = 0$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0$$

Secular determinant

Acc to Hückel -

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0$$

$$\left. \begin{aligned} H_{11} &= \alpha \\ H_{12} &= \beta \\ S_{11} &= 1 \\ S_{21} &= 0 \end{aligned} \right\}$$

$$\psi = C_1\phi_1 + C_2\phi_2 + C_3\phi_3 \dots + C_n\phi_n$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & H_{13} - ES_{13} & \dots & H_{1n} - ES_{1n} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & H_{23} - ES_{23} & \dots & \vdots \\ H_{31} - ES_{31} & H_{32} - ES_{32} & H_{33} - ES_{33} & \dots & \vdots \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ H_{n1} - ES_{n1} & H_{n2} - ES_{n2} & \dots & \dots & H_{nn} - ES_{nn} \end{vmatrix}$$

The resulting determinant can be solved to obtain the energies. When arranged in increasing order of energy each state has the energy higher than the true energy but in variation theorem we choose minimum value of energy, so smallest root of the eqn give the energy

* If in data the value of S_{ij} & S_{ji} is not given then we apply condition of orthonormal set $S_{ij} = 1$ $S_{ij} = 0$

Qus-

The trial wave function of a system is expanded as

$$\psi = c_1 \phi_1 + c_2 \phi_2$$

$$\langle \phi_1 | H | \phi_1 \rangle = 0 = H_{11}$$

$$\langle \phi_2 | H | \phi_1 \rangle = 2 = \langle \phi_1 | H | \phi_2 \rangle = H_{21} \text{ OR } H_{12}$$

$$\langle \phi_2 | H | \phi_2 \rangle = 3 = H_{22}$$

Soln-

$$E = \begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix}$$

$$= \begin{vmatrix} 0 - E \cdot 1 & 2 - E \cdot 0 \\ 2 - E \cdot 0 & 3 - E \cdot 1 \end{vmatrix} = 0$$

$$\begin{vmatrix} -E & 2 \\ 2 & 3-E \end{vmatrix} = 0$$

$$-3E + E^2 - 4 = 0$$

$$E^2 - 3E - 4 = 0$$

$$E^2 - 4E + E - 4 = 0$$

$$E(E-4) + 1(E-4) = 0$$

$$E = 4, -1$$

$$\begin{matrix} E = 4 \\ E = -1 \end{matrix}$$

E = -1 (minimum energy)

DPP - 13

⑥ In linear combination two function will be of same character.

$$\begin{matrix} c_1 = 1 \\ c_2 = 0 \end{matrix}$$

$$\begin{matrix} c_1 = 1 \\ c_2 = 1 \end{matrix}$$

$$\psi = e^{-x} + e^{-x/2} \quad \text{ⓧ}$$

\downarrow \downarrow
 ψ_{1s} ψ_{2s}

IMP

⑭

→ To obtain the approximate wavefunction for a particular state we substitute the appropriate energy in secular eqn & solve the coefficient (c_i)

$$(H_{11} - ES_{11})c_1 + (H_{12} - ES_{12})c_2 = 0$$

$$(H_{21} - ES_{21})c_1 + (H_{22} - ES_{22})c_2 = 0$$

$E = -1$	$c_1 \ \& \ c_2$	$\psi = c_1\phi_1 + c_2\phi_2$
$E = 4$	$c_1 \ \& \ c_2$	$\psi = c_1\phi_1 + c_2\phi_2$

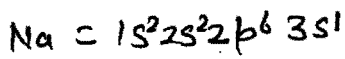
(13)

$$E_n = -13.6 \frac{Z^2}{n^2}$$

Hydrogenic atom
1e system
www.chemistryABC.com

$$E_n = -13.6 \frac{Z_{eff}^2}{n^2}$$

Multi e (Hartree)



$$Z_{eff} = 1.84$$

$$= \frac{-13.6 \times (1.84)^2}{(1)^2}$$

(14)

$$H_{11} = -15$$

$$H_{12} = H_{21} = -1$$

$$H_{22} = -3$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0$$

$$\begin{vmatrix} -15 - E & -1 \\ -1 & -3 - E \end{vmatrix} = 0$$

$$(15 + E)(3 + E) - 1 = 0$$

$$45 + 18E + E^2 - 1 = 0$$

$$E^2 + 18E + 44 = 0$$

DPP-14 Quantum Mechanics

1. Consider the statements

- (a) $2p_z$ and $2p_x$ orbital have same radial part of function, but $2s$ Orbital has different radial part.
 (b) The maximum angular node corresponding to e in orbital of H atom which have the radial part of function $r^2 e^{-r/3a_0}$ is 2. The degeneracy corresponding to this function is 9.
 (c) The degeneracy corresponding to energy of rotating particle with energy $56B$ is 15 where B is rotational constant.

which of the above statement is true (1) a,b (2) b,c (3) a,c (4) a,b,c (5) a only (6) b only (7) none

2. Consider the statement

a) The first order correction to the ground state energy of SHO when it is governed by potential energy $0.5x^2 (k+bx^2)$ bx^2 is 0.

b) The tunneling is more sensitive to the width of the barrier than the height of the barrier.

Incorrect statement of above are (1) a,b (2) b, (3) a only (4) none

3. A quantum mechanical particle of mass m free to rotate on the surface of radius r is in the state with energy $10\hbar^2/mr^2$. The degeneracy of this state is $E = \frac{\hbar^2 J(J+1)}{2I}$ IIT JAM 2010

a) 20 (b) 10 (c) 9 (d) 4

4. A particle in 1D box (potential energy between to infinite outside) has the ground state energy $E = (0.125\hbar^2/8ml^2)$. The expectation value of the above Hamiltonian with $\psi(x) = x(x-a)$ yields an energy E_1 . Using a linear combination of two even function $x(x-a)$ and $x^2(x-a)^2$, we obtain variation minimum to the ground state energy as E_2 the relation between E_0 , E_1 and E_2 is

a) $E_0 < E_1 < E_2$ b) $E_0 < E_2 < E_1$ c) $E_1 < E_0 < E_2$ d) $E_2 < E_0 < E_1$ CSIR NET CH

5. For some one-electron system with $l=0, m=0$ the function $N_0 e^{-\sigma}$ and $N_1 (2-\sigma)e^{-\sigma/2}$ refers respectively to the ground state energy E_0 and first excited state energy level E_1 . If a variation wave function is $N_2 (3-\sigma)e^{-\sigma}$ yield an average energy E than it will satisfy CSIR NET CH

a) $E \geq 0$ b) $0 \leq E \leq E_0$ c) $E \geq E_1$ d) $E_0 \leq E \leq E_1$

6. The ground state energy of the attractive delta potential $V(x) = -b\delta(x)$ where $b > 0$, calculated with variational trial wave function $\psi(x) = A \cos(\pi x/2a)$ $-a < x < a$ is CSIR NET PY

a) $-(mb^2/\pi^2\hbar^2)$ b) $-(2mb^2/\pi^2\hbar^2)$ c) $-(mb^2/2\pi^2\hbar^2)$ d) $-(mb^2/4\pi^2\hbar^2)$

7. For a particle in a box problem in $(0, L)$ an approximate wave function is given as $x(.5L-x)$

$(L-x)$ The average energy E for this state is CSIR NET CH

a) $(\hbar^2/8ml^2) < E < (\hbar^2/2ml^2)$ b) $E > (\hbar^2/2ml^2)$
 c) $(\hbar^2/4ml^2) < E < (\hbar^2/2ml^2)$ d) $0 < E < (\hbar^2/8ml^2)$

8. Two trial wave functions $\phi_1 = c_1 x(a-x)$ and $\phi_2 = c_1 x(a-x) + c_2 x^2(a-x)^2$ give ground state energies E_1 and E_2 , respectively, for the microscopic particle in a 1-D box by using the variation method. If the exact ground state energy is E_0 , the correct relationship between E_0 , E_1 and E_2 is

(A) $E_0 = E_1 = E_2$ (B) $E_0 < E_1 < E_2$ (C) $E_0 < E_2 < E_1$ (D) $E_0 > E_2 = E_1$ IIT GATE

9. If the perturbation $H' = ax$ is added to the infinite square potential $V=0$ for $0 < x < \pi$ and $V = \text{infinite}$ otherwise The first order correction to the ground state energy is NET PHY.

a) $a\pi/2$ b) $a\pi$ c) $a\pi/4$ d) $a\pi/2^{0.5}$

10. Write the principle of variational principle.

11. An electron is in a state described by the wave function

$\Psi = (1/4\pi)^{0.5} (\cos\theta + e^{-i\Phi} \sin\theta) R(r)$ Where θ and Φ are the corresponding angle.

i) What are the possible value of L_z

ii) What is the probability of obtaining each of the value of L_z .

12 An 1eV electron got trapped inside the surface of the metal . If the potential barrier is 4 eV and the width of the barrier is 2 \AA calculate the probability of transmission.

13 Evaluate the most probable distance of the electron of hydrogen atom in its 2p state what is the radial density at this distance.

14 The unperturbed wavefunction of a particle is trapped in a 1 D Box of length a , if the floor of the box is raised by constant amount V then what is second order correction to the ground state.

15 A particle of mass m confined to move in a potential $V=0$ for $0 < x < a$ and $V=\infty$ otherwise the wavefunction of the particle at time $t=0$ is

$$\Psi(x,0) = A[2 \sin(\pi x/a) + \sin(3\pi x/a)]$$

(a) Normalise the wavefunction at $t=0$. (ii) find $\Psi(x,t)$

16 An electron is confined in the ground state of 1D SHO such that $\Delta x = 10^{-10}$ m. assuming $\langle T \rangle = \langle V \rangle$ find the energy in electron volt required to excite it to first excited state .

17 At time $t=0$ the wavefunction $\Psi(r,0) = 1/(10)^{0.5} [2\psi_{1,0,0} + \psi_{2,1,0} + (2)^{-0.5} \psi_{2,1,1} + (3)^{0.5} \psi_{2,1,-1}]$ where subscript are value of quantum number n,l,m what is the expectation value of energy of the system , what is the probability of finding the system with $l=1$ and $m=1$.

18 Consider the statements

i) Schrodinger equation for a quantum system is linear differential of the type second order in space and second order in time.

ii) The expectation value of z coordinate in the ground state $\psi = Ae^{-z/a}$ is 0. CSIR NET PH

Correct statement is (a) i, (b) ii, (c) i,ii (d) none

19 The root of determinant in case of ethylene molecule in Huckel theory is

(a) $\alpha + \beta, \alpha - \beta$ (b) $\alpha + 2\beta, \alpha - \beta$ (c) $\alpha + 2\beta, \alpha - 2\beta$ (d) $\alpha + \beta, \alpha - 2\beta$ CSIR NET CH

20 .Consider the statement

i) Coulomb integrals for all the carbon atoms are assumed to be identical. CSIR NET CH

ii) On-diagonal elements incorporate the Coulomb integrals for each atom and Off-diagonal elements consist of the resonance integrals;

iii) for an n -atom chain, in which each atom contributes one atomic orbital to the conjugated π -system, there will be n overlapping atomic orbitals giving rise to n molecular orbitals.

Correct statement above are (a) i,ii (b) ii,iii (c) i,iii (d) i,ii,iii

* Huckel theory -

Huckel theory is a simplified version of the linear variation method which can be applied to simple conjugated π -system.

We assume σ - π separability which means that nuclei, e s of the atomic ~~and~~ inner shells and localised σ bonds, provide an effective field in which the remaining πe move

Next simplification is to approximate the π -molecular orbital as linear combination of atomic orbital.

In a minimal set calculation of a planar conjugated hydrocarbon the only atomic orbital with π -symmetry are $2p$ orbitals on carbon.

* Huckel MO treatment of -

Ethylene



$$\begin{vmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \end{vmatrix}$$

$$c_{11} = c_{22} = c_{33} \dots c_{ii} = \alpha$$

$$c_{12} = c_{21} = \beta$$

$$c_{ij} = \beta$$

if i & j direct connected

$$0$$

if i & j not direct

connected

$$S_{ii} = 1$$

$$S_{ij} = 0$$

orthonormal

$$\begin{vmatrix} \alpha & \beta \\ \beta & \alpha \end{vmatrix}$$

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0$$

divide by β

$$\begin{vmatrix} \frac{\alpha - E}{\beta} & 1 \\ 1 & \frac{\alpha - E}{\beta} \end{vmatrix} = 0$$

Put $\frac{\alpha - E}{\beta} = x$

$$E = \alpha - x\beta$$

$$\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0$$

$$x^2 - 1 = 0$$

$$x = \pm 1$$

$$x = +1$$

$$E = \alpha - \beta$$

$$\text{————— } \alpha - \beta$$

$$x = -1$$

$$E = \alpha + \beta$$

$$\text{————— } \alpha + \beta$$

β is always
-ve

α is considered as energy of isolated π electron

So π bond formation energy

$$= \text{Energy of ethylene} - \text{energy of two isolated } \pi e^-$$

$$= 2(\alpha + \beta) - 2\alpha$$

$$= 2\alpha + 2\beta - 2\alpha$$

$$= 2\beta$$

∴ ethylene become stable by energy = 2β

= -150 kJ/mol approx.

To determine the value of wave function ψ -

Find the value of c_1 and c_2 as

$$\psi = c_1\phi_1 + c_2\phi_2$$

$$c_1^2 + c_2^2 = 1$$

ψ is normalized only when $c_1^2 + c_2^2 = 1$ — (1)

as

$$\begin{vmatrix} c_1 & c_2 \\ x & 1 \\ 1 & x \end{vmatrix} = 0$$

So $c_1x + c_2 = 0$ — (2)

$$c_1 + c_2x = 0$$
 — (3)

for energy level $E = \alpha + \beta$

$x = -1$ put this value in eqn (2) & (3)

$$c_1(-1) + c_2 = 0$$

$$c_1 + c_2(-1) = 0$$

$$\begin{aligned} c_1 &= c_2 \\ c_1 &= c_2 \end{aligned}$$

$$c_1^2 + c_2^2 = 1$$

$$c_1^2 + c_1^2 = 1$$

$$2c_1^2 = 1$$

$$c_1 = \frac{1}{\sqrt{2}}$$

$$c_2 = \frac{1}{\sqrt{2}}$$

$$\psi = c_1 \phi_1 + c_2 \phi_2$$

$$\psi = \frac{1}{\sqrt{2}} \phi_1 + \frac{1}{\sqrt{2}} \phi_2$$

for energy level $E = \alpha - \beta$ $x = +1$ put this value in eqn (2) & (3)

$$c_1(+1) + c_2 = 0$$

$$c_1 + c_2(-1) = 0$$

$$\begin{cases} c_1 = -c_2 \\ c_1 = -c_2 \end{cases}$$

$$c_1^2 + c_2^2 = 1$$

$$c_1^2 + c_2^2 = 1$$

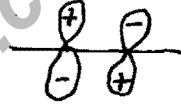
$$\begin{cases} c_1 = \frac{1}{\sqrt{2}} & c_2 = -\frac{1}{\sqrt{2}} \end{cases}$$

$$\psi = c_1 \phi_1 + c_2 \phi_2$$

$$\psi = \frac{1}{\sqrt{2}} \phi_1 - \frac{1}{\sqrt{2}} \phi_2$$

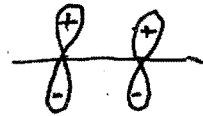
$$x = +1 \quad \text{---} \quad \alpha - \beta$$

$$\psi = \frac{1}{\sqrt{2}} \phi_1 - \frac{1}{\sqrt{2}} \phi_2$$

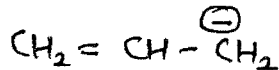
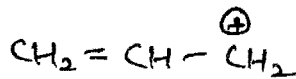
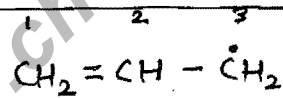


$$x = -1 \quad \text{---} \quad \alpha + \beta$$

$$\psi = \frac{1}{\sqrt{2}} \phi_1 + \frac{1}{\sqrt{2}} \phi_2$$



Allyl system—



$$\begin{vmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{vmatrix} \Rightarrow \begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} = 0$$

Divide by β

$$\begin{vmatrix} \frac{\alpha-E}{\beta} & 1 & 0 \\ 1 & \frac{\alpha-E}{\beta} & 1 \\ 0 & 1 & \frac{\alpha-E}{\beta} \end{vmatrix} = 0$$

Put $\frac{\alpha-E}{\beta} = x$

$$E = \alpha - x\beta$$

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0$$

$$= x \begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} - 1 \begin{vmatrix} 1 & 1 \\ 0 & x \end{vmatrix} + 0 \begin{vmatrix} 1 & x \\ 0 & 1 \end{vmatrix}$$

$$= x(x^2 - 1) - 1(x - 0) + 0$$

$$= x^3 - x - x = 0$$

$$x^3 - 2x = 0$$

$$x^2(x - 2) = 0$$

$$x = 0$$

$$x = \pm \sqrt{2}$$

$$E = \alpha - \beta x$$

$$x = 0 \quad E = \alpha$$

$$x = \sqrt{2} \quad E = \alpha - \sqrt{2}\beta$$

$$x = -\sqrt{2} \quad E = \alpha + \sqrt{2}\beta$$

$$\text{_____ } \alpha - \sqrt{2}\beta$$

$$\text{_____ } \alpha$$

$$\text{_____ } \alpha + \sqrt{2}\beta$$

Allyl cation

$$\text{_____ } \alpha - \sqrt{2}\beta$$

$$\text{_____ } \alpha$$

$$\text{16 _____ } \alpha + \sqrt{2}\beta$$

Allyl anion

$$\text{_____ } \alpha - \sqrt{2}\beta$$

$$\text{16 _____ } \alpha$$

$$\text{16 _____ } \alpha + \sqrt{2}\beta$$

Radical

$$\text{_____ } \alpha - \beta$$

$$\text{16 _____ } \alpha$$

$$\text{16 _____ } \alpha + \beta$$

π -Bond formation energy -

Allyl cation

Energy of allyl cation - energy of $2\pi e^-$

$$\begin{aligned} & 2(\alpha + \sqrt{2}\beta) - 2(\alpha) \\ &= 2\alpha + 2\sqrt{2}\beta - 2\alpha \\ &= 2\sqrt{2}\beta \end{aligned}$$

Delocalisation energy -

Energy of allyl cation - energy of ethylene

$$\begin{aligned} & 2(\alpha + \sqrt{2}\beta) - 2(\alpha + \beta) \\ &= 2\sqrt{2}\beta - 2\beta \\ &= 2\beta(\sqrt{2} - 1) = 2\beta(0.414) = 0.828\beta \end{aligned}$$

Allyl anion -

π -bond formation energy

$$\begin{aligned} & [2(\alpha + \sqrt{2}\beta) + 2\alpha] - 4\alpha \\ &= 2\sqrt{2}\beta \end{aligned}$$

Delocalisation energy

Energy of allyl anion - energy of ethylene + $2e^-$

$$\begin{aligned} & [2(\alpha + \sqrt{2}\beta) + 2\alpha] - [2(\alpha + \beta) + 2\alpha] \\ &= 2\sqrt{2}\beta - 2\beta \\ &= 0.828\beta \end{aligned}$$

Allyl radical -

π -bond formation energy

Delocalization energy

Delocalization energy per electron (DEPE) -

$$\text{Allyl radical} = \frac{0.828\beta}{3} = \underline{0.276\beta}$$

$$\text{Allyl cation} = \frac{0.828\beta}{2} = \underline{0.414\beta}$$

$$\text{Allyl anion} = \frac{0.828\beta}{4} = \underline{0.207\beta}$$

Higher the value of β , ^{coefficient} Higher the stability.

β is always -ve

To determine the function -

$$\psi = c_1\phi_1 + c_2\phi_2 + c_3\phi_3$$

As we know

$$c_1^2 + c_2^2 + c_3^2 = 1$$

$$\begin{vmatrix} c_1 & c_2 & c_3 \\ \alpha & 1 & 0 \\ 1 & \alpha & 1 \\ 0 & 1 & \alpha \end{vmatrix}$$

$$\alpha = \sqrt{2} \quad \alpha - \sqrt{2}\beta$$

$$\alpha = 0 \quad \alpha$$

$$\alpha = -\sqrt{2} \quad \alpha + \sqrt{2}\beta$$

$$c_1\alpha + c_2 = 0$$

$$c_1 + c_2\alpha + c_3 = 0$$

$$c_2 + c_3\alpha = 0$$

for $E = \alpha + \sqrt{2}\beta \quad \alpha = -\sqrt{2}$

$$c_1(-\sqrt{2}) + c_2 = 0 \quad \text{--- (2)} \quad c_2 = \sqrt{2}c_1$$

$$c_1 + c_2(-\sqrt{2}) + c_3 = 0 \quad \text{--- (3)} \quad c_2 = \sqrt{2}c_3$$

$$c_2 + c_3(\sqrt{2}) = 0 \quad \text{--- (4)}$$

$$c_1 = c_3$$

Putting in eqn (1)

$$c_1^2 + (\sqrt{2}c_1)^2 + c_1^2 = 1$$

$$c_1^2 = \frac{1}{4}$$

$$c_1 = \frac{1}{2}$$

$$c_3 = \frac{1}{2}$$

$$c_2 = \frac{1}{\sqrt{2}}$$

$$\psi = \frac{1}{2} \phi_1 + \frac{1}{\sqrt{2}} \phi_2 + \frac{1}{2} \phi_3$$

(ii) $E = \alpha$ $C_1(\alpha) + C_2 = 0$ $C_2 = 0$
 $\alpha = 0$ $C_1 + C_2(\alpha) + C_3 = 0$ $C_1 + C_3 = 0 \Rightarrow C_1 = -C_3$
 $C_2 + C_3(\alpha) = 0$ $C_2 = 0$

Putting in eqn ①

$$C_1^2 + C_1^2 = 1$$

$$2C_1^2 = 1 \quad C_1 = \frac{1}{\sqrt{2}} \quad C_3 = -\frac{1}{\sqrt{2}} \quad C_2 = 0$$

$$\psi = \frac{1}{\sqrt{2}} \phi_1 - \frac{1}{\sqrt{2}} \phi_3$$

(iii) $E = \alpha - \sqrt{2} \beta$ $\alpha = +\sqrt{2}$
 $C_1(\sqrt{2}) + C_2 = 0$ $C_2 = -\sqrt{2} C_1$
 $C_1 + \sqrt{2} C_2 + C_3 = 0$
 $C_2 + \sqrt{2} C_3 = 0$ $C_2 = -\sqrt{2} C_3$ $C_1 = C_3$

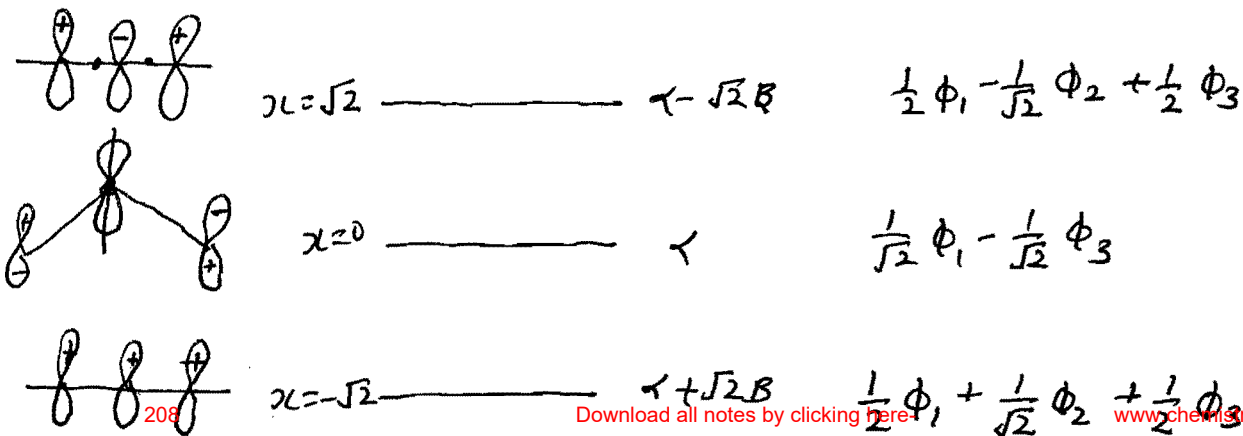
Putting in eqn ①

$$C_1^2 + (\sqrt{2} C_1)^2 + C_1^2 = 1$$

$$C_1^2 + 2C_1^2 + C_1^2 = 1 \Rightarrow 4C_1^2 = 1$$

$$C_1 = \frac{1}{2} \quad C_3 = \frac{1}{2} \quad C_2 = -\frac{1}{\sqrt{2}}$$

$$\psi = \frac{1}{2} \phi_1 - \frac{1}{\sqrt{2}} \phi_2 + \frac{1}{2} \phi_3$$

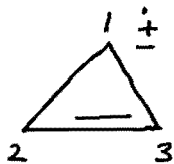


Cyclobutadiene -



Cyclopropyl -

Anion, cation, radical



$$\begin{vmatrix} C_{11} & C_{12} & C_{13} \\ C_{21} & C_{22} & C_{23} \\ C_{31} & C_{32} & C_{33} \end{vmatrix} \Rightarrow \begin{vmatrix} \alpha-E & \beta & \beta \\ \beta & \alpha-E & \beta \\ \beta & \beta & \alpha-E \end{vmatrix} \Rightarrow \begin{vmatrix} \frac{\alpha-E}{\beta} & 1 & 1 \\ 1 & \frac{\alpha-E}{\beta} & 1 \\ 1 & 1 & \frac{\alpha-E}{\beta} \end{vmatrix} = 0$$

$$\frac{\alpha-E}{\beta} = x \quad E = \alpha - \beta x$$

$$\begin{vmatrix} x & 1 & 1 \\ 1 & x & 1 \\ 1 & 1 & x \end{vmatrix} = 0$$

$$\begin{aligned}
 x(x^2-1) - 1(x-1) + 1(1-x) &= 0 \\
 x^3 - x - x + 1 + 1 - x &= 0 \\
 \boxed{x^3 - 3x + 2 = 0} &\text{ --- (1)}
 \end{aligned}$$

$$x = 1$$

$x-1=0$ is a soln of above eqn

$$\frac{x^3 - 3x + 2}{x-1} = (x-1)(x^2 + x - 2) = 0$$

$$(x-1)(x^2 + 2x + x - 2) = 0$$

$$(x-1)(x+2)(x+1) = 0$$

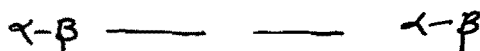
$$\left. \begin{aligned} x &= 1 \\ x &= -2 \\ x &= +1 \end{aligned} \right\}$$

$$\underline{x = -2}$$

$$E = \alpha + 2\beta$$

$$\underline{x = 1}$$

$$E = \alpha - \beta$$

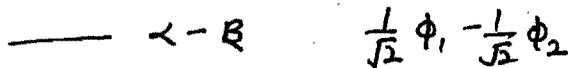


$$\underline{x = 1}$$

$$E = \alpha - \beta$$

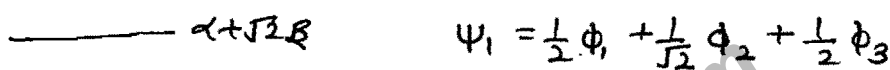
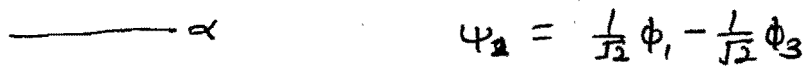
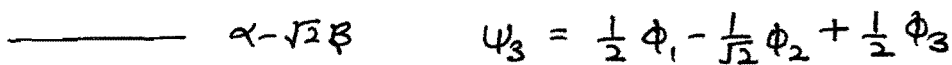


☆ (i) ethylene -



Ethylene = $2\alpha + 2\beta$

(ii) Allyl -



(iii)



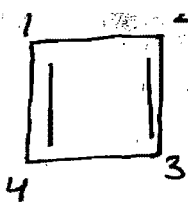
(iv) $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$



$E = 2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta)$

$= 4\alpha + 4.472\beta$

(V)



$$\begin{array}{c} \alpha - 2\beta \\ \leftarrow \quad \uparrow \quad \uparrow \quad \leftarrow \\ \alpha + 2\beta \end{array}$$

$$\begin{vmatrix} \alpha - E & \beta & 0 & \beta \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ \beta & 0 & \beta & \alpha - E \end{vmatrix} = 0$$

★ To determine the value of energy -

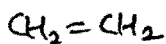
Non-cyclic -

$$E = \alpha + 2\beta \cos \frac{k\pi}{n+1}$$

n = no. of carbon atoms

$k = 1, 2, 3, \dots$

(i) ethylene -



$$n = 2$$

$$E = \alpha + 2\beta \cos \frac{k\pi}{3}$$

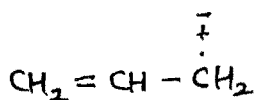
$$k = 1 \quad E = \alpha + 2\beta \cos \frac{\pi}{3} = \alpha + \beta$$

$$k = 2 \quad E = \alpha + 2\beta \cos \left(\frac{2\pi}{3}\right) = \alpha - \beta$$

cos	0	30	45	60	90	120	135
	1	$\frac{\sqrt{3}}{2}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2}$	0	$-\frac{1}{2}$	$-\frac{1}{\sqrt{2}}$

(iii)

Allyl -



$$n = 3$$

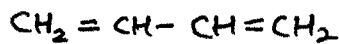
$$E = \alpha + 2\beta \cos \frac{k\pi}{4}$$

$$k_1 = 1 \quad = \alpha + 2\beta \cos \frac{\pi}{4} = \alpha + \sqrt{2}\beta$$

$$k = 2 \quad = \alpha + 2\beta \cos \frac{2\pi}{4} = \alpha$$

$$k = 3 \quad = \alpha + 2\beta \cos \frac{3\pi}{4} = \alpha - \sqrt{2}\beta$$

(ii) 1,3 butadiene -



$$n=4$$

$k=1$	$E = \alpha + 2\beta \cos \frac{\pi}{5}$	$= \alpha + 1.618\beta$	$\cos 36^\circ$
$k=2$	$E = \alpha + 2\beta \cos \frac{2\pi}{5}$	$= \alpha + 0.618\beta$	$\cos 72^\circ$
$k=3$	$E = \alpha + 2\beta \cos \frac{3\pi}{5}$	$= \alpha - 0.618\beta$	$\cos 108^\circ$
$k=4$	$E = \alpha + 2\beta \cos \frac{4\pi}{5}$	$= \alpha - 1.618\beta$	$\cos 144^\circ$

Cyclic -

$$E = \alpha + 2\beta \cos \frac{2k\pi}{n} \quad k = 0, \pm 1, \pm 2, \pm 3, \dots$$

(i) Cyclopropyl -

$$n=3$$

$$E = \alpha + 2\beta \cos \frac{2k\pi}{3}$$

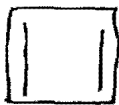
$$k=0 = \alpha + 2\beta \cos 0 = \alpha + 2\beta$$

$$k=+1 = \alpha + 2\beta \cos \frac{2\pi}{3} = \alpha - \beta$$

$$k=-1 = \alpha + 2\beta \cos \left(-\frac{2\pi}{3}\right) = \alpha - \beta$$

degenerate $\overline{\alpha - \beta} \quad \alpha - \beta$
 $\underline{\alpha - \beta} \quad \alpha + 2\beta$

(ii)



$$n=4$$

$$E = \alpha + 2\beta \cos \frac{2k\pi}{4}$$

$$k=0 = \alpha + 2\beta$$

$$k=\pm 1 = \alpha + 2\beta \cos \frac{2\pi}{4} = \alpha$$

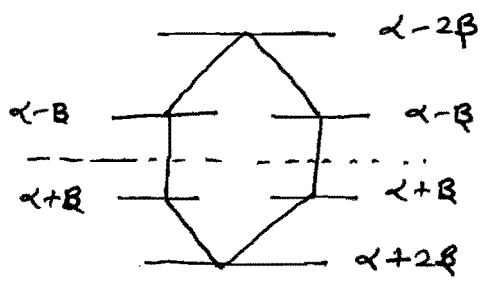
$$k=+2 = \alpha + 2\beta \cos \frac{4\pi}{4} = \alpha - 2\beta$$

(ii)



$n=6$

$$\begin{aligned}
 k=0 &= \alpha + 2\beta \cos \frac{0\pi}{6} = \alpha + 2\beta \\
 k=\pm 1 &= \alpha + 2\beta \cos \frac{2\pi}{6} = \alpha + 2\beta \cos \frac{\pi}{3} = \alpha + \beta \\
 k=\pm 2 &= \alpha + 2\beta \cos \frac{4\pi}{6} = \alpha + 2\beta \cos \frac{2\pi}{3} = \alpha - \beta \\
 k=\pm 3 &= \alpha + 2\beta \cos \frac{6\pi}{6} = \alpha + 2\beta \cos \pi = \alpha - 2\beta
 \end{aligned}$$



π -bond formation energy-

$$\begin{aligned}
 &= E_{1,3 \text{ Buta.}} - \text{Energy of 4 isolated } \pi e^- && \alpha - 1.618\beta \\
 &= (4\alpha + 4.472\beta) - 4\alpha && \alpha - 0.618\beta \\
 &= 4.472\beta && 1\beta \quad \alpha + 0.618\beta \\
 &&& 4\beta \quad \alpha + 1.618\beta
 \end{aligned}$$

Resonance energy-

$$\begin{aligned}
 &= E_{1,3 \text{ butadiene}} - 2 \times \text{Energy of 1 ethylene} \\
 &= 4\alpha + 4.472\beta - 2[2(\alpha + \beta)] \\
 &= 4\alpha + 4.472\beta - 4\alpha - 4\beta \\
 &= 0.472\beta
 \end{aligned}$$

$\alpha - \beta$
 $\alpha + \beta$

(7) (ii) $E = 6\alpha + 8\beta - 6\alpha = 8\beta$

delocalization = $6\alpha + 8\beta - 3(2\alpha + 2\beta)$
 $= 2\beta$

(iii)

$$\begin{array}{c} \text{---} \alpha - 2\beta \\ \frac{1}{\text{---}} \alpha \quad \frac{1}{\text{---}} \alpha \\ \frac{1\beta}{\text{---}} \alpha + 2\beta \end{array} \quad \begin{array}{l} 2\alpha + 4\beta + 2\alpha - 2(2\alpha + 2\beta) \\ = 4\alpha + 4\beta - 4\alpha - 4\beta \\ = 0 \end{array}$$

(9)

$$\begin{array}{c} \text{---} \alpha - 1.618\beta \\ \text{---} \alpha - 0.618\beta \\ \frac{1\beta}{\text{---}} \alpha + 0.618\beta \\ \frac{1\beta}{\text{---}} \alpha + 1.618\beta \end{array} \quad \begin{array}{l} E = 4\alpha + 4.472\beta - 2\alpha - 4\beta \\ E = 0.472\beta \\ = 0.472 \times 75 \\ = 35.4 \text{ kJ/mol} \end{array}$$

(10)

(ii) $E_T = 10\alpha + 13.68\beta$

delocalization energy = $10\alpha + 13.68\beta - 5(2(\alpha + \beta))$
 $= 3.68\beta$

(12) (iii)

$$\begin{array}{c} \text{---} \alpha - 2\beta \\ \frac{\uparrow}{\text{---}} \alpha \quad \frac{\uparrow}{\text{---}} \alpha \\ \frac{1\beta}{\text{---}} \alpha + 2\beta \end{array}$$

★ To determine orbital coefficient - (C₁, C₂, ...)

To determine function corresponding to energy level we have to determine orbital coefficient.

Orbital Coefficients are:

$$C_s \propto \frac{\sin \pi k s}{n+1}$$

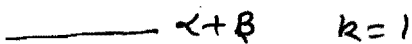
n = no. of carbon atom

k = based on energy level

s = for carbon atom

e.g. C₁ = s = 1

C₂ = s = 2




(eg.)

E = α + β k = 1 n = 2

C₁ ∝ $\frac{\sin \pi \cdot 1 \cdot 1}{3}$

C₁ ∝ $\sin \frac{\pi}{3}$

C₁ ∝  $\frac{\sqrt{3}}{2}$

C₂ ∝ $\frac{\sin \pi \cdot 1 \cdot 2}{3}$

C₂ ∝ $\sin \frac{2\pi}{3}$

C₂ ∝  $\frac{\sqrt{3}}{2}$

Let us consider we have to determine the value of C₁, C₂ & C₃ for highest energy MO of 3 carbon chain (n=3) (k=3)

$$C_s \propto \frac{\sin \pi k s}{n+1}$$

n = 3

k = 3

s = 1

$$C_1 = \frac{\sin \pi \cdot 1}{4} = \frac{\sin 3\pi}{4} = \frac{1}{\sqrt{2}}$$

s = 2

$$C_2 = \frac{\sin 6\pi}{4} = \frac{\sin 3\pi}{2} = -1$$

s = 3

$$C_3 = \frac{\sin 9\pi}{4} = \frac{1}{\sqrt{2}}$$

$$\psi = \frac{1}{\sqrt{2}} \phi_1 - \phi_2 + \frac{1}{\sqrt{2}} \phi_3$$

It is not normalized because

$$c_1^2 + c_2^2 + c_3^2 \neq 1$$

$$\left(\frac{1}{\sqrt{2}}\right)^2 + 1^2 + \left(\frac{1}{\sqrt{2}}\right)^2 \neq 1$$

$$\frac{1}{2} + 1 + \frac{1}{2}$$

$$= 2$$

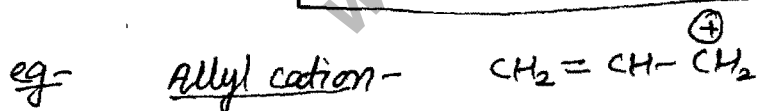
multiplied by $\left(\frac{1}{\sqrt{2}}\right)$

$$\psi = \frac{1}{2} \phi_1 - \frac{1}{\sqrt{2}} \phi_2 + \frac{1}{2} \phi_3$$

★ To determine the charge density & Bond order by Huckel -

To determine the value of charge density we have to focus on orbital coefficient corresponding to carbon to which we have to determine charge density and the no. of e^- present in the every energy state

$$q_i = \sum \text{no. of } e^- c_{ni}^2$$



$$\psi_3 = \frac{1}{2} \phi_1 - \frac{1}{\sqrt{2}} \phi_2 + \frac{1}{2} \phi_3$$

$$\psi_2 = \frac{1}{\sqrt{2}} \phi_1 - \frac{1}{\sqrt{2}} \phi_3$$

$$\psi_1 = \frac{1}{2} \phi_1 - \frac{1}{\sqrt{2}} \phi_2 + \frac{1}{2} \phi_3$$

$$q_1 = \text{no. of } e^- c_{11}^2 + \text{no. of } e^- c_{21}^2 + \text{no. of } e^- c_{31}^2$$

$$= 2 \times \left(\frac{1}{2}\right)^2 + \left(0 \times \left(\frac{1}{\sqrt{2}}\right)^2\right) + 0 \times \left(\frac{1}{2}\right)^2$$

$$= \frac{2 \times 1}{4} = \frac{1}{2}$$

$$q_2 = \text{no. of } e^- \times C_{12}^2 + \text{no. of } e^- \times C_{22}^2 + \text{no. of } e^- \times C_{32}^2$$

$$= 2 \times \left(\frac{1}{\sqrt{2}}\right)^2$$

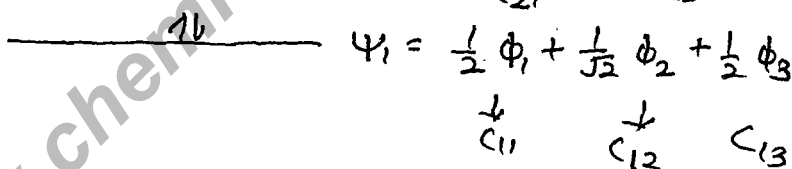
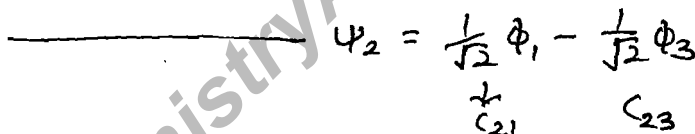
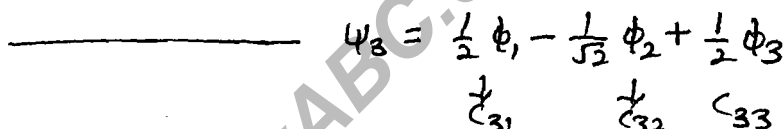
$$= 2 \times \frac{1}{2} = 1$$

$$q_3 = \text{no. of } e^- \times C_{13}^2 + \text{no. of } e^- \times C_{23}^2 + \text{no. of } e^- \times C_{33}^2$$

$$= 2 \times \left(\frac{1}{2}\right)^2$$

$$q_3 = \frac{1}{2}$$

Bond orders →



$$p_{rs} = \sum \text{no. of } e^- \times C_{rn} \times C_{ns}$$

$$p_{12} = \text{no. of } e^- \times C_{11} \times C_{22} + \text{no. of } e^- \times C_{21} \times C_{22} + \text{no. of } e^- \times C_{31} \times C_{32}$$

$n=1 \quad \quad \quad n=2 \quad \quad \quad n=3$

eg- Allyl cation-

$$p_{12} = 2 \times \frac{1}{2} \times \frac{1}{\sqrt{2}} + 0 \times \frac{1}{2} \times 0 + 0 \times \frac{1}{2} \times \left(-\frac{1}{\sqrt{2}}\right)$$

$$p_{12} = \frac{1}{\sqrt{2}}$$

$$p_{23} = 2 \times \frac{1}{\sqrt{2}} \times \frac{1}{2} + 0 \times 0 \times \left(-\frac{1}{\sqrt{2}}\right) + 0 \times \frac{1}{\sqrt{2}} \times \frac{1}{2}$$

(11) $\psi_1 = \frac{1}{\sqrt{6}} (x_1 + x_2 + x_3 + x_4 + x_5 + x_6)$

$\psi_2 = \frac{1}{\sqrt{4}} (x_2 + x_3 - x_5 - x_6)$

$\psi_3 = \frac{1}{\sqrt{3}} (x_1 + \frac{1}{2}x_2 - \frac{1}{2}x_3 - x_4 - \frac{1}{2}x_5 + \frac{1}{2}x_6)$

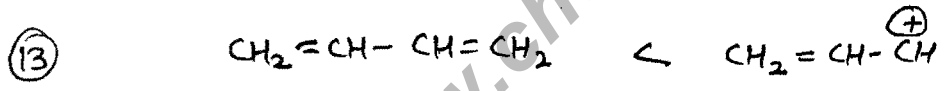
$P_{12} = 2 \times \frac{1}{\sqrt{6}} \times \frac{1}{\sqrt{6}} + 2 \left(\frac{1}{\sqrt{4}} \times \frac{1}{\sqrt{4}} \right) + 2 \left(\frac{1}{\sqrt{3}} \right) \left(\frac{1}{2\sqrt{3}} \right) = \frac{2}{3}$

$P_{23} = 2 \times \frac{1}{\sqrt{6}} \times \frac{1}{\sqrt{6}} + 2 \left(\frac{1}{\sqrt{4}} \right) \left(\frac{1}{\sqrt{4}} \right) + 2 \left(\frac{1}{2\sqrt{3}} \right) \left(-\frac{1}{2\sqrt{3}} \right) = \frac{1}{6} + \frac{1}{2} = \frac{2}{3}$

$q_1 = 2 \times C_{11}^2 + 2 C_{21}^2 + 2 C_{31}^2$
 $= 2 \times \left(\frac{1}{\sqrt{6}} \right)^2 + 2 \times 0 + 2 \times \left(\frac{1}{\sqrt{3}} \right)^2$

$q_1 = 1$

$q_2 = 1$

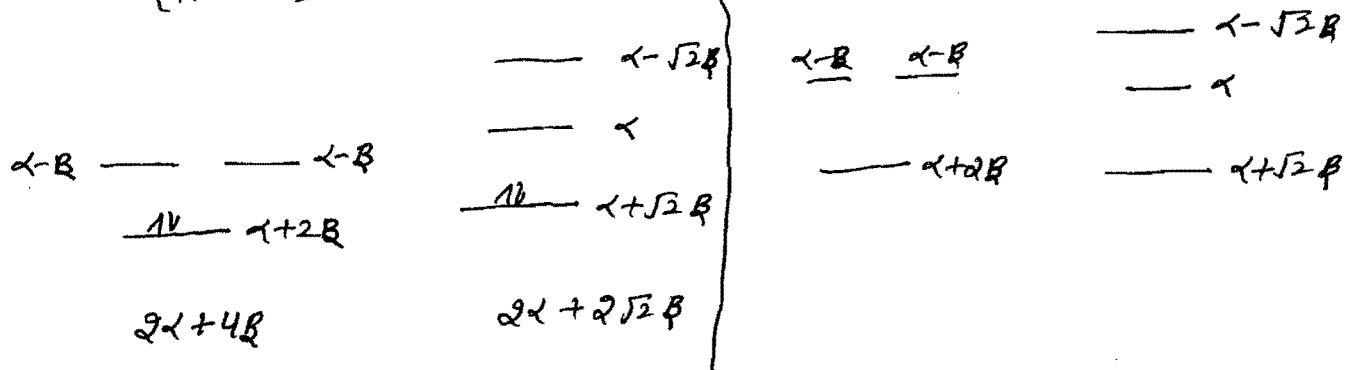
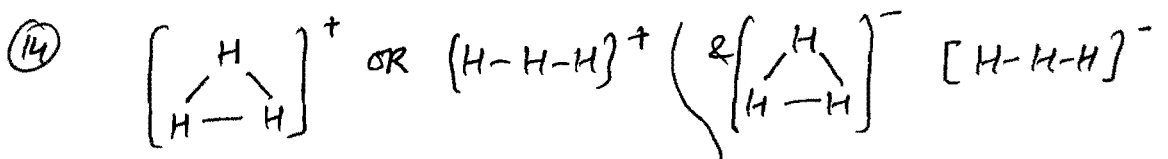


$DE = \frac{0.472\beta}{4}$

$= 0.118\beta$

$DE = \frac{0.828\beta}{2}$

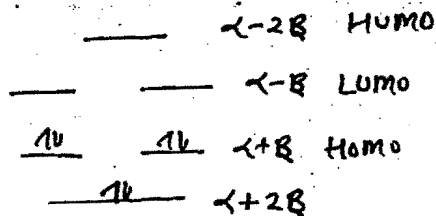
$= 0.414\beta$



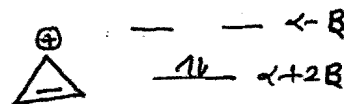
218 more stable

$$-2\beta = 150$$

$$-3\beta = 225$$



$$\alpha - \beta - \alpha - 2\beta = -3\beta$$



DPP 15 Quantum mechanics

1. The energy for a single electron excitation in cyclopropene according to Huckel theory

(a) β (b) 2β (c) 3β (d) 4β CSIR NET

2. The resonance integral for benzene in the Huckel model is -75 KJ/mole the energy required for the transition from HOMO to LUMO and to the highest unoccupied MO respectively will be

(a) 150 and 225 KJ/mole (b) 75 and 150 KJ/mole (c) 150 and 300 KJ/mole (d) 75 and 225 KJ/mole IIT GATE

3 Simple Huckel Molecular Orbital Theory CSIR NET

(a) consider electron electron repulsion explicitly (b) distinguish cis butadiene and trans butadiene

(c) distinguish cis butadiene and cyclobutadiene (d) has different coulomb integral for non equivalent carbon

4. As per Huckel theory, π electron energy of cyclobutadiene are IIT GATE

(a) $\alpha + 2\beta, \alpha + \beta, \alpha - \beta, \alpha - 2\beta$ (b) $\alpha + 2\beta, \alpha - \beta, \alpha - \beta, \alpha - 2\beta$ (c) $\alpha + 2\beta, \alpha, \alpha, \alpha - 2\beta$ (d) $\alpha + \beta, \alpha - \beta, \alpha - \beta, \alpha - 2\beta$

5. Consider the statement

i) Coulomb integrals for all the carbon atoms are assumed to be identical. T

ii) On-diagonal elements incorporate the Coulomb integrals for each atom and Off-diagonal elements consist of the resonance integrals; T

iii) for an n-atom chain, in which each atom contributes one atomic orbital to the conjugated π -system, there will be n overlapping atomic orbitals giving rise to n molecular orbitals. T

Correct statement above are (a) i,ii (b) ii,iii (c) i,iii (d) i,ii,iii

6 The root of determinant in case of ethylene molecule in Huckel theory is CSIR NET

(a) $\alpha + \beta, \alpha - \beta$ (b) $\alpha + 2\beta, \alpha - \beta$ (c) $\alpha + 2\beta, \alpha - 2\beta$ (d) $\alpha + \beta, \alpha - 2\beta$

7 consider the statement

i) The concept of π bond formation energy is different than delocalization energy. T

ii) The π bond formation energy in benzene is 6β . F

iii) The delocalization energy for cyclobutadiene molecule is zero. T

Correct statement above are (a) i,ii (b) ii,iii (c) i,iii (d) all (e) none

8. The electronic charge corresponding to central carbon atom in allyl cation is

(a) 1 (b) 0.5 (c) $1/\sqrt{2}$ (d) none CSIR NET

9. Consider the statements

i) Huckel allow us to determine the energies and wavefunction for the π molecular orbital without specifying the Hamiltonian operator. T

ii) The delocalization energy of butadiene is of the order of 65 kJ/mole. F

iii) Compared with the π electron energy of three ethane molecule the delocalization energy in benzene is 3β . F

The correct statement above are (a) i,ii (b) ii,iii (c) i,iii (d) i,ii,iii

10. Consider the statement

i) The delocalization energy corresponding to cyclobutadiene molecule is 0.472β . F

ii) The total π electron energy of naphthalene $E_\pi = 10\alpha + 13.68\beta$ delocalization energy of it is 1.68β F

iii) Secular determinant simplifies if the trial wave function is the linear combination of orthonormal function. T

The correct statements above are (a) i,ii (b) ii,iii (c) i,iii (d) i,ii,iii

11. In case of Huckel molecular orbital treatment of benzene

i) The total π electronic charge on nth carbon atom to be $1/6$. So we see that π electron are uniformly distributed around the benzene ring. **F**

ii) From the bond order ($P=2/3$) calculation in benzene we find that all bond are equivalent. **T**

iii) If $\beta = -75$ kJ/mole then benzene is stabilized by about 150 kJ/mole. **T**

The true statement above are (a) i,ii (b) ii,iii (c) i,iii (d) i,ii,iii (e) none

12. Consider the statement

i) The delocalization energy for allylcation, allyl anion and allyl radical are same but stability for all these species differ, so Huckel method can not explain the stability order of these species. **F (DEPE)**

ii) If the energy of two electron one in each side of two isolated non interacting $2p_z$ atomic orbital is 2α then net gain in energy on the formation of ethylene system is 2β . **T** $2(\alpha+\beta) - 2\alpha = 2\beta$

iii) The ground state of cyclobutadiene is a triplet state biradiacal. **T**

The correct statement above are (a) i,ii (b) ii,iii (c) i,iii (d) i,ii,iii (e) none

13. Consider the statement

i) Butadiene is somewhat stabilized by delocalization (relative to ethylene), it is much less conjugated than allylcation. $\rightarrow 0.828\beta$ **T**

ii) Huckel theory is an approximation formulae, the concept of bathochromic shift that was studied during $\pi \rightarrow \pi^*$ can not be explained by Huckel method. **F**

iii) The value of Huckel parameter α and β are different in case of hetro atom. **T**

The correct statement above are (a) i,ii (b) ii,iii (c) i,iii (d) i,ii,iii (e) ii (f) iii (g) i

14 Using extended huckel theory determine the linear or the triangular state of H_3^+ is the more stable state. Repeat the calculation for H_3 and H_3^- . \rightarrow Extended HMO Theory applicable on H_3^+ bond also.

15. Consider the statement

i) Huckel molecular orbital theory is based on σ - π seperability. **T**

ii) The value of resonance energy generally remain in the form of resonance integral **T**

iii) The approximation of considering overlap integral zero in Huckel molecular orbital theory is a bad approximation. **T** $S_{11}=1$ $S_{12}=0.25$ $S_{13}=0.09$, Can't be neglected

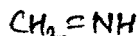
The correct statement above are (a) i,ii (b) ii,iii (c) i,iii (d) all (e) none

16. The bond order between first and second carbon atom in allyl radical is

17 The energy required for the transition from homo to luma in ethylene molecule is ... **150 kJ/mole**

18 The energy level corresponding to methyleneimine if $\alpha_N = \alpha + 0.5\beta$ is ... **$\alpha + 1.28\beta$**

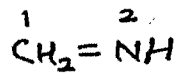
19 The energy level corresponding to allylcation is as **$\alpha - 0.78\beta$**



gate
2002

Setup the Hückel determinate form for methylenediamine

& find the corresponding energy level if $\alpha_N = \alpha + 0.5\beta$



$$\beta_{C-N} = 1.0\beta$$

$$\begin{vmatrix} C_{11} & C_{12} \\ C_{21} & C_{22} \end{vmatrix} \Rightarrow \begin{vmatrix} \alpha_C - E & \beta_{C-N} \\ \beta_{N-C} & \alpha_N - E \end{vmatrix} = 0$$

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha + 0.5\beta - E \end{vmatrix} = 0$$

Divide by β

$$\begin{vmatrix} \frac{\alpha - E}{\beta} & 1 \\ 1 & \frac{\alpha + 0.5\beta - E}{\beta} \end{vmatrix} = 0 \Rightarrow \begin{vmatrix} \frac{\alpha - E}{\beta} & 1 \\ 1 & \frac{\alpha - E + 0.5\beta}{\beta} \end{vmatrix} = 0$$

Put $\frac{\alpha - E}{\beta} = x$ $E = \alpha - \beta x$

$$\begin{vmatrix} x & 1 \\ 1 & x + 0.5 \end{vmatrix} = 0$$

$$x^2 + 0.5x - 1 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$\begin{aligned} a &= 1 \\ b &= 0.5 \\ c &= -1 \end{aligned}$$

$$= \frac{-0.5 \pm \sqrt{2.5 - 4 \times 1 \times (-1)}}{2}$$

$$= \frac{-0.5 \pm \sqrt{2.5 + 4}}{2}$$

$$\begin{aligned} x &= -1.28 \\ x &= 0.78 \end{aligned}$$

$$E = \alpha - \beta x$$

$$x = -1.28$$

$$E = \alpha + 1.28\beta$$

$$x = 0.78$$

$$E = \alpha - 0.78\beta$$

Huckel Theory - (Qualitative Theory)

HMO is applicable for planar conjugated hydrocarbon molecule, method assumes that π -system of conjugated ~~system~~ molecule may be treated independently of the σ -bonding. π -e are delocalised over the framework of molecule and play important role in every rxn. The σ e can be considered as relatively unreactive. σ bond framework lie in x-y plane and $2p_x$ & $2p_y$ orbital were used to construct the hybrid orbitals. Then $2p_z$ orbital on each carbon atom is still available for bonding. σ - π separability is permissible for planar conjugated system. π -e move in a fixed effective electrostatic potential due to electrostatic σ framework, that provide the platform for movement of π -e.

HMO method each carbon atom contributes one π -e and one atomic orbital (usually $2p_z$) to the molecular orbital of the system which is approximated by linear combination of atomic orbital (LCAO) procedure and using linear variation principle -

$$\psi_j = \sum_{\mu=1}^n c_{j\mu} \phi_{\mu}$$

$$\psi_1 = c_{11}\phi_1 + c_{12}\phi_2 + c_{13}\phi_3$$

where the sum extend for no. of carbon atom (n) & ϕ_{μ} is the $2p_z$ atomic orbital located at carbon at μ .

Molecular orbital energy may be obtained by linear variation principle

$$E_j = \frac{\langle \psi_j | H | \psi_j \rangle}{\langle \psi_j | \psi_j \rangle}$$

In Huckel method the integral (integral Hamiltonian & overlap) was simplified as

(i) The overlapping integral for 2 atomic orbital located on 2 different centre is taken to be zero.

$$\int \phi_\mu \phi_\nu d\tau = 0 \quad S_{\mu\nu} = 0$$

(ii) $2p_z$ atomic orbital on the same carbon atom are normalized

$$S_{\mu\mu} = 1$$

$$S_{\nu\nu} = 1$$

(iii) Neglecting of overlap integral is over simplification & it is considered in inappropriate simplification.

The interaction b/w atomic orbital i.e. ϕ_μ & ϕ_ν centred at μ & ν are defined in HMO theory as

$$\int \phi_\mu H \phi_\nu d\tau = \langle \phi_\mu | H | \phi_\nu \rangle = H_{\mu\nu} = \beta$$

This represent the interaction energy b/w two atomic orbitals ϕ_μ & ϕ_ν centred at μ & ν respectively & termed as resonance integral

if μ & ν are non-adjacent neighbours, by convention this interaction is neglected

$$\int \phi_\mu H \phi_\nu d\tau = 0 \quad (\text{non-adjacent neighbours})$$

The energy of e^- moving acc. to atomic orbital ϕ_μ in the field of nucleus at the centre μ is

$$\int \phi_{\mu} H \phi_{\mu} d\tau = \langle \phi_{\mu} | H | \phi_{\mu} \rangle = H_{\mu\mu} = \alpha$$

This represents the energy of ψ in an atomic orbital ϕ_{μ} centred at μ & referred as Coulomb integral.

Coulomb integral (α) is the measurement of binding energy of $2p \psi$ of the carbon

$$\boxed{-\frac{1}{\alpha} \rightarrow \text{ionisation energy}}$$

Thus the value of α depends on substitution attached to the carbon & hybrid. of carbon. It is also approximated as valence orbital ionisation energy.

The assumption that all resonance value of β for C-C bond is an oversimplified.

As β value vary with the bond length so 2 value of β should be used for butadiene. However in simple HMO method all value of α & β in a carbon system are taken as same.

α is the -ve of ionisation energy, generally have -ve value.

β describe the additional stabilisation arising from the delocalization of the ψ over neighbouring atomic orbitals

β is also -ve but smaller magnitude than the α . The reference point,

α is used as reference point $\alpha = 0$ as the value of energy &

value of β are determined by experiments (Spectroscopy, Thermometry)

for C-C

$$\boxed{\beta = -75 \text{ kJ/mole}}$$

When these 3 simple postulates of HMO

$$(i) S_{\mu\nu} = 0, S_{\mu\mu} = 1, S_{\nu\nu} = 1$$

$$(ii) H_{\mu\nu} = \beta, H_{\nu\nu} = 0 \text{ (not directly attached)}$$

$$(iii) H_{\nu\nu} = \alpha, H_{\mu\mu} = \alpha$$

When these values are replaced in secular determinate from linear variation principle, the assumption results in following structure:

All on-diagonal elements become $\alpha - E$

Off-diagonal elements b/w neighbouring atom becomes β

All other elements = 0

By solving this determinant we set up the energy pattern and by calculating orbital coeff. we determine function corresponding to every energy state.

Huckel method has wide applicability in determining, bond order, ρ density, delocalization energy, dipole moment & energy required for π - π interaction, also.

Simple HMO is limited to planar system & can't differentiate b/w cis & trans geometry of di-enes.



In case of Heteroatom the parameters β & α differ & generally measured in the term of α for carbon β for C-C

$$(i) \alpha_{\text{Hetro}} = \alpha_c + h\beta$$

$$(ii) \beta_{\text{C-Hetro}} = k\beta_{\text{C-C}}$$

The value of parameters h & k are based on characteristic of hetero atom, two sets of value for heteroatom such as $\textcircled{\text{N}}$ & $\textcircled{\text{O}}$ are given, depending on whether heteroatom contribute 1 or 2 e^- in the system.

$$\left. \begin{array}{l} \alpha_{\text{N}}(1) = \alpha_{\text{C}} + 0.5\beta \\ \alpha_{\text{N}}(2) = \alpha_{\text{C}} + 1.5\beta \end{array} \right\} \begin{array}{l} \text{No. of } e^- \\ \text{CH}_2 = \text{NH} \\ \text{[Diagram of a five-membered ring with a nitrogen atom and a double bond]} \end{array}$$

$$\left. \begin{array}{l} \alpha_{\text{O}}(1) = \alpha_{\text{C}} + 1.0\beta \\ \alpha_{\text{O}}(2) = \alpha_{\text{C}} + 2.0\beta \end{array} \right\}$$

$$\left. \begin{array}{l} \beta_{\text{C-N}} = 0.8\beta \\ \beta_{\text{C=N}} = 1.0\beta \end{array} \right\}$$

$$\left. \begin{array}{l} \beta_{\text{C=O}} = 0.8\beta \\ \beta_{\text{C=O}} = 1.0\beta \end{array} \right\}$$

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★ Molecular Orbital Theory - (MOT)

Qus - gate - 2006

To demonstrate the variational principle a trial wave function

$$\psi = c_1 \frac{\psi_{2s} + \psi_{3s}}{\sqrt{2}} + c_2 \frac{\psi_{2s} - \psi_{3s}}{\sqrt{2}} \quad \psi = c_1 \phi_1 + c_2 \phi_2$$

Secular determinant for H-atom in ev.

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix}$$

$$H_{11} = \int \phi_1 H \phi_1 d\tau$$

$$= \int \frac{\psi_{2s} + \psi_{3s}}{\sqrt{2}} \hat{H} \frac{\psi_{2s} + \psi_{3s}}{\sqrt{2}} d\tau$$

$$= \frac{1}{2} \int (\psi_{2s} + \psi_{3s}) \hat{H} (\psi_{2s} - \psi_{3s}) d\tau$$

$$= \frac{1}{2} \left[\int \psi_{2s} \hat{H} \psi_{2s} d\tau + \int \psi_{2s} \underbrace{H \psi_{3s}}_{E \psi_{3s}} d\tau + \int \psi_{3s} H \psi_{3s} d\tau + \int \psi_{3s} H \psi_{2s} d\tau \right]$$

$$= \frac{1}{2} \left[-\frac{13.6}{4} + \left(-\frac{13.6}{9} \right) \right]$$

$$= \frac{-3.4 \left(1 + \frac{4}{9} \right)}{2}$$

$$\begin{aligned}
 H_{22} &= \int \phi_2 H \phi_2 d\tau \\
 &= \int \frac{\psi_{2s} - \psi_{3s}}{\sqrt{2}} H \frac{\psi_{2s} - \psi_{3s}}{\sqrt{2}} d\tau \\
 &= \frac{-3.4 \left(1 + \frac{4}{9}\right)}{2}
 \end{aligned}$$

$$\begin{aligned}
 H_{12} &= \int \phi_1 H \phi_2 d\tau \\
 &= \frac{1}{2} \left[\int \phi \psi_{2s} H \psi_{2s} d\tau - \int \psi_{2s} H \psi_{3s} d\tau + \int \psi_{3s} H \psi_{2s} d\tau \right. \\
 &\quad \left. - \int \psi_{3s} H \psi_{3s} d\tau \right] \\
 &= \frac{1}{2} \left(\frac{-13.6}{4} - \frac{13.6}{9} \right) \\
 &= \frac{-3.4 \left(1 + \frac{4}{9}\right)}{2}
 \end{aligned}$$

$$\begin{vmatrix}
 \frac{-3.4 \left(1 + \frac{4}{9}\right)}{2} - E & \frac{-3.4 \left(1 - \frac{4}{9}\right)}{2} \\
 \frac{-3.4 \left(1 - \frac{4}{9}\right)}{2} & \frac{-3.4 \left(1 + \frac{4}{9}\right)}{2} - E
 \end{vmatrix}$$

Ans

★ MOT —

$$\psi_{mo} = c_1 \phi_1 + c_2 \phi_2$$

Two atomic orbital ϕ_1 & ϕ_2 are linearly combined to form molecular orbital function ψ

ψ_{mo} is normalized only when

$$\int \psi_{mo} \psi_{mo} d\tau = 1$$

OR

$$\int (c_1 \phi_1 + c_2 \phi_2) (c_1 \phi_1 + c_2 \phi_2) d\tau = 1$$

$$\int c_1 \phi_1 c_1 \phi_1 d\tau + \int c_1 \phi_1 c_2 \phi_2 d\tau + \int c_2 \phi_2 c_1 \phi_1 d\tau + \int c_2 \phi_2 c_2 \phi_2 d\tau = 1$$

$$c_1^2 \int \phi_1 \phi_1 d\tau + c_1 c_2 \int \phi_1 \phi_2 d\tau + c_1 c_2 \int \phi_1 \phi_2 d\tau + c_2^2 \int \phi_2 \phi_2 d\tau = 1$$

$$c_1^2 + 2c_1 c_2 \int \phi_1 \phi_2 d\tau + c_2^2 = 1$$

$$c_1^2 + c_2^2 + 2c_1 c_2 S = 1$$

CSIR

Qus- $\psi_{mo} = 0.4 \phi_1 + 0.8 \phi_2$ is a normalized MO of diatomic molecule constructed from ϕ_1 & ϕ_2 which are normalized. The overlap b/w ϕ_1 & ϕ_2 find $S = ?$ (overlapping integral)

$$(0.4)^2 + 2 \times 0.4 \times 0.8 S + (0.8)^2 = 1$$

$$c_1^2 + c_2^2 + 2c_1 c_2 (S) = 1 \quad S = 0.31$$

Probability corresponding to ϕ_1 i.e. probability of finding e^- corresponding to (1) atom in mo & (2) atom

$$P_1 = c_1^2 + c_1 c_2 S \quad \checkmark$$

$$P_2 = c_2^2 + c_1 c_2 S$$

$$P_1 + P_2 = 1$$

$$c_1^2 + c_2^2 + 2c_1 c_2 S = 1$$

CSIR

Qus- ~~7/10~~ = One molecular orbital of polar molecule AB has the form $C_A \psi_A + C_B \psi_B$ where ψ_A & ψ_B are normalized atomic orbital centred on A & B. The e^- in this orbital is found on atom B with probability 90%. Neglecting the overlap a possible set of C_A & C_B is

Solⁿ -

$$\psi_{MO} = C_A \psi_A + C_B \psi_B$$

$$P_A = C_A^2 = .10$$

$$C_A = \sqrt{.10} = 0.32$$

$$P_B = C_B^2 = .90$$

$$C_B = \sqrt{\frac{9}{10}} = .95$$

$$C_A^2 + C_B^2 = 1 \quad [\because S=0]$$

$$C_A = 0.32 \quad C_B = 0.95$$

★ How to write wave function for MO —

diatomic molecule having $1e^-$ (H_2^+) The wave function corresponding wave function to it

$$\psi_{MO} = C_1 \phi_1 + C_2 \phi_2$$

A = Hydrogen

B = Hydrogen

Normalized only when

$$\int \psi_{MO} \psi_{MO}^* d\tau = 1$$

$$C_1 = C_2 \quad (\text{Both are Hydrogen})$$

$$C_1^2 + C_2^2 + 2C_1 C_2 S = 1$$

$$C_1^2 + C_1^2 + 2C_1^2 S = 1$$

$$2C_1^2 (1+S) = 1$$

$$C_1 = \frac{1}{\sqrt{2(1+S)}}$$

$$\psi_{MO} = \frac{1}{\sqrt{2(1+S)}} [\phi_1 + \phi_2]$$

★ for diatomic with 2e⁻

$$= \frac{1}{\sqrt{2(1+S)}} [\phi_A(1) + \phi_B(1)] \cdot \frac{1}{\sqrt{2(1+S)}} [\phi_A(2) + \phi_B(2)]$$

★ In VBT

diatomic with 1e⁻ (Not possible) or Not valid
 ↓
 Below VBT

Diatomic with 2e⁻

follows mono-centric approach

- ① A
- ② B

$$\psi_{VB} = \phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1) \quad (\text{Bonding})$$

$$= \phi_A(1)\phi_B(2) - \phi_A(2)\phi_B(1) \quad (\text{Anti-Bonding})$$

★ How to write the wave function corresponding to molecular orbital

2 atom, 1e⁻ (H₂⁺)

$$\psi_{MO} = \frac{1}{\sqrt{2(1+S)}} [\phi_1 + \phi_2]$$

atom e⁻ C₁=C₂

3 atom, 2e⁻

$$\psi_{MO} = [\phi_A(1) + \phi_B(1) + \phi_C(1)] [\phi_A(2) + \phi_B(2) + \phi_C(2)]$$

MO follows multicentric approach

→ Let us normalize wave function corresponding to VBT for 2 atom $2e^-$ system

$$\int \Psi_{VBT} \Psi_{VBT} d\tau = 1$$

$$\int N [\phi_A(1)\phi_B(2) + \phi_A(2) + \phi_B(1)] N [\phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)] = 1$$

$$= N^2 \left[\int \phi_A(1)\phi_B(2) \cdot \phi_A(1)\phi_B(2) d\tau + \int \phi_A(1)\phi_B(2) \phi_A(2)\phi_B(1) \right. \\ \left. + \int \phi_A(2)\phi_B(1) \phi_A(2)\phi_B(1) + \int \phi_A(2)\phi_B(1) \phi_A(1)\phi_B(2) d\tau \right] = 1$$

$$\int \phi_A \phi_A = 1 \quad \int \phi_A(1) \phi_A(1) d\tau = 1$$

$$\int \phi_B \phi_B = 1$$

$$\int \phi_A \phi_B = S$$

$$N^2 [1 + S^2 + 1 + S^2] = 1$$

$$N^2 [2 + 2S^2] = 1$$

$$N = \frac{1}{\sqrt{2+2S^2}}$$

$$\text{OR } N = \frac{1}{\sqrt{2(1+S^2)}}$$

Qus - The simplest ground state VB wavefunction of a diatomic molecule like HCl is given as

$$\Psi = \Psi_H(1s,1) \Psi_{Cl}(3p_z,2) + B$$

Where B stands for

- ① $\Psi_H(3p_z,2) \Psi_{Cl}(1s,1)$ ③ $\Psi_{Cl}(1s,2) \Psi_H(3p_z,1)$
 ② $\Psi_H(1s,2) \Psi_{Cl}(3p_z,1)$ ④ $\Psi_{Cl}(1s,1) \Psi_H(3p_z,2)$

Qus - Sp hybrid orbital are of the form

$$C_1 2s + C_2 2p_z$$

The coefficient of Normalized form of the above Sp hybrid orbital

(a) $C_1 = \frac{1}{\sqrt{2}} \quad C_2 = \pm \frac{1}{\sqrt{2}}$

$$C_1^2 + C_2^2 = 1$$

(b) $C_1 = \frac{1}{2} \quad C_2 = \pm \frac{1}{2}$

(c) $C_1 = \frac{1}{\sqrt{2}} \quad C_2 = \pm \frac{1}{2}$

(d) $C_1 = \frac{1}{2} \quad C_2 = \pm \frac{1}{\sqrt{2}}$

★ Comparison of MOT & VBT -

By taking into consideration two atom @ e⁻ system.

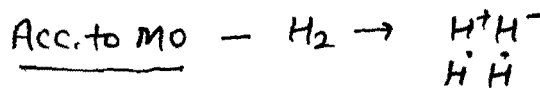
Let us consider @ atom @ e⁻ system

$$\Psi_{MO} = [\phi_A(1) + \phi_B(1)] [\phi_A(2) + \phi_B(2)]$$

$$\Psi_{VBT} = \underbrace{[\phi_A(1) \phi_B(2)] [\phi_A(2) \phi_B(1)]}_{\downarrow \text{Covalent}} \quad 100\% \text{ Covalent}$$

$$\Psi_{MO} = \underbrace{\phi_A(1) \phi_A(2)}_{\downarrow \text{ionic}} + \underbrace{\phi_A(1) \phi_B(2) + \phi_B(1) \phi_A(2)}_{\downarrow \text{Covalent}} + \underbrace{\phi_B(1) \phi_B(2)}_{\downarrow \text{ionic}}$$

50% Covalent
50% Ionic



The wavefunction corresponding to MOT, Ψ_{MO} is containing of 50% Covalent ~~ionic~~ term $(\phi_A(1) \phi_B(2) + \phi_B(1) \phi_A(2))$ & 50% ionic term

So acc to MOT wavefunction when molecule H_2 dissociate there should be 50% chance of H^+H^- & 50% chance of H^-H^+ but experimentally we found two (H) forms when H_2 molecule dissociate, so in MOT ionic term is overemphasized & it should be modified. It is corrected by taking the concept of configuration interaction into account.

In VBT Total function ψ is containing of covalent term but molecule also exist as ionic, so we have to correct it by adding ionic part as

$$\psi = \psi_{\text{covalent}} + d \psi_{\text{ionic}}$$

d is the parameter that determines the % ionic character

ψ is normalized only when $c_1^2 + c_2^2 = 1$ if $c_1^2 + c_2^2 \neq 1$ then

$$1^2 + d^2 \neq 1$$

reverse of value

&

SQRT & multiply with function

multiply by

$$\psi = \frac{1}{\sqrt{1^2 + d^2}} \psi_{\text{covalent}} + \frac{d}{\sqrt{1^2 + d^2}} \psi_{\text{ionic}}$$

$$\% \text{ ionic character} = c_2^2 \times 100 = \frac{d^2}{1+d^2} \times 100$$

Qus - In the formation of H_2 molecule from 2H atom placed at a position A & B are separated by a distance r_{AB} a part of spatial wave function

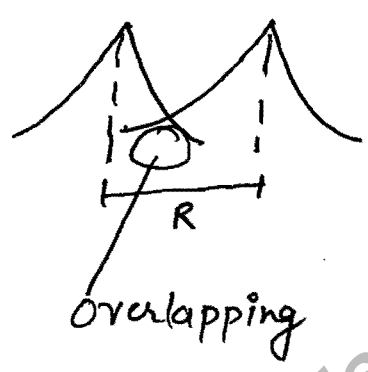
$$\psi = \phi_A(1) \phi_B(2) + \phi_B(1) \phi_A(2)$$

- ① This is covalent term and is important $\lambda_{AB} \rightarrow \infty$
- ② This " ionic " " " " " $\lambda_{AB} \rightarrow \infty$
- ③ " " covalent " " " " $\lambda_{AB} \rightarrow 0$
- ④ " " ionic " " " " $\lambda_{AB} \rightarrow 0$

$$S = \left(1 + R + \frac{R^2}{3}\right) e^{-R}$$

R = internuclear distance
b/w two atoms

$$1 > S > 0$$



$R \rightarrow \infty$ S ↑ as $\lambda_{AB} \rightarrow \infty$
→ Ionic Term

$$-\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_a} - \frac{e^2}{4\pi\epsilon_0 r_b} + \frac{e^2}{R_{AB}}$$

Gate-2008

wave function of a diatomic molecule has the form

$$\psi = 0.89 \psi_{\text{covalent}} + 0.45 \psi_{\text{ionic}}$$

The chance that both electron of the bond will be found on the same atom in 100 inspections of the molecule approximately is ionic

$$(0.45)^2 \times 100 = 0.2025 \times 100 = 20.25$$

(45)² → 20 से
20,50 से कितना
= 2025 (5) → 5² = 25

★ Theoretical Treatment of MOT -

MOT is based on the principle of

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LCAO - MO model, in theory e^{\ominus} is associated with a wavefunction that is delocalized over the entire molecule. MO's are polycentric, they involve more than one nucleus while AO's are monocentric, as they involve only one nucleus.

generally MO's are developed by two methods: LCAO & United atom method. LCAO has a good deal of similarity with valence bond method.

LCAO - The combination b/w two orbitals b/w A & B will be effective if the following ③ conditions are satisfied

Energy (E)

Overlapping (O)

Symmetry (S)

EOS

- ① Combining wavefunction should be of comparable energy.
- ② A significant extent of overlapping needed.
- ③ lobes of combining AO's must have same symmetry w.r.t bond axis.

If we consider H_2^+ molecule

the Hamiltonian of the molecule is

$$H = \frac{-\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 a} - \frac{e^2}{4\pi\epsilon_0 b} + \frac{e^2}{4\pi\epsilon_0 R}$$

$$\psi_{1s} = c_1 \phi_a + c_2 \phi_b \quad \text{OR} \quad \psi_{1s} = \frac{\phi_a + \phi_b}{\sqrt{1+S}}$$

The sum of the wavefunction by variation principle leads to secular determinant

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0$$

$$H_{11} = \int \phi_a H \phi_a d\tau = \alpha, \quad H_{12} = \int \phi_a H \phi_b d\tau = \beta, \quad S_{12} = \int \phi_a \phi_b d\tau = S$$

$$S_{22} = S_{11} = \int \phi_a \phi_a d\tau = 1$$

$$\begin{vmatrix} \alpha - E & \beta - ES \\ \beta - ES & \alpha - E \end{vmatrix} = 0 \quad \left. \begin{array}{l} E_+ = \frac{\alpha + \beta}{1+S} \\ E_- = \frac{\alpha - \beta}{1-S} \end{array} \right\}$$

$$(\alpha - E)^2 - (\beta - ES)^2 = 0$$

$$\alpha - E = \pm (\beta - ES)$$

evaluation of α , β & S

$$\alpha = H_{11} = \int \psi_{1s(a)} H \psi_{1s(a)} d\tau$$

$$= \int \psi_{1s(a)} \left(-\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_a} - \frac{e^2}{4\pi\epsilon_0 r_b} + \frac{e^2}{4\pi\epsilon_0 R} \right) \psi_{1s(a)} d\tau$$

$$= \int \psi_{1s(a)} \left(-\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_a} \right) \psi_{1s(a)} d\tau + \int \psi_{1s(a)} \left(-\frac{e^2}{4\pi\epsilon_0 r_b} \right) \psi_{1s(a)} d\tau$$

(I) (II)

$$+ \int \psi_{1s(a)} \frac{e^2}{4\pi\epsilon_0 R} \psi_{1s(a)} d\tau$$

(III) ↓
fixed (R)

Hamiltonian of an isolated H atom is

$$H^0 = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_a}$$

So (I) Term of equation denotes the energy of 1s orbital of isolated (H) atom it is denoted by (E_H)

The 2nd integral considers the electrostatic interactions b/w 1s e^- of (a) & nucleus (b) & considered as Coulomb electrostatic interaction & denoted by (J) & generally -ve quantity

$$\alpha = E_H + J + \frac{e^2}{4\pi\epsilon_0 R}$$

R - resonance integral is given by

$$R = \int \psi_{1s}(a) H \psi_{1s}(b) d\tau$$

$$= \int \psi_{1s}(a) \left(-\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_a} - \frac{e^2}{4\pi\epsilon_0 r_b} + \frac{e^2}{4\pi\epsilon_0 R} \right) \psi_{1s}(b) d\tau$$

The resonance integral is consisting of term exchange integral A that may be obtained by breaking hamiltonian operator

as

$$\int \psi_{1s}(a) \left(-\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\epsilon_0 r_b} \right) \psi_{1s}(b) d\tau + \int \psi_{1s}(a) -\frac{e^2}{4\pi\epsilon_0 r_a} \psi_{1s}(b) d\tau$$

↓ (I)

$$+ \int \psi_{1s}(a) \frac{e^2}{4\pi\epsilon_0 R} \psi_{1s}(b) d\tau$$

$$\int \psi_{1s}(a) H^0 \psi_{1s}(b) d\tau$$

↓

$$\int \psi_{1s}(a) E_H \psi_{1s}(b) d\tau \rightarrow E_H \int \psi_{1s} \psi_{1s}(b) d\tau$$

$E_H S$

First term represents the original Hamiltonian operating on nucleus (b) 103

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$$\int \Psi_{1s}(a) H^0 \Psi_{1s}(b) d\tau = E_H S$$

2nd integral give the exchange integral K, which consider exchange of α by nuclei a & b, physically it depends on overlap of orbitals, it is -ve quantity it is favoured maximum if the orbital overlapping of the same energy, when we replace the value α & β in expression

$$E_+ = \frac{\alpha + \beta}{1 + S}$$

$$E_- = \frac{\alpha - \beta}{1 - S}$$

$$E = E_H + \frac{e^2}{4\pi\epsilon_0 R} + \frac{J+K}{1+S}$$

$$E_+ = E_H + \frac{1}{R} + \frac{J+K}{1+S}$$

$$E_- = E_H + \frac{1}{R} + \frac{J-K}{1-S}$$

J & K generally both are -ve quantities.

The value of J, K & S also expressed in terms of R as

$$J = - \left[\frac{1}{R} (1 - (1+R)e^{-2R}) \right]$$
$$K = - (1+R)e^{-R}$$
$$S = \left(1+R + \frac{R^2}{3} \right) e^{-R}$$

* Important aspects of LCAO-MO -

molecular orbital are developed

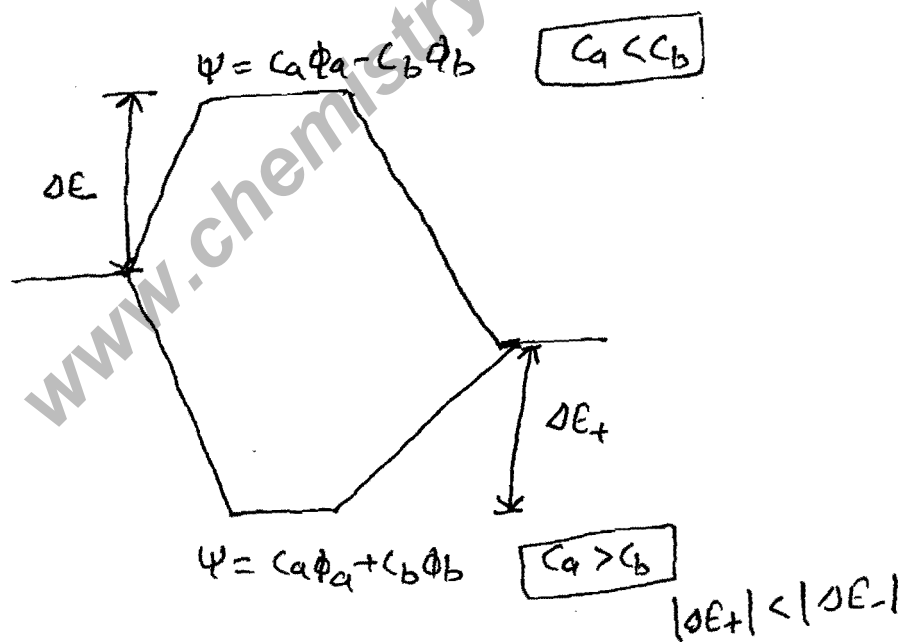
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from the atomic orbitals which nuclei are at the fixed position, through the LCAO method, thus the MO's are polycentric (involve more than one nucleus) which AOs are monocentric, the energy of MO that has the form $\psi = c_a \phi_a + c_b \phi_b$ with in phase of AOs is lower than that of lower lying orbital by ΔE_+ , this MO is called bonding.

The energy of MO which has the form

$$\psi = c_a \phi_a - c_b \phi_b$$

with out of phase AO is higher than that of higher lying atomic orbital by ΔE_- , this is called anti-bonding MO



ΔE_+ & ΔE_- increases with the overlap, the inequality is always satisfied the value of ΔE_+ & ΔE_- can be calculated by determining value of J & K

The contribution of AO in MO is measured by their relative coeff. C_a & C_b ? this coeff can be calculated by secular eqn.

If two AOs have the same energy then their coeff. are equal, but if energy of AOs are not equal the magnitude of coeff. of lower lying AO orbital is greater in bonding MO & smaller in anti-bonding MO.

The probability that the e^- described by MO is located on one of the two atom is proportional to

$$C_1^2 + C_1 C_2 S$$

$$C_2^2 + C_1 C_2 S$$

these probabilities are equal if both orbital are same & not same then probability finding the e^- on the atom with lower atomic orbital energy is higher in bonding state & lower in the anti-bonding state.

No. of molecular orbitals are equal to total no. of AOs

For an effective combination of AOs they must satisfy EOS condition.

Depending on the overlap integral MO are classified as

Bonding, anti-bonding & non-bonding

$$S > 0 \quad \text{bonding}$$

$$S < 0 \quad \text{Anti-Bonding}$$

$$S = 0 \quad \text{Non-bonding}$$

All the MOs are normalized & bonding & anti-bonding orbitals are mutually orthogonal.

After construction of MOs e^- are filled acc. to Aufbau & Pauli principle.

MOs are also defined by four quantum no., as AO's,

$$m_l = -l \text{ to } +l$$

$$l = \pm 1$$

(*) generally n & l are retained from the starting AO's & they

have same significance, the magnetic quantum no. of MO are represented by l

for $l=0$ the orbitals are symmetrical around the reference axis & called σ orbital

for $l=\pm 1$ - referred as π orbital

$l=\pm 2$ - δ orbital

& the fourth quantum no. has same significance as in AO's.

σ bond arises overlapping of 1 lobe - 1 lobe

π bond - 2 lobes + 2 lobes

δ bond - 4L + 4L

ϕ bond - 6 lobes + 6 lobes

S-orbital can have only σ type interaction

p ————— σ & π both

d ————— σ , π & δ

f ————— σ , π , δ & ϕ type interaction

The different MO have different symmetry elements, they can be classified as (based on symmetry) gerade and ungerade

* Introduction of spin in VBT -

Electron spin & Pauli principle -

A fourth quantum no, called spin quantum no, is required when the relativistic motion of e^- are taken into consideration. This concept of e^- spin was postulated by Goudsmit & Uhlenback in order to explain the fine structure of line spectra of alkali atom, eg. - The sodium D-lines which arises from the transition b/w 3s & 3p orbitals have doublet, to explain this doublet, first time concept of spin was introduced. It is the intrinsic property of microscopic particle & there is no classical analog to the spin & it is strictly a quantum mech. phenomenon, if microscopic particle have spin then there is corresponding spin angular momentum also exist. If there is spin there is introduction of 4th quantum no. is needed. So 6th postulates in QM was introduced to define the spin part of the state in total wave function & the operator corresponding to spin angular momentum was proposed, the tool used for this purpose is called matrix mechanics. The basic idea of matrix mechanics is to replace wave function with a vector in the form of matrix, operator are represented by matrix & function also represented by matrix also

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

$$\sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$$

$$\sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

$$\left. \begin{aligned} S_x &= \frac{1}{2} \hbar \sigma_x \\ S_y &= \frac{1}{2} \hbar \sigma_y \\ S_z &= \frac{1}{2} \hbar \sigma_z \end{aligned} \right\}$$

Operator of spin angular momentum is represented by Pauli spin matrix. It is dimensionless. σ_x, σ_y & σ_z

In 1928, P. Dirac developed a relativistic theory of QM from which the concept of spin generated naturally.

$$[\sigma_x, \sigma_y] = 2i\sigma_z$$

$$[\sigma_y, \sigma_z] = 2i\sigma_x$$

$$[\sigma_z, \sigma_x] = 2i\sigma_y$$

$$\sigma^2 = \sigma_x^2 + \sigma_y^2 + \sigma_z^2 = 3 \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

$$\sigma_x^2 = \sigma_x \sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

$$\sigma_y^2 = \sigma_y \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

$$\sigma_z^2 = \sigma_z \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

$$[S_x, S_y] = i\hbar S_z$$

$$[S_y, S_z] = i\hbar S_x$$

$$[S_z, S_x] = i\hbar S_y$$

$$\begin{aligned} [S_x, S_y] &= \left[\frac{1}{2}\hbar\sigma_x, \frac{1}{2}\hbar\sigma_y \right] = \frac{1}{2}\hbar \cdot \frac{1}{2}\hbar [\sigma_x, \sigma_y] \\ &= \frac{1}{2}\hbar \frac{1}{2}\hbar 2i\sigma_z \\ &= \frac{2i\hbar}{2} \frac{1}{2}\hbar\sigma_z \\ &= \underline{\underline{i\hbar S_z}} \end{aligned}$$

When spin part of the wavefunction was introduced in the total wave function then the symmetry of wavefunction, is mentioned in postulate (6)

Postulate (6) The total wave function must be anti-symmetric w.r.t. to interchange of ^{all} co-ordinates of ① fermion with that of another fermion.

The Pauli exclusion principle which states that no two \ominus within an atom can't have same set of four quantum no. This is a direct result of this anti-symmetric principle.

$$\begin{array}{ccc} & 1 & 2 \\ \hbar & \rightarrow q_1 & q_2 \rightarrow \hbar \\ \theta & & \theta \\ \phi & & \phi \\ \sigma & & \sigma \end{array}$$

$$\sigma(q_1, q_2) = -\sigma(q_2, q_1) \quad (\text{Antisymmetric})$$

$$q_1 \neq q_2$$

$$\text{If } q_1 = q_2 = q \quad \sigma(q, q) + \sigma(q, q) = 0$$

Let us consider q_1 & q_2 are co-ordinates corresponding to \bar{e} (1) & (2)

$$q_1(n_1, l_1, m_{l_1}, m_{s_1}) ; q_2(n_2, l_2, m_{l_2}, m_{s_2})$$

Acc. to postulate (6) the wavefunction must be anti-symmetric
If all four quantum no., co-ordinates corresponding to q_1 & q_2
are equal then

$$q_1 = q_2 = q$$

$$\sigma(q_1, q_1) = -\sigma(q_2, q_2)$$

$$\sigma(q, q) = -\sigma(q, q)$$

$$\sigma(q, q) + \sigma(q, q) = 0$$

$$2\sigma(q, q) = 0$$

$$\Rightarrow \sigma = 0$$

If spin part of wave function is zero (0) Then total function
become zero \Rightarrow not acceptable.

$$\Psi_{\text{Total}} = \Psi_{\text{Space}} + \sigma_{\text{Spin}}$$

$\hookrightarrow \Psi_T$ must be anti-symmetric
for a fermion containing
system.

For two atom two \bar{e} system -

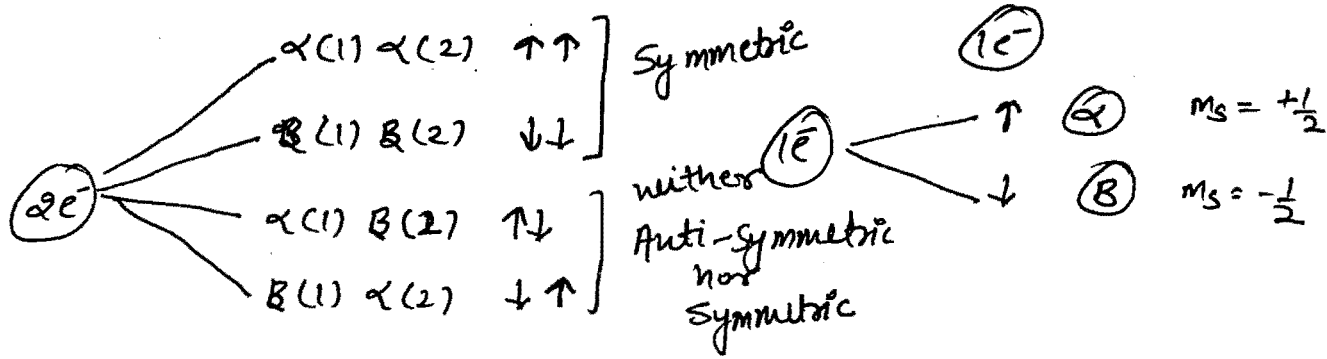
(UBT)

$$\Psi = \left. \begin{array}{l} \phi_a(1) \phi_b(2) \\ \phi_a(2) \phi_b(1) \\ \phi_a(1) \phi_b(2) + \phi_a(2) \phi_b(1) \\ \phi_a(1) \phi_b(2) - \phi_a(2) \phi_b(1) \end{array} \right\} \text{Space part}$$

Symmetric \rightarrow

Anti-symmetric \rightarrow

Spin part for two e⁻ system there are four possible states.



$$\Psi_T = \Psi_{space} + \sigma_{Spin}$$

Out of these 4 spin state first two ($\alpha(1)\alpha(2), \beta(1)\beta(2)$) are ~~system~~ symmetric as we operate spin exchange operator on the function and change the spin remain same

Symmetric $\left[\begin{array}{l} P_{12} \alpha(1)\alpha(2) = \alpha(2)\alpha(1) \\ \uparrow\uparrow \rightarrow \uparrow\uparrow \end{array} \right.$

Symmetric $\left[\begin{array}{l} P_{12} \beta(1)\beta(2) = \beta(2)\beta(1) \\ \downarrow\downarrow = \downarrow\downarrow \end{array} \right.$

The symmetry of two states $\alpha(1)\beta(2)$ & $\beta(1)\alpha(2)$ can not be determine because when we operate the spin exchange operator on the function neither get same state nor we get same with -ve (i.e anti-symmetric)

$$\left. \begin{array}{l} P_{12} \alpha(1)\beta(2) = \beta(2)\alpha(1) \\ \uparrow\downarrow = \downarrow\uparrow \\ P_{12} \alpha(2)\beta(1) = \beta(1)\alpha(2) \\ \uparrow\downarrow = \downarrow\uparrow \end{array} \right\} \begin{array}{l} \text{neither symmetric} \\ \text{nor anti-symmetric} \end{array}$$

To define the symmetry of the state we take the linear combination of above two states

$$\alpha(1)\beta(2) + \beta(1)\alpha(2)$$

$$\alpha(1)\beta(2) - \beta(1)\alpha(2)$$

When we operate spin exchange operators on the above two states we get

$$\alpha(1)\beta(2) + \beta(1)\alpha(2) \quad \underline{\text{Symmetric}}$$

$$P_{12} [\alpha(1)\beta(2) + \beta(1)\alpha(2)] = \alpha(2)\beta(1) + \beta(2)\alpha(1) \\ = \beta(2)\alpha(1) + \alpha(2)\beta(1)$$

$$P_{12} [\uparrow\downarrow + \downarrow\uparrow] = \downarrow\uparrow + \uparrow\downarrow \\ = \uparrow\downarrow + \downarrow\uparrow$$

$$(ii) P_{12} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] = \alpha(2)\beta(1) - \beta(2)\alpha(1) \\ \uparrow\downarrow - \downarrow\uparrow = - [\beta(2)\alpha(1) - \alpha(2)\beta(1)] \\ = \downarrow\uparrow - \uparrow\downarrow \\ = - [\uparrow\downarrow - \downarrow\uparrow] \quad \underline{\text{Anti-symmetric}}$$

$$\left. \begin{array}{l} \alpha(1)\alpha(2) \\ \beta(1)\beta(2) \\ \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)] \end{array} \right\} \rightarrow \text{Symmetric}$$

$$\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \rightarrow \text{Anti-symmetric}$$

$$M_S = \frac{1}{2} + \frac{1}{2} = 1 \quad \text{Triplet State } S=1 \\ M_S = \frac{1}{2} - \frac{1}{2} = 0 \\ M_S = -1 \\ M_S = 0$$

$$\left[\begin{array}{l} S^2 \alpha(1)\alpha(2) = 2\hbar^2 \alpha(1)\alpha(2) \\ S^2 \beta(1)\beta(2) = 2\hbar^2 \beta(1)\beta(2) \\ S^2 [\alpha(1)\beta(2) + \beta(1)\alpha(2)] = 2\hbar^2 [\alpha(1)\beta(2) + \beta(1)\alpha(2)] \end{array} \right.$$

$$\hat{S}^2 [\alpha(1)\beta(2) - \alpha(2)\beta(1)] = 2\hbar^2 [\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

When we operate the total spin angular momentum operator \hat{S}^2 on states, eigen value corresponding to each state $2\hbar^2$.

As the eigen value corresponding to $L^2 = l(l+1)\hbar^2$ in very same way eigen value corresponding $S^2 = s(s+1)\hbar^2$

$$s(s+1)\hbar^2 = 2\hbar^2$$

$$s = 1$$

$2s+1 = 3$ Triplet state.

$$s = 1 \quad m_s = 1, 0, -1$$

$$\left. \begin{array}{l} \alpha(1)\alpha(2) \\ \beta(1)\beta(2) \\ \alpha(1)\beta(2) + \beta(1)\alpha(2) \end{array} \right\} \begin{array}{l} m_s = +1 \\ m_s = -1 \\ m_s = 0 \end{array} \quad \boxed{s=1} \quad \text{Triplet state}$$

⊗ In the very same way when we operate \hat{S}^2 operator on the state

$$\alpha(1)\beta(2) - \beta(1)\alpha(2)$$

$$S^2 [\alpha(1)\beta(2) - \beta(1)\alpha(2)] = 0 [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

$$s(s+1)\hbar^2 = 0$$

$$s = 0 \\ m_s = 0$$

$$2s+1 = 1 \quad \text{Singlet state}$$

Acc. to postulate ① total wave function for a fermion containing system must be anti-symmetric.

The possible wavefunction from above spatial and spin states are

$$\Psi_{T, \text{anti}} = \phi_a(1) \phi_b(2) \times \alpha(1) \beta(2) - \beta(1) \alpha(2)$$

$$\Psi_{T, \text{anti}} = \phi_a(2) \phi_b(1) \times \alpha(1) \beta(2) - \beta(2) \alpha(1)$$

$$\Psi_{T, \text{anti}} = \phi_a(1) \phi_b(2) + \phi_a(2) \phi_b(1) \times \alpha(1) \beta(2) - \beta(2) \alpha(1)$$

$$\Psi_{T, \text{anti}} = [\phi_a(1) \phi_b(2) - \phi_a(2) \phi_b(1)] \times [\alpha(1) \alpha(2)]$$

$$\Psi_{T, \text{anti}} = [\phi_a(1) \phi_b(2) - \phi_a(2) \phi_b(1)] \times [\beta(1) \beta(2)]$$

$$\Psi_{T, \text{anti}} = [\phi_a(1) \phi_b(2) - \phi_a(2) \phi_b(1)] \times [\alpha(1) \beta(2) + \beta(1) \alpha(2)]$$

★ Slater Determinant -

We have introduced spin, we have seen that we must use antisymmetric wave function, acc to postulate ⑥ All electronic wave function must be anti-sym. It is easy to write anti-sym $2e^-$ wave function by inspection but what if we have a set of n -spin orbitals & we need to construct an anti-sym $n e^-$ wave function, in early 1930 Slater introduced the use of determinants to construct anti-symmetric wave function, if we use

$$1s(1) 1s(2) [\alpha(1) \beta(2) - \beta(1) \alpha(2)]$$

for $2e^-$ system

We can write

$He = 1s^2$

$$\begin{vmatrix} 1s\alpha(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\beta(2) \end{vmatrix}$$

So Slater determinant is antisymmetric wave function that represent the electronic wave function & follow the Pauli-exclusion principle.

* How to construct a wave function using determinant

First we construct a matrix of spin orbital, in first row of matrix we put the orbital that the first e^- can occupy & assign the first e^- to them, thus for He, we have 2 orbital $1s(\alpha)$ & $1s(\beta)$, The first row of matrix become

$$1s\alpha(1) \quad 1s\beta(1)$$

In the second row of matrix we put the same orbital but assign them to the 2nd e^- since the 2nd e^- also could be in these orbital, thus the 2nd row for matrix become

$$1s\alpha(2) \quad 1s\beta(2)$$

$$\begin{vmatrix} 1s\alpha(1) & 1s\beta(1) \\ 1s\alpha(2) & 1s\beta(2) \end{vmatrix}$$

$$1s\alpha(1)1s\beta(2) - 1s\alpha(2)1s\beta(1)$$

All wave function generated by determinant will be anti-symmetric

We can see this because interchange of e^- in wave function produce same with -ve state, it may be equivalent (represented) by

the property of interchanging of rows in the matrix, if we change rows in the matrix then it means we are going to change e^- which change the sign of wave function.

$$\begin{vmatrix} \alpha(1) & \beta(1) \\ \alpha(2) & \beta(2) \end{vmatrix} \rightarrow \begin{vmatrix} \alpha(2) & \beta(2) \\ \alpha(1) & \beta(1) \end{vmatrix}$$

In the case of Lithium we construct a matrix with three lowest available spin orbitals $1s\alpha$, $1s\beta$, $2s\alpha$

Our first row will be

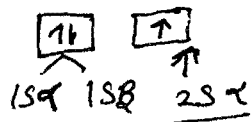
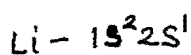
$$1s\alpha(1) \quad 1s\beta(1) \quad 2s\alpha(1)$$

& our 2nd & 3rd row will be, we put 2nd & 3rd e^- in same orbital

$$1s\alpha(2) \quad 1s\beta(2) \quad 2s\alpha(2)$$

$$1s\alpha(3) \quad 1s\beta(3) \quad 2s\beta(3)$$

$$\begin{vmatrix} 1s\alpha(1) & 1s\beta(1) & 2s\alpha(1) \\ 1s\alpha(2) & 1s\beta(2) & 2s\alpha(2) \\ 1s\alpha(3) & 1s\beta(3) & 2s\alpha(3) \end{vmatrix}$$



To ~~det~~ write the determinantal wave function for $n e^-$ atom

first of all we list out (n) orbitals $(\phi_1, \phi_2, \phi_3, \dots)$

e.g. in case of Be $1s^2 2s^2$ with $4e^-$ what spin orbital could we use?

$1s\alpha$ $1s\beta$ $2s\alpha$ $2s\beta$

The first row in all n orbital with e^- one in them

2nd

 2

This is continued until one row for each e^-

	$\phi_1(1)$	$\phi_2(1)$	\dots	$\phi_n(1)$
	\downarrow	\downarrow		
	$1s\alpha$	$1s\beta$		
$\phi_1(1)$	$\phi_2(1)$	$\phi_3(1)$	\dots	$\phi_n(1)$
$\phi_1(2)$	$\phi_2(2)$	$\phi_3(2)$	\dots	$\phi_n(2)$
\vdots	\vdots	\vdots	\vdots	\vdots
$\phi_1(n)$	$\phi_2(n)$	\dots	\dots	$\phi_n(n)$

Thus our Slater matrix for Be is

$1s\alpha(1)$	$1s\beta(1)$	$2s\alpha(1)$	$2s\beta(1)$
$1s\alpha(2)$	$1s\beta(2)$	$2s\alpha(2)$	$2s\beta(2)$
$1s\alpha(3)$	$1s\beta(3)$	$2s\alpha(3)$	$2s\beta(3)$
$1s\alpha(4)$	$1s\beta(4)$	$2s\alpha(4)$	$2s\beta(4)$

To get the antisymmetrized wave function we just solve the determinant.

The only step we have left is to normalize the wave function, it is easy

To normalize, for n e^- atom we multiply by $\frac{1}{\sqrt{n!}}$ to

the Slater determinant

$$He = \frac{1}{\sqrt{2!}}$$

$$Li = \frac{1}{\sqrt{3!}}$$

$$Be = \frac{1}{\sqrt{4!}}$$

DPP-18

$$(5) \quad S_z = \hbar \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$$(4) \quad (\hat{u}_i) \begin{vmatrix} \alpha(1) & \beta(1) \\ \alpha(2) & \beta(2) \end{vmatrix}$$

$$\alpha = \beta \quad (\text{if})$$

$$\begin{vmatrix} \alpha(1) & \alpha(1) \\ \alpha(2) & \alpha(2) \end{vmatrix} = 0$$

DPP 18

1. Consider the statement

- (i) For one spin system there are two spin state ,for two spin system there are four spin wavefunction. **T**
- (ii) $\alpha_1 \alpha_2$ and $\beta_1 \beta_2$ are symmetric wave function whereas $\alpha_1 \beta_2$ and $\beta_1 \alpha_2$ are antisymmetric in nature with respect to spin exchange operator. **F**
- (iii) In triplet state the function corresponding to $m_s = 0$ does not exist. **F**

The true statements above are (a) i,ii (b) i,iii (c) ii,iii (d) i,ii,iii (e) I only (f) ii only (g) iii only

2 Consider the statement

- (i) The spin operators satisfy the same general equations that we developed for the angular momentum operators. **T**
- (ii) The value of commutator $[S_z, S_+]$ is $-(\hbar/2\pi)S_+$. **F**
- (iii) normalization constant of an $N \times N$ Slater determinant of orthonormal spin orbitals is $1/(N!)^{0.5}$. **F**

The true statement above are (a) i,ii (b) i,iii (c) ii,iii (d) i,ii,iii (e) I only (f) ii only (g) iii only

3 Consider the statement

- (i) when we operate the operator S^2 on state $\alpha_1 \alpha_2$ then eigenvalue is 0. **F**
- (ii) The spin angular momentum operator is generally represented by pauli spin matrix. **T**
- (iii) For being total function antisymmetric if space part is symmetric then spin part may be symmetric may be ant symmetric. **F**

The true statement above are (a) i,ii (b) i,iii (c) ii,iii (d) i,ii,iii (e) I only (f) ii only (g) iii only

4 Consider the statement

- (i) only the magnitude of the spin angular momentum and one of its components can be known simultaneously. **F**
- (ii) Pauli exclusion principle requires that each orbital have a maximum occupancy of two electrons may be explained by Slater determinant. **T**
- (iii) The two electron with same spin in a state have zero probability. **T**

Correct statements above are (a) i,ii (b) i,iii (c) ii,iii (d) i,ii,iii (e) I only (f) ii only (g) iii only

5. In certain axis of quantization z component of spin angular momentum have the following representation

$S_z = \hbar \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$ what would be the trace of the matrix S_x^2 is **Sum of all diagonal element**

(a) $0 \hbar^2$ (b) $1 \hbar^2$ (c) $2 \hbar^2$ (d) none of the above

$\sigma_x^2 = \sigma_y^2 = \sigma_z^2$
 $S_x^2 = S_y^2 = S_z^2$

6. A random distribution of error obey the Gaussian form as $(A/\pi)^{0.5} e^{-Ax^2}$, The mean and standard deviation of this distribution obeys **gaussian**
- (a) $\langle x \rangle = 0$, $\sigma_x = 1/(A)^{0.5}$
 - (b) $\langle x \rangle \neq 0$, $\sigma_x = 1/(A)^{0.5}$
 - (c) $\langle x \rangle = 0$, $\sigma_x = (A)^{0.5}$
 - (d) $\langle x \rangle = 0$, $\sigma_x = (A)$

7. Fill in the blanks

- i) The wave function corresponding to helium atom including spin is
- ii) Normalisation constant corresponding to lithium atom in slater determinant is
- iii) The $N \times N$ slater determinant may be written as
- iv) percent ionic character may be obtained by parameter λ as $\frac{\lambda^2}{1+\lambda^2} = \gamma$ ionic
- v) In MOT the covalent term and ionic corresponding to two atom two electron system may be written as
- vi) The spin angular momentum operator in z direction in form of pauli matrix is $S_z = \frac{1}{2} \hbar \sigma_z$ [!]
- vii) When we operate S_z operator on α spin then corresponding eign value is

$S_z \alpha = \frac{1}{2} \hbar \alpha$
 $S_z \beta = -\frac{1}{2} \hbar \beta$

$S_z = m_s \hbar$

Q.8 - which of the following statement is incorrect

- (a) A Slater determinant is an antisymmetrized wave function T
- (b) Electronic wave function should be represented by Slater determinant. T
- (c) A Slater determinant always corresponds to a particular spin state F TWO
- (d) A Slater determinant obey the Pauli exclusion principle. T

Q.9 A Slater determinant corresponding to the ionic part of ground state valence bond wave function of H₂ molecule is [1S_aα, 1S_aβ, 1S_bα, 1S_bβ] are atomic spin orbitals of Hydrogen atom a and b of the hydrogen molecule)

CSIR DEC 2017

- (a) $\begin{vmatrix} 1S_a \alpha(1) & 1S_a \beta(1) \\ 1S_a \alpha(2) & 1S_a \beta(2) \end{vmatrix}$
- (b) $\begin{vmatrix} 1S_a \alpha(1) & 1S_b \beta(1) \\ 1S_a \alpha(2) & 1S_b \beta(2) \end{vmatrix}$
- (c) $\begin{vmatrix} 1S_a \alpha(1) & 1S_b \alpha(1) \\ 1S_a \alpha(2) & 1S_b \alpha(2) \end{vmatrix}$
- (d) $\begin{vmatrix} 1S_a \alpha(1) & 1S_b \beta(1) \\ 1S_a \alpha(1) & 1S_b \beta(2) \end{vmatrix}$

Q.10 The spatial part of the wave function of the atom in its ground state is 1S(1)1S(2) The spin part would be

CSIR JUNE-2017

- (a) α(1)α(2)
- (b) β(1)β(2)
- (c) $\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)]$
- (d) $\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$

Q.11 For H₂ molecule, the ground state wave function is $\Psi(1,2) = \phi(1,2) \sigma(1,2)$ where φ refers to the space part and σ refers to the spin part. Given that φ(1,2) = φ(2,1) the form σ(1,2) would be

CSIR JUNE-2011

- (a) α(1)β(2)
- (b) α(2)β(1)
- (c) $\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$
- (d) $\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)]$

Q.12 An excited state Triplet state wave function of Hydrogen molecule with the electronic configuration σ_g¹σ_u¹ has the following space part

CSIR DEC 2011

- (a) σ_g(1)σ_u(2)
- (b) σ_g(1)σ_u(2) + σ_u(1)σ_g(2)
- (c) σ_g(1)σ_g(2) + σ_u(1)σ_u(2)
- (d) σ_g(1)σ_g(2) - σ_u(1)σ_u(2)

Q.13 For H₂ molecule in the excited state σ_g¹σ_g¹ the spin part of the triplet state with m_s = 0 is proportional to

CSIR JUNE 2012

- (a) α(1)β(2)
- (b) α(1)β(2) - β(1)α(2)
- (c) α(1)α(2)
- (d) $\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)]$

Q.14 In the formation of H₂ molecule the 2s atoms placed at position A and B and separated by distance r_{AB}. A part of spatial wave function is

$\phi_A(1)\phi_A(2) + \phi_B(1)\phi_B(2)$
This is a (ionic/covalent) term and it is important as (r_{AB} → ∞)

Q.15 Write the Normalised Slater Determinant for beryllium in the 1s²2s² configuration. Do not expand the Determinant

Q.16 Write down the Slater Determinant for Slater Determinant

Q.17 For n e⁻ atom the Normalisation constant for Slater Determinant is $\frac{1}{\sqrt{n!}}$

Q.18 For two atom two e⁻ system the triplet state corresponding to spin part of wave function is $\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)]$

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DPP 17 Regular Batch

1. Consider the statements

(i) Overlapping S_{ab} can have value between zero and one. In order to have a chemical bond it is necessary that $S_{ab} > 0$. T(ii) The bonding orbital change sign on inversion in p_x and p_y orbital so it is ungerade, and antibonding orbital remain same on inversion so it is gerade. T

(iii) Bonding orbital show a build up a electron density in an internuclear region while antibonding orbital show a decrease of electron density in internuclear region. T

Correct statements above are (a) i, ii (b) ii, iii (c) i, ii, iii (d) none

2. Consider the statement

(i) In the case of bonding orbital of HF molecule $N(C_1\psi_1 + C_2\psi_2)$ $C_1 \ll C_2$ T

(ii) Photoelectron spectra generally support the existence of molecular orbital. T

(iii) For Heteroatomic molecule higher atomic orbital contribute more to antibonding MO and lower atomic orbital contribute to bonding. T

Correct statement above are (a) i, ii (b) ii, iii (c) i, ii, iii (d) none

3. Consider the statement

(i) Virial theorem apply to atom and molecule described by either by exact wavefunction or by approximate wavefunction. T

(ii) Orbitals are conserved and generally probability amplitude can be positive or negative. T(iii) Size and energy of any atomic orbital are generally determined by quantum number n , and both play a crucial role in determining the significant interaction between AO. T

Correct statement above are (a) i, ii (b) ii, iii (c) i, ii, iii (d) none

4. Consider the statements

(i) The sign of the wave function does not indicate anything about charge. T

(ii) In a 2p orbital, it is just as probable to find electron density in the negative lobe as it is to find electron density in the positive lobe. T

(iii) A molecular orbital cannot hold more than two electrons. T

Correct statements above are (a) i, ii (b) ii, iii (c) i, ii, iii (d) none

5. Consider the statements

(i) An antibonding molecular orbital (designated with an *) occurs when the electron density of the orbital is concentrated in regions of space outside the area between the atomic nuclei T

(ii) rotating sigma bond does not decrease the overlap of the orbitals involved T

(iii) pi bonds cannot rotate around the bond axis. T

The true statement above are (a) i, ii (b) ii, iii (c) i, ii, iii (d) none

6 Consider the statements

(i) For bonding MO $S_{ab} > 0$, for antibonding $S_{ab} < 0$. T(ii) Bonding and antibonding molecular orbital are orthogonal. T(iii) The magnetic quantum number in molecular orbital is denoted by λ , if $\lambda = 0$ the orbital symmetrical with respect to reference axis. T

Correct statements above are (a) i, ii (b) ii, iii (c) i, ii, iii (d) none

7 Normalize the molecular orbital ψ_+ in case of H_2^+ molecule if $S = 0.59$.

8 (I) Bonding molecular orbital leads to accumulation of electron density between the nuclei to minimize nucleus nucleus repulsion. (T/F) T

(II) Compared to H_2^+ the bond energy of H_2 is greater. T

To prove BMO & ABMO

orthogonal we take

minimum $\int \psi_+ \psi_-$ 

Nucleus - nucleus Repulsion



9. Consider the statements

(i) In VB theory, a bond forms when an electron in an atomic orbital on one atom pairs its spin with that of an electron in an atomic orbital on another atom. **T**

(ii) In MO theory the covalent and ionic term have equal weight. **T**

(iii) VBT asserts that electron pairs occupy directed orbitals delocalized on a particular atom. **T**

The true statements above are (a) i,ii (b) ii,iii (c) i,iii (d) all (e) none **immocudric**

10. Consider the statements

(i) According to the Pauli exclusion principle when electrons are exchanged Ψ must change sign $\Psi(1,2) = -\Psi(2,1)$. **T**

(ii) For the molecule to be stable $\Delta E_{total} < 0$, $\Delta E_{kinetic} < 0$, $\Delta E_{potential} < 0$. **F** *ve ab ho sakti*

(iii) Slater determinants are used to express wave functions of many electron systems, and by many electron we mean more than one electron. **T**

Correct statements above are (a) I,ii (b) ii,iii (c) I,iii (d) all (e) none

11. Consider the statements

(i) wavefunction describing many electron system must change sign under the exchange of any two electron. **T** *(anti-symmetric)*

(ii) The integral H_{11} represents the binding energy of the electron in the 1s state to nucleus 1. **T**

(iii) overlap of the orbitals becomes 0 when the atoms are separated by an infinite distance. **T**

The true statement above are (a) i,ii (b) ii,iii (c) i,iii (d) all (e) none

12. Consider the statement

(i) H_2 molecule, the two electrons reside in the $1\sigma_g$ molecular orbital and the configuration is $(1\sigma_g)^2$. **T**

(ii) A purely covalent structure with equal sharing of the bonding electron pair would result in a dipole moment of 0 for the molecule. **T**

(iii) for most heteronuclear diatomic molecules and write the wave function as $\psi_{molecule} = \psi_{covalent} + \lambda\psi_{ionic}$. **T**

The correct statements above are (a) i,ii (b) ii,iii (c) i,iii (d) all (e) none

13. For a molecule XY, $\psi_{molecule} = \psi_{covalent} + 0.50\psi_{ionic}$. Calculate the percent ionic character of the X-Y bond.

14. Consider the statement

(i) Ionic term dominates in molecular orbital method so we need correction in theory. **T**

(ii) If the electron in the HF molecule is described by $\psi = 0.34\Phi_{H(1s)} + 0.84\Phi_{F(2p_z)}$ then probability of finding the electron on H atom is 21%.

(iii) In the VB model the molecular wavefunction are generated from AO whereas in MO model the molecular wave function are generated from MO, which are linear combination of AO. **T**

Correct statement is (a) i,ii (b) ii,iii (c) i,iii (d) all (e) none

15. Consider the statement

(i) the energy of the MO that has form $\psi = C_1\psi_1 + C_2\psi_2$ in-phase atomic orbital is lower than that of lower lying orbital by ΔE_+ . **T** *-bonding*

(ii) The energy splitting $\Delta E_+ + \Delta E_-$ always increase with overlapping integral. **T**

(iii) The negative of α is generally considered the ionization energy. **T**

Correct statement is (a) i,ii (b) ii,iii (c) i,iii (d) all (e) none

16. Normalization constant for $[\Phi_a(1)\Phi_b(2) + \Phi_a(2)\Phi_b(1)]$ for a homonuclear diatomic molecule according to valence bond theory if $S=0.59$.

$$\frac{1}{\sqrt{2(1+S^2)}}$$

(6)

$$\phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1)$$

$$S = 0.59$$

$$N = \frac{1}{\sqrt{2(1+S^2)}} = \frac{1}{\sqrt{2(1+(0.59)^2)}}$$

(3) (ii)

$$(0.34)^2 + (0.84)^2 + 2 \times 0.34 \times 0.84 S = 1$$

$$S = ?$$

$$P_H = C_1^2 + C_1 C_2 S$$

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