**COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH
UNIVERSITY GRANTS COMMISSION**

CHEMICAL SCIENCES   CODE:01

2.1. Basic principles of Quantum Mechanics

At a Glance

de-Broglie Hypothesis, Heisenberg uncertainty principle, Photoelectric effect, what is wave function and development of Schrödinger equation, Postulates of quantum mechanics, Normalization, Orthogonality, Hermitian operator, Eigen function and Eigen value, PARTICLE IN A BOX, Simple Harmonic Oscillator (S.H.O), Virial Theorem, Hydrogen atom, Tunneling,

Key Statements

Basic Key Statements: de-Broglie Hypothesis (2.1.1), Heisenberg uncertainty principle (2.1.2), Photoelectric effect (2.1.4), The Schrödinger equation (2.1.6), Postulates of quantum mechanics (2.1.7), Probability (2.1.8), Linear operator (2.1.11), Eigen function and Eigen value (2.1.14), Average value (2.1.15), Three dimensional Simple Harmonic Oscillator (S.H.O) (2.1.24)

Standard Key Statements: Wave function (ψ) (2.1.5), Normalization (2.1.9), Orthogonality (2.1.10), Hermitian operator (2.1.12), Commutator algebra (2.1.13), Orthonormal condition (2.1.16), PARTICLE IN A BOX (2.1.17), Virial Theorem (2.1.25), Angular momentum (2.1.27), Tunneling (2.1.28)

Advance Key Statements: Particle in one dimensional box (2.1.18), Particle in a symmetrical one dimensional box (2.1.19), Particle in two dimensional box (2.1.20), Particle in three dimensional box (2.1.21), Hydrogen atom (2.1.26)

Key Facts

2.1.1.   de-Broglie Hypothesis:

According to de-Broglie for a sub-microscopic particle the dual nature is observed. One is particle nature another is wave nature.

Mathematical expression: $\lambda = \frac{h}{mv} = \frac{h}{p}$

$$\boxed{Wave\ nature} \propto \frac{1}{\boxed{Particle\ nature}}$$

Where, λ = de-Broglie wavelength

   h = Plank's constant

   m = mass of particle with velocity v.

   p = momentum of particle

2.1.2.   Heisenberg uncertainty principle:

According to this principle for a sub-microscopic particle the position and momentum cannot be calculated accurately simultaneously.

The mathematical form reveals with three different type

I. $\Delta x . \Delta p_x \geq \frac{h}{4\pi}$

II. $\Delta x . \Delta v_x \geq \frac{h}{4\pi m}$

III. $\Delta E . \Delta t \geq \frac{h}{4\pi}$

   Where, Δx is the measurement of uncertainty of position along X-axis, Δp_x is the measurement of uncertainty of momentum along X-axis, Δv_x is the measurement of uncertainty of velocity along X-axis, ΔE and Δt is the measurement of uncertainty of energy and time respectively.

2.1.3.   Other expressions for de-Broglie wavelength:

If the kinetic energy will be E_K, then momentum, $p = \sqrt{2mE_K}$ and wavelength, $\lambda = \frac{h}{\sqrt{2mE_K}}$.

If a q charge particle is allowed to pass through a potential difference V, then, wavelength, $\lambda = \frac{h}{\sqrt{2mqV}}$.

2.1.4. Photoelectric effect:

When a metal surface is been exposed by a high energy beam of light source, some phenomena is been found. When the frequency of light is sufficiently high, electrons are emitted from the metal surface.

The phenomena in which electrons are emitted from the metal surface when irradiated with Photon is called "Photoelectric effect".

The metals which exhibit this phenomenon are called "Photo-sensitive materials" and the emitted electrons are called "Photo-electrons".

Mathematical expression: $\frac{1}{2}mv_{max}^2 = h\nu - h\nu_0$

Where, ν and ν_0 is the frequency of the energy source and threshold frequency respectively.

2.1.5. Wave function(ψ):

The behavior of electrons, by now known to have wave like properties can be described by a mathematical expression called a wave function (ψ).

It contains within it all possible information that can be known about a system.

These are not arbitrary mathematical functions but must satisfy certain simple conditions such that:

i.   It must be single valued.

ii.   The first derivative must be continuous.

iii. It must be quadratically integrable. $\int |\psi|^2 d\tau$ is a finite number.

iv.   It must be finite in any region of space but zero at infinity.

ψ itself doesn't have any physical significance but $|\psi|^2$ measures the total probability of find out an electron in a particular space.

2.1.6. The Schrödinger equation:

This equation is a second order differential equation used to calculate the wave function of a system.

Mathematical expression:

In cartesian co-ordinate (3D):

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

Where, E and V are total and potential energy;

∇^2 is Laplacian operator $= \left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}\right)$

In polar co-ordinate:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{8\pi^2\mu}{h^2}\left(E + \frac{e^2}{r}\right)\psi = 0$$

2.1.7.   **Postulates of quantum mechanics**:
   A. Every state of a dynamical system can be described by a function ψ, known as wave function. The wave function is a function of coordinates and time and the quantity ψψ* (or ψ²) denote the probability density and ψ itself denotes **probability amplitude**.
   B. **Operator postulate:** For every physically measurable quantities office system there exist a corresponding linear Hermitian operator. The operator on the wave function gives the magnitude of the corresponding observable quantity of the system.
   C. ψ must be well behaved.
   D. Every physical property can be associated with a corresponding operator Â which is linear and Hermitian and the average value of the physical quantity can be calculated by

$$\langle a \rangle = \frac{\int \psi^* \hat{A} \psi \, dv}{\int \psi^* \psi \, dv}$$

   E. When state of system becomes time dependent the following wave function ψ can be found out by solving Schrödinger equation.

2.1.8.   **Probability:**
   Probability of finding a particle within a limit from lower limit to upper limit may be calculated as: $\boxed{\int_{LL}^{UL} \psi^* \psi \, d\tau}$ **NOTE:** ψ must be normalized.

2.1.9.   Normalization:

Any given function ψ_i is said to be normalized if $\int \psi_i^* \psi_i dv = 1$.

$\int \psi_i^* \psi_i dv \neq 1$ then, it is not normalized.

Say, $\int \psi_i^* \psi_i dv = n$

Then, $\frac{1}{n} \int \psi_i^* \psi_i dv = 1$

i.e., $\int \left(\psi_i^* + \frac{1}{\sqrt{n}}\right) \left(\psi_i + \frac{1}{\sqrt{n}}\right) dv = 1$

Here $\frac{1}{\sqrt{n}}$ is called normalization constant.

2.1.10.   Orthogonality:

Any two wave functions ψ_i and ψ_j corresponding to the energy value E_i and E_j respectively the following condition must be full filled:

$$\boxed{\int \psi_i \psi_j dv = 0}$$

such a condition is called condition of orthogonality of wave function; the two functions ψ_i and ψ_j are said to be orthogonal to each other.

2.1.11.   Linear operator:

Any operator $\hat{p}$ is said to be a linear operator if

$\hat{p} (\psi_i + \psi_j) = \hat{p}\, \psi_i + \hat{p}\, \psi_j$ or $\hat{p} (c\psi_i) = c\hat{p}\, \psi_i$ [c is constant].

Let, $\hat{p} = \frac{d}{dx}$ then it is a linear operator

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

2.1.12.   Hermitian operator:

Any operator $\hat{p}$ is said to be Hermitian if

$\int \psi_i^* (\hat{p}\psi_j) dv = \int (\hat{p}^* \psi_i^*) \psi_j dv$ [p* is the complex conjugate of p]

2.1.13.   Commutator algebra:

Two operators may commute or main not commute.

$\hat{P}$ is said to be comute with $\hat{Q}$ if $\hat{P}\hat{Q} = \hat{Q}\hat{P}$ i.e., $\hat{P}\hat{Q}\psi(x) = \hat{Q}\hat{P}\psi(x)$

And, denoted by $[\hat{P}, \hat{Q}] = 0$

Let us assume $\hat{P} = \dfrac{d}{dx}$ and $\hat{Q} = \dfrac{d}{dy}$ and $\psi = x^2 + y^2$

$$\hat{P}\hat{Q}\psi(x) = \frac{d}{dx}\frac{d}{dy}(x^2 + y^2) = \frac{d}{dx}(2y) = 0$$

$$\hat{Q}\hat{P}\psi(x) = \frac{d}{dy}\frac{d}{dx}(x^2 + y^2) = \frac{d}{dy}(2x) = 0$$

Therefore, $\hat{P}\hat{Q} = \hat{Q}\hat{P}$

Properties of comutators:

Using the computer we can establish the following properties.

- Antisymmetric: $[\hat{P}, \hat{Q}] = -[\hat{Q}, \hat{P}]$
- Linearity: $[\hat{P}, \hat{Q} + \hat{R} + \hat{S} + \cdots] = [\hat{P}, \hat{Q}] + [\hat{P}, \hat{R}] + [\hat{P}, \hat{S}] + \cdots$
- Hermitian conjugate of a commutator: $[\hat{P}, \hat{Q}]^{\dagger} = [\hat{Q}^{\dagger}, \hat{P}^{\dagger}]$
- Distributivity: $[\hat{P}, \hat{Q}\hat{R}] = [\hat{P}, \hat{Q}]\hat{R} + \hat{Q}[\hat{P}, \hat{R}]$
- Jacobi identity: $\left[\hat{P}, [\hat{Q}, \hat{R}]\right] + \left[\hat{Q}, [\hat{P}, \hat{R}]\right] + \left[\hat{R}[\hat{P}, \hat{Q}]\right] = 0$

2.1.14.   Eigen function and Eigen value:

Eigen function is the function when operated by an operator generates the same function multiplied by a constant. The constant is called eigen value. Eigen value of any operator is the value of the corresponding property.

Let $\hat{P} = \dfrac{d}{dx}$ and $\psi_i = \sin x$

So, $\hat{P}\psi_i = \dfrac{d}{dx}(\sin x) = \cos x$. So non eigen.

Let $\hat{P} = \dfrac{d^2}{dx^2}$ and $\psi_i = \sin x$

So, $\hat{P}\psi_i = \dfrac{d^2}{dx^2}(\sin x) = -\cos x$. So eigen.

2.1.15.   Average value:

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

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

2.1.16.   **Orthonormal condition:**
If two wave function ψ_m and ψ_n are such that
$\int \psi_m^* \psi_n d\tau = 0$
Then ψ_m and ψ_n are said to be Orthogonal.
$\int \psi_m^* \psi_n d\tau = 1$ (Normalized)
If the both the condition for orthogonal and normalization are achieved then it is said to be Orthonormal.

2.1.17.   **PARTICLE IN A BOX:**
Ongoing detailed explanation let a short look on the different types of particle in a box. It may be divided into three parts
- Particle in one dimensional box
- Particle in a two dimensional box
- Particle in a three dimensional box

2.1.18.   **Particle in one dimensional box:**
In this problem a particle of mass m is placed in a one dimensional box of length l. Particle is free to move. The box has infinite walls.
By the use of time independent one dimensional Schrödinger equation we have $\psi(x) = A \sin \frac{n\pi x}{l}$
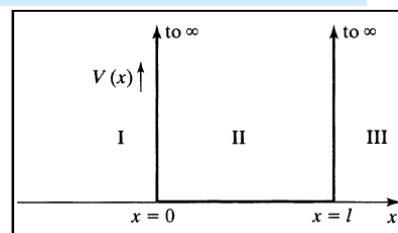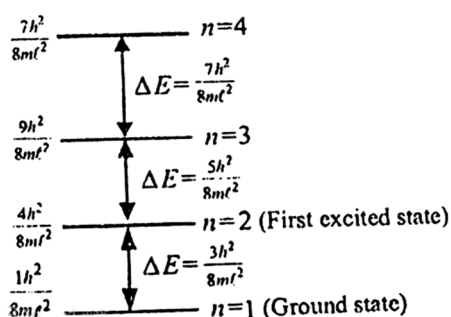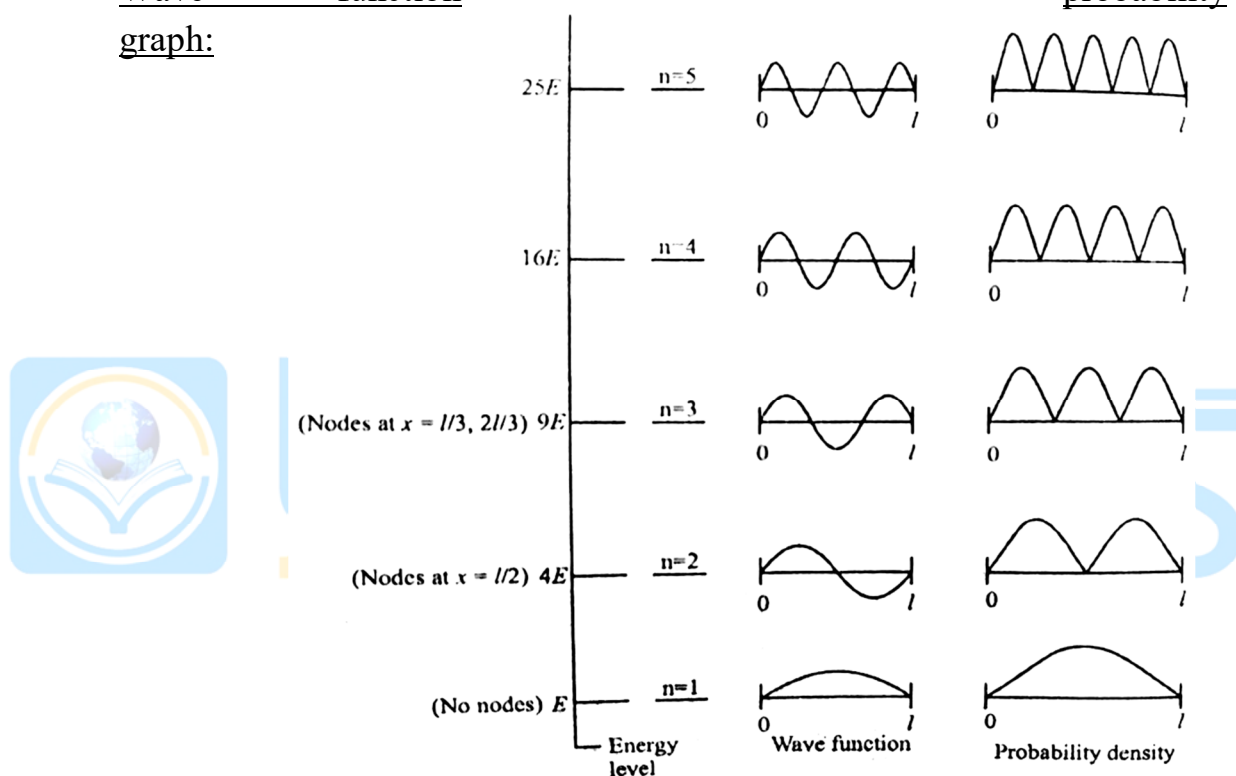
Applying Normalization, $\int \psi^* \psi dv = 1$, we have $A = \sqrt{\frac{2}{l}}$

So, $\boxed{\psi = \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l}}$ and energy, $E = \frac{n^2 h^2}{8ml^2}$

Therefore, $\Delta E = E_{n+1} - E_n = \frac{(2n+1)h^2}{8ml^2}$

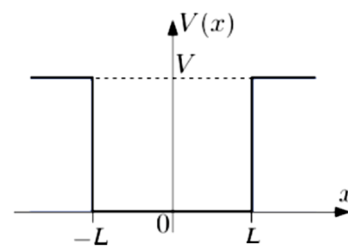Zero point energy, $E_0 = \frac{h^2}{8ml^2}$

Energy level Diagram:

$$\frac{7h^2}{8ml^2} \quad \overline{\quad\quad} \quad n=4$$

$$\Delta E = \frac{7h^2}{8ml^2}$$

$$\frac{9h^2}{8ml^2} \quad \overline{\quad\quad} \quad n=3$$

$$\Delta E = \frac{5h^2}{8ml^2}$$

$$\frac{4h^2}{8ml^2} \quad \overline{\quad\quad} \quad n=2 \text{ (First excited state)}$$

$$\Delta E = \frac{3h^2}{8ml^2}$$

$$\frac{1h^2}{8ml^2} \quad \overline{\quad\quad} \quad n=1 \text{ (Ground state)}$$

Wave function graph: probability

2.1.19. **Particle in a symmetrical one dimensional box:**

   V= 0 (Inside the box)
   V= ∞ (Outside the wall)

Applying boundary condition, we have, $\psi(x) = B\cos\left(\frac{n\pi x}{2l}\right)$; $[n = 1,3,5 \dots]$

$\psi(x) = A\sin\left(\frac{n\pi x}{2l}\right)$; $[n = 2,4,6 \dots]$

Applying normalization we have

$$\psi(x) = \frac{1}{\sqrt{l}} \sin\left(\frac{n\pi x}{2l}\right); [n = 2, 4, 6 \dots] \text{ and}$$

$$\psi(x) = \frac{1}{\sqrt{l}} \cos\left(\frac{n\pi x}{2l}\right); [n = 1, 3, 5 \dots].$$

Again energy, $\boxed{E = \frac{n^2 h^2}{32ml^2}}$.

2.1.20.   **Particle in two dimensional box:**

$V(x, y) = 0$; 0<x<l$_x$, 0<x<l$_y$.

$\quad\quad\quad = \infty$; otherwise.

From Schrodinger wave equation and normalization

$$X(x) = \sqrt{\frac{2}{l_x}} \sin \frac{n_x \pi x}{l_x}; \text{ and energy, } E_x = \frac{n_x^2 h^2}{8ml_x^2}$$

$$Y(y) = \sqrt{\frac{2}{l_y}} \sin \frac{n_y \pi y}{l_y}; \text{ and energy, } E_y = \frac{n_y^2 h^2}{8ml_y^2}.$$

So, $\psi = X(x) \times Y(y) = \frac{2}{\sqrt{l_x l_y}} \sin \frac{n_x \pi x}{l_x} \sin \frac{n_y \pi y}{l_y}$ and energy, $= \left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2}\right)\frac{h^2}{8m}$.

Zero point energy: $E_{11} = \frac{h^2}{4ml^2}$

Degeneracy:

Degeneracy in 2-D box

2.1.21.   **Particle in three dimensional box:**

From Schrodinger wave equation and normalization

$$X(x) = \sqrt{\frac{2}{l_x}} \sin \frac{n_x \pi x}{l_x}; \text{ and energy, } E_x = \frac{n_x^2 h^2}{8ml_x^2}$$

$$Y(y) = \sqrt{\frac{2}{l_y}} \sin \frac{n_y \pi x}{l_y}; \text{ and energy, } E_y = \frac{n_y^2 h^2}{8ml_y^2}$$
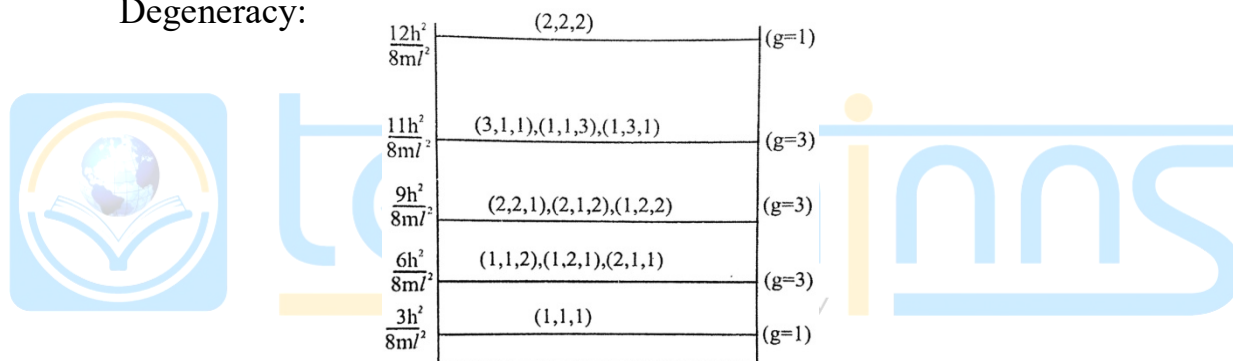
$$Z(z) = \sqrt{\frac{2}{l_z}} \sin \frac{n_z \pi z}{l_z}; \text{ and energy, } E_z = \frac{n_z^2 h^2}{8ml_z^2}$$

So, $\psi = X(x) \times Y(y) \times Z(zx) = \sqrt{\frac{8}{l_x l_y l_z}} \sin \frac{n_x \pi x}{l_x} \sin \frac{n_y \pi y}{l_y} \sin \frac{n_z \pi z}{l_z}$ and

energy, $= \left(\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2} + \frac{n_z^2}{l_z^2} \right) \frac{h^2}{8m}$.

Zero point energy: $E_{111} = \frac{3h^2}{8ml^2}$.

Degeneracy:

2.1.22.   **One dimensional Simple Harmonic Oscillator (S.H.O):**

The potential energy of a molecule is given by

$$V(x) = \frac{1}{2} k x^2$$

Therefore, oscillation frequency, $\nu = \frac{1}{2\pi} \left(\frac{k}{\mu} \right)^{1/2}$.

Using one dimensional Schrodinger wave equation the normalized function of S.H.O is $\psi_n(\xi) = \left[\frac{\beta^{1/2}}{2^n n! \sqrt{\pi}} \right]^{1/2} e^{-\xi^2/2} H_n(\xi)$, n= 0,1,2,3…

And, energy, $E_n = \left(n + \frac{1}{2} \right) h\nu$, n= 0, 1, 2, 3…

Therefore, zero point energy, $E_0 = \frac{1}{2} h\nu$.

This means at ground state no molecules are there in complete rest.

Graph of variation of wave function and probability density with states of energy:
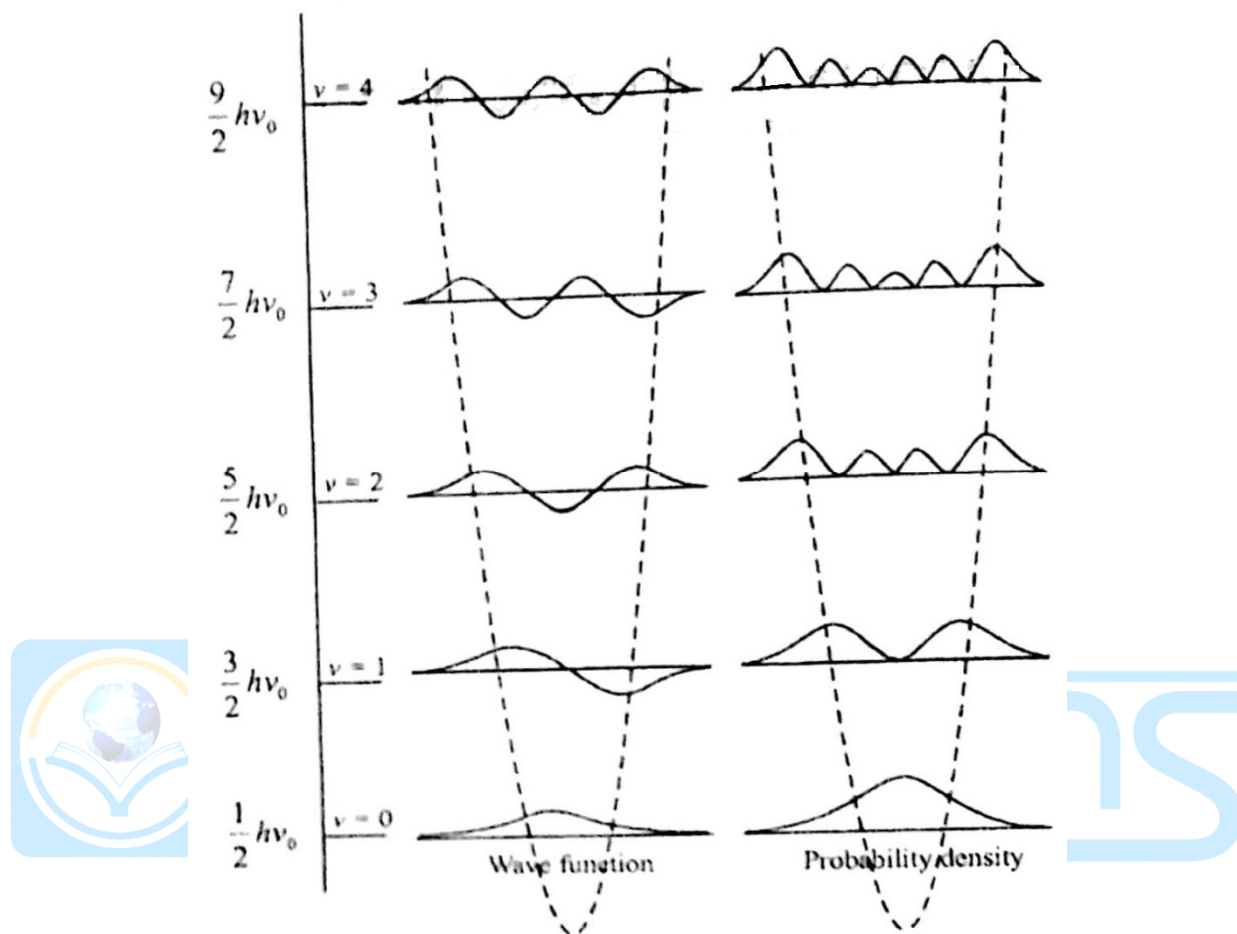
2.1.23. Two dimensional Simple Harmonic Oscillator (S.H.O):

Energy, $E_{total} = E_x + E_y = \left(n_x + \frac{1}{2}\right)hv + \left(n_y + \frac{1}{2}\right)hv$ i.e $(n_x + n_y + 1)hv$
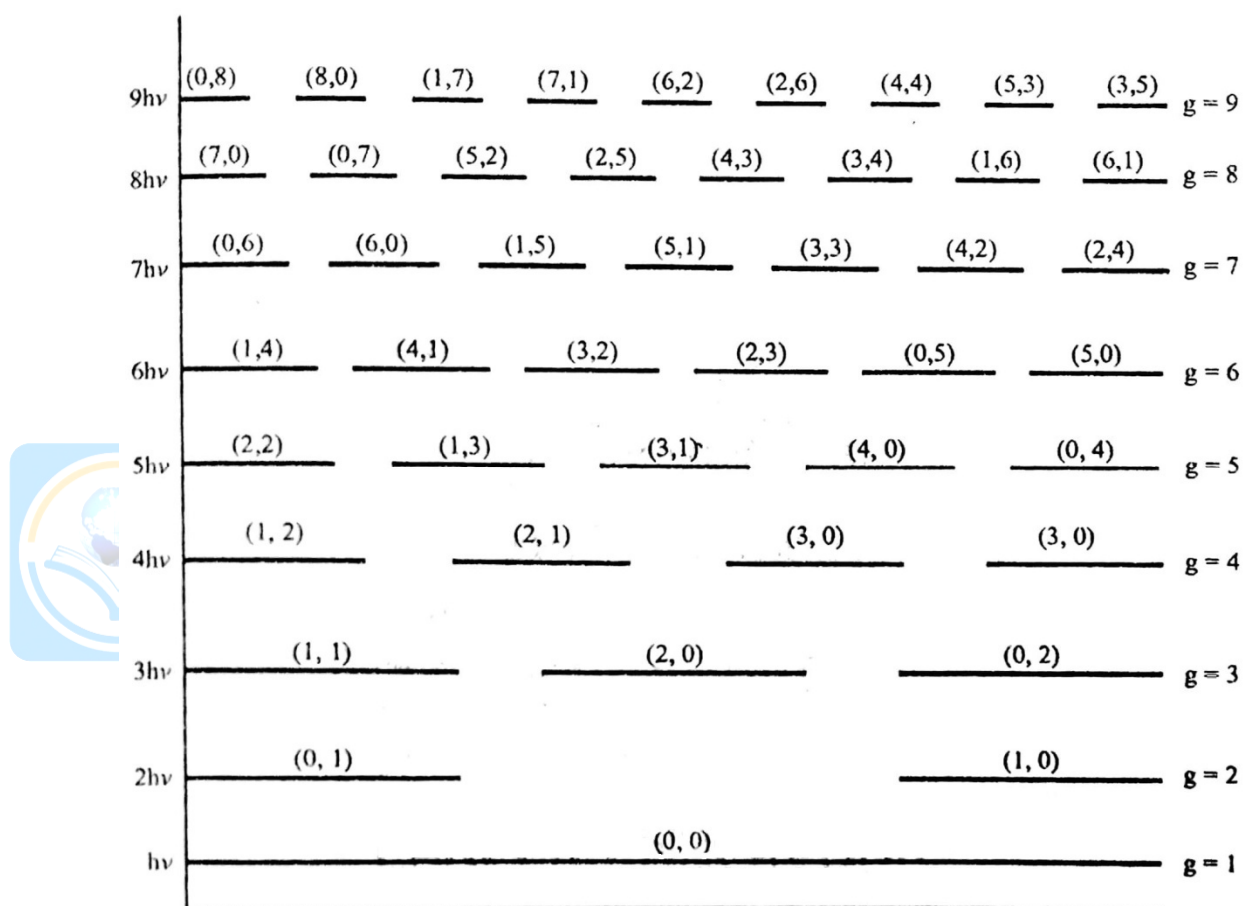
Degeneracy curve:

2.1.24. Three dimensional Simple Harmonic Oscillator (S.H.O):

Energy, $E_{total} = E_x + E_y + E_z = \left(n_x + \frac{1}{2}\right)hv + \left(n_y + \frac{1}{2}\right)hv + \left(n_z + \frac{1}{2}\right)hv$ i.e $(n_x + n_y + n_y + \frac{3}{2})hv$

Degeneracy curve:

2.1.25. Virial Theorem:

As per SHO we have $V \propto x^n$ i.e., $n = 2$

Now, $2\langle T \rangle = n\langle V \rangle = 2\langle V \rangle$

So, $\langle T \rangle = \langle V \rangle$ …………..(i)

i.e, $\frac{\langle T \rangle}{\langle V \rangle} = 1:1$

Now we have $\langle E \rangle = \langle V \rangle + \langle T \rangle$
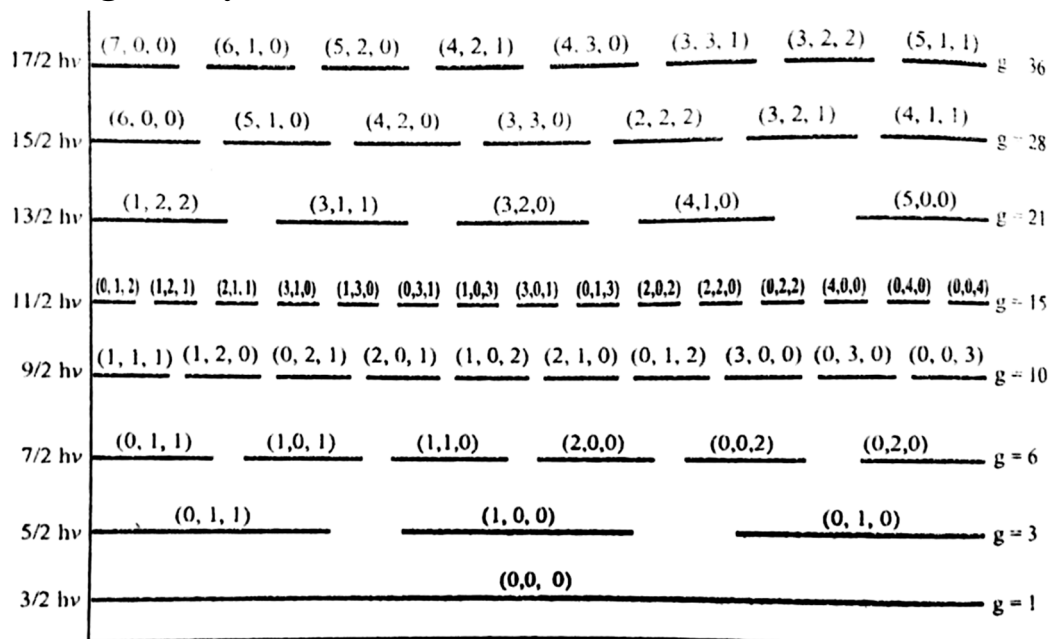
So, $\frac{\langle E \rangle}{\langle V \rangle} = \frac{\langle V \rangle + \langle T \rangle}{\langle V \rangle}$ …………(ii)

Comparing (i) and (ii) we have

$\frac{\langle E \rangle}{\langle V \rangle} = 2:1$

2.1.26. Hydrogen atom:

The electron and the proton in a hydrogen atom interact through a coulombic potential:

$$V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}$$

The Hamiltonian operator for a hydrogen atom is

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}$$

and the Schrodinger equation is

$$-\frac{\hbar^2}{2m_e}\nabla^2\psi(r,\theta,\phi) + V(r)\psi(r,\theta,\phi) = E\psi(r,\theta,\phi)$$

If we use the polar form we have

$$-\frac{\hbar^2}{2m_e}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right]$$
$$+ V(r)\psi(r,\theta,\phi) = E\psi(r,\theta,\phi)$$

i.e.,

$$-\hbar^2\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) - \hbar^2\left[\frac{1}{\sin\theta}\left(\frac{\partial}{\partial\theta}\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right] + 2m_e r^2[V(r) - $$
$$E]\psi(r,\theta,\phi) = 0 \text{ [multiplying both sides by } 2m_e r^2 \text{ and rearranged]}$$

The first part is θ and ϕ independent but the second one is dependent. That is why the first one known as radial and second one is angular part ad represented as

$$\psi(r,\theta,\phi) = R(r)Y_l^{m_l}(\theta,\phi)$$

Therefore the equation after splitting we get

$$-\frac{\hbar^2}{2m_e r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \left[\frac{\hbar^2 l(l+1)}{2m_e r^2}V(r) - E\right]R(r) = 0 \text{ [Radial part]}$$

Energy, $E_n = -\frac{m_e e^4}{8\varepsilon_0^2 h^2 n^2} = -\frac{m_e e^4}{32\pi^2\varepsilon_0^2\hbar^2 n^2}$, n= 1, 2, 3…

The radial *wave functions,* depend on two quantum numbers *n* and *l* and are given by

$$R_{nl}(r) = -\left\{\frac{(n-l-1)!}{2n[(n+1)!]^3}\right\}^{1/2}\left(\frac{2}{ma_0}\right)^{l+3/2}r^l e^{-r/na_0}L_{n+1}^{2l+1}\left(\frac{2r}{na_0}\right)$$

Where, L_{n+1}^{2l+1} are called associated Laguerre polynomials.
The first few Spherical Harmonics are

$Y_0^0 = \frac{1}{(4\pi)^{1/2}}$	$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$
$Y_1^1 = \left(\frac{3}{8\pi}\right)^{1/2}\sin\theta\, e^{i\phi}$	$Y_1^{-1} = \left(\frac{3}{8\pi}\right)^{1/2}\sin\theta\, e^{-i\phi}$
$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2}(\cos^2\theta - 1)$	$Y_2^1 = \left(\frac{15}{8\pi}\right)^{1/2}\sin\theta\cos\theta\, e^{i\phi}$
$Y_2^{-1} = \left(\frac{15}{8\pi}\right)^{1/2}\sin\theta\cos\theta\, e^{-i\phi}$	$Y_2^2 = \left(\frac{15}{32\pi}\right)^{1/2}\sin^2\theta\, e^{2i\phi}$

$$Y_2^{-2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta \, e^{-2i\phi}$$

The Hydrogen-like Radial Wave Functions, for n = 1, 2, and 3

$$R_{10}(r) = 2\left(\frac{Z}{a_0}\right)^{3/2} e^{-\rho}$$

$$R_{20}(r) = \left(\frac{Z}{2a_0}\right)^{3/2}(2-\rho)e^{-\rho/2}$$

$$R_{21}(r) = \frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{3/2}\rho e^{-\rho/2}$$

$$R_{30}(r) = \frac{2}{27}\left(\frac{Z}{3a_0}\right)^{3/2}(27-18\rho+2\rho^2)e^{-\rho/3}$$

$$R_{31}(r) = \frac{1}{27}\left(\frac{2Z}{3a_0}\right)^{3/2}\rho(6-\rho)e^{-\rho/3}$$

$$R_{32}(r) = \frac{4}{27\sqrt{10}}\left(\frac{Z}{3a_0}\right)^{3/2}\rho^2 e^{-\rho/3}$$

Where, $\rho = \frac{Zr}{a_0}$.

Now,

$$\psi_{nlm_l}(r,\theta,\phi) = R_{nl}(r)Y_l^{m_l}(\theta,\phi)$$

Therefore, first few hydrogen atomic wave functions are

$$\psi_{100} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}e^{-\rho}$$

$$\psi_{200} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}(2-\rho)e^{-\rho/2}$$

$$\psi_{210} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\rho e^{-\rho/2}\cos\theta$$

$$\psi_{21\pm1} = \pm\frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\rho e^{-\rho/2}\sin\theta \, e^{\pm i\phi}$$

$$\psi_{300} = \frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{3/2}(27-18\rho+2\rho^2)e^{-\rho/3}$$

$$\psi_{310} = \frac{2}{81\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \rho(6-\rho)e^{-\rho/3}\cos\theta$$

$$\psi_{31\pm1} = \pm\frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \rho(6-\rho)e^{-\rho/3}\sin\theta\, e^{\pm i\phi}$$

$$\psi_{320} = \frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \rho^2 e^{-\rho/3}(3\cos^2\theta - 1)$$

$$\psi_{32\pm1} = \pm\frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \rho^2 e^{-\rho/3}\sin\theta\cos\theta\, e^{\pm i\phi}$$

$$\psi_{32\pm2} = \pm\frac{1}{162\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} \rho^2 e^{-\rho/3}\sin^2\theta\, e^{\pm 2i\phi}$$

Where, $\rho = \frac{Zr}{a_0}$.

2.1.27. **Angular momentum:**

The classical definition of angular momentum $\vec{L} = \vec{r} \times \vec{p}$ depends upon six parameters r_x, r_y, r_z, p_x, p_y, p_z.

- Position Vector:
  $[x, y] = 0$; $[y, z] = 0$; $[x, x] = 0$
- Linear momentum:
- $[p_x, p_y] = 0$; $[p_x, p_x^2] = 0$; $[x, p_x] \neq 0$; $[x, p_y] = 0$; $[x^2, p_y] = 0$
  $[p_x, x^2] \neq 0$; $[x, p_x] = i\hbar$.
- Angular momentum:
  Therefore, $\vec{L} = L_x\hat{\imath} + L_y\hat{\jmath} + L_z\hat{k}$
  $\vec{r} = x\hat{\imath} + y\hat{\jmath} + z\hat{k}$
  $\vec{p} = p_x\hat{\imath} + p_y\hat{\jmath} + p_z\hat{k}$
  So, $\vec{L} = \begin{vmatrix} \hat{\imath} & \hat{\jmath} & \hat{k} \\ x & y & z \\ p_x & p_y & p_z \end{vmatrix} = \hat{\imath}(yp_z - zp_y) + \hat{\jmath}(zp_x - xp_z) + \hat{k}(xp_y - yp_x)$
  $$= L_x\hat{\imath} + L_y\hat{\jmath} + L_z\hat{k}$$
  $L_x = -i\hbar\left(y\frac{\partial}{\partial z} - z\frac{\partial}{\partial y}\right)$; $L_y = -i\hbar\left(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z}\right)$; $L_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$
  So, $[L_x, L_y] = i\hbar L_z$; $[L_x, y] = i\hbar z$; $[L_x, x] = 0$;
  Again two ladder operator, $L_+ = L_x + iL_y$; $L_- = L_x - iL_y$
  So, $[L_z, L_+] = [L_z, L_x + iL_y] = \hbar L_+$

Similarly, $[L_z, L_-] = [L_z, L_x - iL_y] = -\hbar L_-$

And $[L_+, L_-] = [(L_x + iL_y), (L_x - iL_y)] = 2\hbar L_z$

- Spin matrices:

  They also can be represented as per their component like, S_x, S_y, S_z.

  $[S_x, S_y] = i\hbar S_z; [S_y, S_z] = i\hbar S_x; [S_z, S_x] = i\hbar S_y$.

  Now we define a new operator, $\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2$.

  So, $[\hat{S}^2, S_x] = [\hat{S}^2, S_y] = [\hat{S}^2, S_z] = 0$

  Now we define two new operator, S_+ and S_- as raising and lowering operator respectively, where,

  $S_+ = S_x + iS_y$ and $S_- = S_x - iS_y$.

  Therefore, $(S_+ . S_-) = \hat{S}^2 - \hat{S}_z^2 + \hbar S_z$.

  Similarly, $(S_- . S_+) = \hat{S}^2 - \hat{S}_z^2 - \hbar S_z$

  Now, $[S_+, S_z] = -\hbar S_+$

2.1.28. Tunneling:
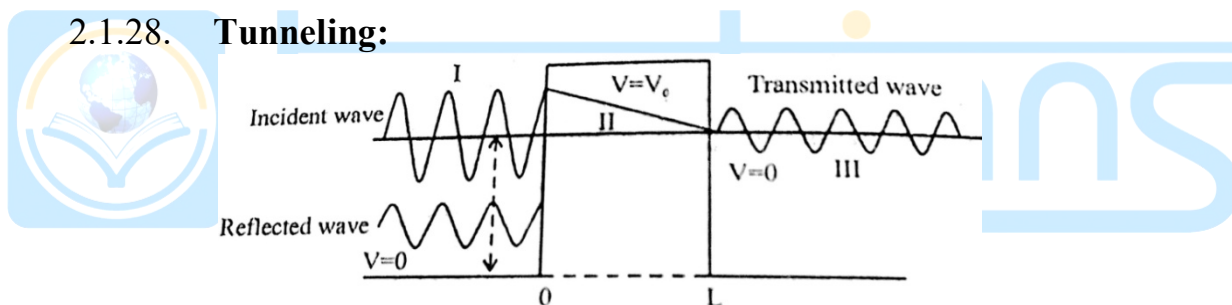
Barrier: V=0; for x<0: Region I

    = V_0; for 0<x<L: Region II

    = 0; for x>L: Region III

Now, for the first region we have the possible solution as,

$$\psi_I = Ae^{ik_1 x} + Be^{-ik_1 x}$$

Or, $\psi_I = Ae^{ip_1 x/\hbar} + Be^{-ip_1 x/\hbar} \left[where, p_1 = \sqrt{2mE}, k_1 = \frac{p_1}{\hbar} \right]$

For second region we have,

$$\psi_{II} = Ce^{ik_2 x} + De^{-ik_2 x}$$

Or, $\psi_{II} = Ce^{ip_2 x/\hbar} + De^{-ip_2 x/\hbar} \left[where, p_2 = \sqrt{2m(V_0 - E)}, k_2 = \frac{p_2}{\hbar} \right]$

For, third region we have,

$$\psi_{III} = Ee^{ik_3 x} + Fe^{-ik_3 x}$$

Or, $\psi_{III} = Ee^{ip_3 x/\hbar} + Fe^{-ip_3 x/\hbar}$

$$\psi_{III} = E e^{ip_3 x/\hbar} \qquad [\text{Because, } F e^{-ip_3 x/\hbar} = 0]$$

Where, $p_1 = \sqrt{2mE}, k_3 = \dfrac{p_3}{\hbar}$

Now reflectance, $R = \dfrac{|B|^2}{|A|^2}$ and transmittance, $T = \dfrac{|E|^2}{|A|^2}$.

The value of T can be evaluated as

$$T = \frac{4E(V_0 - E)}{4E(V_0 - E) + V_0^2 \sinh^2\left(\sqrt{\dfrac{2m(V_0-E)L^2}{\hbar^2}}\right)}$$

Previous Year Questions Analysis

NET JUNE 2014

Q. The spatial part of the wave function of the atom in its ground state is $1s(1)1s(2)$. The spin part would be—

(a) $\alpha(1)\alpha(2)$

(b) $\beta(1)\beta(2)$

(c) $\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$

(d) $\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$

Ans. The four normalized two electrons spin eigen functions with correct exchange properties are—

$$\alpha(1)\alpha(2)$$

Symmetric: $\beta(1)\beta(2)$

$$\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$

Antisymmetric: $\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$

Thus, $\psi^0 = 1s(1)1s(2).\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$

So, spin part $= \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$

Spatial part $= 1s(1)1s(2)$ [as $\psi^{total} = \psi^{spin} \times \psi^{spatial}$]

Correct option is (d).

Q. A particle in a one-dimensional box (potential zero between 0 to a and infinite outside) has the ground state energy $E_0 = \dfrac{0 \cdot 125 h^2}{ma^2}$. 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 functions $x(x-a)$ and $x^2(x-a)^2$, we obtain variational minimum to the ground state energy as E_2. Which of the following relations holds for E_0, E_1 and E_2 ?

(A) $E_0 < E_1 < E_2$

(B) $E_0 < E_2 < E_1$

(C) $E_1 < E_0 < E_2$

(D) $E_2 < E_0 < E_1$

Ans.

$$E_0 = \frac{0 \cdot 125 h^2}{ma^2}$$

$$\psi(x) = x(x-a), E_1$$

linear combination of $x(x-a)$ and $x^2(x-a)^2$, E_2

Variational principle tells that ground state energy is always less than other higher level energies.

So, $E_0 < (E_1, E_2)$

Now, E_2 is obtained from even functions (two), it have high value than E1

Thus, $\boxed{E_0 < E_1 < E_2}$

Correct option is (b).

Q. The ground state energy of hydrogen atom is $-13 \cdot 598$ eV. The expectation values of kinetic energy, $\langle T \rangle$ and potential energy, $\langle V \rangle$, in units of eV, are—

(a) $\langle T \rangle = 13 \cdot 598$, $\langle V \rangle = -27 \cdot 196$

(b) $\langle T \rangle = -27 \cdot 196$, $\langle V \rangle = 13 \cdot 598$

(c) $\langle T \rangle = -6 \cdot 799$, $\langle V \rangle = -6 \cdot 799$

(d) $\langle T \rangle = 6 \cdot 799$, $\langle V \rangle = -20 \cdot 397$

Ans. We know that for H-atom, energy, K.E. and P.E. holds following relation

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

Given that $\langle E \rangle = -13 \cdot 598$

$\because \langle T \rangle = -\langle E \rangle$

$\therefore \langle T \rangle = 13 \cdot 598$

and $\langle V \rangle = 2\langle E \rangle$

$= 2 \times (-13 \cdot 598)$

$\boxed{\langle V \rangle = -27 \cdot 196}$

Correct option is (a).

Q. If $\psi = 0{\cdot}8\ \phi\ A + 0{\cdot}4\ \phi B$ is a normalized molecular orbital of a diatomic molecule AB, constructed from ϕA and ϕB which are also normalized, the overlap between ϕA and ϕB is—

(a) 0·11   (b) 0·31   (c) 0·51   (d) 0·71

Ans. $\psi\ =\ 0\cdot 8\ \phi A\ +\ 0\cdot 4\ \phi B$ – normalized M.O.

ϕA and ϕB are also normalized.

An overlap integral is a direct measure of the extent of the overlap of the orbitals centered on two different nuclei. We know that,

$$\psi\ =\ a\phi_A\ +\ b\phi_B$$

$$a\ =\ 0\cdot 8, b\ =\ 0\cdot 4$$

Thus, overlap integral,

$$S_{AB}\ =\ \int a\phi_A\,.\,b\phi_B\ dt$$

$$=\ ab\ =\ 0\cdot 8\ \times\ 0\cdot 4$$

$$=\ 0\cdot 32$$

Correct option is (b).

NET DEC 2014

Q. For a particle of mass m confined in a box of length L, assume $\Delta x = L$. Assume further that Δp (min) $= (p^2)^{1/2}$. Use the uncertainty principle to obtain an estimate of the energy of the particle. The value will be—

(a) $\dfrac{h^2}{(8mL^2)}$ (b) $\dfrac{\hbar^2}{(8mL^2)}$ (c) $\dfrac{h^2}{(32mL^2)}$ (d) $\dfrac{h^2}{(2mL^2)}$

Ans. We know, $\Delta x . \Delta p = \dfrac{\hbar}{2}$ i.e., $.\Delta p = \dfrac{\hbar}{2L}$

Energy of the particle $= \dfrac{(\Delta p)^2}{2m} = \left(\dfrac{\hbar}{2L}\right)^2 \dfrac{1}{2m} = \dfrac{\hbar^2}{(8mL^2)}$

Correct option is (b).

Q. The angular momentum operator $L_z = -i\hbar\dfrac{\partial}{\partial\phi}$ has eigenfunctions of the form $\exp[iA\phi]$. The condition that a full rotation leaves such an eigen fuction unchanged is satisfied for all the values of A—

(a) $0, \pm\dfrac{1}{3}, \pm\dfrac{2}{3}, \pm 1, \pm\dfrac{4}{3}, \ldots$ (b) $0, \pm 1, \pm 2, \pm 3, \ldots$

(c) $0, \pm\dfrac{1}{2}, \pm 1, \pm\dfrac{3}{2}, \ldots$ (d) $0, \dfrac{1}{2}, \dfrac{3}{2}, \dfrac{5}{2}, \ldots$

Ans.

$$L_z = -i\hbar\frac{\partial}{\partial\phi}$$

The eigen function equation is

$$L_z Y_l^m = -i\hbar\frac{\partial}{\partial\phi}Y_l^m$$

$$Y_l^m = f_{(0)}e^{iA\phi}$$

f is arbitrary function ϕ must be periodic for Y is to be unchanged with period 2π. Thus, value of A should be A $= 0, \pm 1, \pm 2, \ldots$

Correct option is (b).

Q. Wavelength (λ in nm) of the Lyman series for an one-electron ion is in the range $24 \leq \lambda \leq 30$. The ionization energy of the ion will be closest to ($1J = \frac{10^{19}}{1.6} eV$) —

(a) 32 eV   (b) 42 eV   (c) 52 eV   (d) 62 eV

Ans. I.E. $= \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8 \times 10^{19}}{24 \times 10^{-9} \times 1.6} = 52 \ eV$

Ionization energy is the energy required to remove an electron from outermost orbital of gaseous system.

Correct option is (c).

Q. The probability of finding the harmonic oscillator in the energy level $n = 1$ is (neglect zero point energy and assume $h\nu = k_B T$).

(A) e (B) e^2 (C) $1 - e^{-2}$ (D) $e^{-2}(e-1)$

Ans. $E_n = \left(n + \frac{1}{2}\right) h\nu$

Probability, $P_{(E)} = \dfrac{e^{-E/k_B T}}{\sum_i e^{-E/k_B T}}$

$$= \frac{e^{-3/2}}{e^{-1/2} + e^{-3/2}} = \frac{e^{-1}}{1 + e^{-1}}$$

$$= \frac{e^{-1}.e}{e+1} \times \frac{(e-1)}{(e-1)} = \frac{e-1}{e^2 - 1}$$

Assuming, $e^2 \gg 1$

$$= \frac{e-1}{e^2}$$

Therefore, $P_{(E)} = e^{-2}(e-1)$

Correct option is (d).

Q. A particle in a 1-dimentional box of length L is perturbed by a delta function potential, $\delta(x-\frac{L}{2})$, 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   (c) $\frac{L}{2}$ (d) $\frac{2}{L}$

Ans.

First order energy correction is—

$$E_n^{(1)} = \left\langle \psi_n^{(0)} \left| \bar{H} \right| \psi_n^{(0)*} \right\rangle$$

$$\psi_n^{(0)} = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$$

Thus, $E_n^{(1)} = \frac{2}{L}\int_{-L}^{L} \sin^2\left(\frac{n\pi x}{L}\right)\delta(x-\frac{L}{2})dx$

Now, for ground state, n =1

$$E_n^{(1)} = \frac{2}{L}\int_{-L}^{L} \sin^2\left(\frac{\pi x}{L}\right)\delta(x-\frac{L}{2})dx$$

$\because \int_{+\infty}^{-\infty} \delta(x-a)dx = 1$

Thus, $\boxed{E_n^{(1)} = \frac{2}{L}}$

Correct option is (d).

Q. The operators S± are defined by $S_{\pm} = S_x \pm iS_y$, where S_x and S_y are components of the spin angular momentum operator. The commutator $[S_z, S_+]$ is—

(A) $\hbar S_+$ (B) $\hbar S_-$ (C) $-\hbar S_+$ (D) $-\hbar S_-$

Ans. $[S_z, S_+] = [S_z, S_x] + i[S_z, S_y]$

$$= i\hbar S_y + i(-i\hbar S_x) = \hbar(S_x + iS_y) = \hbar S_{\pm}.$$ **Correct option is (a).**

Q. The character table of C_{2v} point group is given below. In *cis*-butadiene molecule the vibrational modes belonging to A_2 irreducible representation are IR inactive. The remaining IR active modes are—

C_{2v}	E	C_2	σ_v	σ_v'	
A_1	1	1	1	1	z, x^2, y^2, z
A_2	1	1	-1	-1	R_z, xy
B_1	1	-1	1	-1	x, R_y, xz
B_2	1	-1	1	-1	y, R_x, yz

(a) $7A_1 + 5B_1 + 8B_2$ (b) $9A_1 + 4B_1 + 7B_2$

(c) $7A_1 + 3B_1 + 7B_2$ (d) $9A_1 + 3B_1 + 8B_2$

Ans.

1

	E	C_2	σ_v	σ_v'
no. of unshifted atoms	10	0	0	10
Character per atom	3	-1	1	1
	30	0	0	10

order of group, $h = 4$
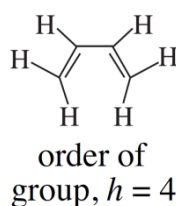
$A_1 = 10$, $A_2 = 5$, $B_1 = 5$, $B_2 = 10$ $l_{\text{trans}} = B_1 + B_2 + A_1$, $l_{\text{rot}} = B_2 + B_1 + A_2$

Thus, IR active model $= 9A_1 + 3B_1 + 8B_2$

Correct option is (d).

Q. The product $\sigma_{xy}.S_z^4$ (S_z^4 is the four fold improper axis of rotation around the z axis, and σ_{xy} is the reflection in the xy plane) is—

(a) C_z^4 (b) $C_z^4.i$ (c) C_y^4 (d) C_z^2

Ans. $\sigma_{xy}.S_z^4 = C_z^4$ (Rotational axis)

Correct option is (a).

Q. The configuration [Ne] $2p^1\ 3p^1$ has a ^3D term. Its levels are—

(a) $^3D_{3/2}, ^3D_{1/2}$

(b) $^3D_{5/2}, ^3D_{3/2}, ^3D_{1/2}$

(c) $^3D_3, ^3D_2, ^3D_1$

(d) $^3D_3, ^3D_2, ^3D_1, ^3D_0$

Ans. [Ne] $2p^1\ 3p^1$, Term $= {}^3D$, S $= n/2 = 1$, L $= 2$(D) J $= (L - S)$ to $(L + S) = 1, 2,$ 3, Thus, $^3D_3, ^3D_2, ^3D_1,$

Correct option is (c).

Q. For some one-electron system with $l = 0$ and $m = 0$, the functions $N_0 e^{-\sigma}$ and $N_1(2 - \sigma)e^{-\sigma/2}$ refer respectively to the ground (E_0) and first excited (E_1) energy levels. If a variational wave function $N_2(3 - \sigma)e^{-\sigma}$ yields and average energy $\bar{E}$, it will satisfy—

(a) $\bar{E} \geq 0$ (b) $0 \leq \bar{E} \leq E_0$ (c) $\bar{E} \geq E_1$ (d) $E_0 \leq \bar{E} \leq E_1$

Ans. Ground state wave function: $N_0 e^{-\sigma}$

First excited wave function: $N_1(2 - \sigma)e^{-\sigma/2}$

Correct option is (c).

Q. The number of microstates that are possible, when two particles are distributed in four states such that the resulting wave functions are antisymmetric with respect to exchange of the particles, is—

(a) 16 (b) 12 (c) 8 (d) 6

Ans. No. of microstates $= \dfrac{4!}{2!(4-2)!} = 6$

Correct option is (d).

Q. A Slater determinant corresponding to the ionic part of the ground state valence bond wave function of H2 molecule is ($1s_a\alpha$, $1s_a\beta$, $1s_b\alpha$, $1s_b\beta$ are atomic spin orbitals of hydrogen atoms a and b of the hydrogen molecule)

(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) $\begin{vmatrix} 1s_a\alpha(1) & 1s_b\beta(1) \\ 1s_a\alpha(1) & 1s_b\beta(2) \end{vmatrix}$

Ans. $\begin{vmatrix} 1s_a\alpha(1) & 1s_a\beta(1) \\ 1s_a\alpha(2) & 1s_a\beta(2) \end{vmatrix} = 1s_a\alpha(1)1s_a\beta(2) - 1s_a\beta(1)1s_a\alpha(2)$

α and β are spin up and down

According to Pauli's principle, 2 electrons in 'a' atomic orbital with spin up and down.

Correct option (a).

Q. According to Huckel theory, the π electron charge on the central carbon atom in propenyl cation $(CH_2CHCH_2)^+$ is (in units of electronic charge).

(a) $\frac{1}{2}$ (b) $\frac{1}{\sqrt{2}}$ (c) 1   (d) 2

Ans. Wave function for central carbon in propenyl cation

$$\psi_2 = \frac{1}{\sqrt{2}}\phi_1 - \frac{1}{\sqrt{2}}\phi_3$$
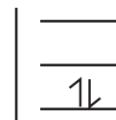
π electron charge,

$$q_r = \sum \eta_i C_{ir}^2$$

$$q_2 = 2 \times \left(\frac{1}{\sqrt{2}}\right)^2 + 0 + 0 = 1$$

Correct option is (c).

NET JUNE 2015

Q. 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—

(a) the total energy becomes zero

(b) the average momentum becomes zero

(c) the wave function becomes zero everywhere

(d) the potential $V_0 \neq 0$

Ans. As we know, $\Psi = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right)$ [n$\neq$0]

then $\Psi = 0$ (*i.e.*, wavefunction become zero) and it is not possible. In I-D box for ground state $n = 1$. $n = 0$ exists only for Simple Harmonic Oscillator.

Correct option is (c).

Q. An eigenstate of energy satisfies $H\Psi_n = E_n \Psi_n$. In the presence of an extra constant potential V_0—

(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 change, but not Ψ_n

(d) only Ψ_n will change, but not E_n

Ans. When we add potential in the Hamaltonian the energy eigen value will shift but the eigen function will not change.

Correct option is (c).

Q. The product $C_2^x . \sigma_{xy}$ (C_2^x is the two-fold rotation axis around the x-axis and σ_{xy} is the xy mirror plane) is—

(a) σ_{xz} (b) σ_{yz} (c) C_2^y (d) C_2^z

Ans. $\begin{vmatrix} x \\ y \\ z \end{vmatrix} \xrightarrow{\sigma_{xy}} \begin{vmatrix} x \\ -y \\ z \end{vmatrix}$; $C_2^x . \sigma_{xy} = \begin{vmatrix} x \\ y \\ z \end{vmatrix} \xrightarrow{C_2^x} \begin{vmatrix} x \\ -y \\ -z \end{vmatrix} \xrightarrow{\sigma_{xy}} \begin{vmatrix} x \\ -y \\ z \end{vmatrix}$; **Correct option is (a).**

Q. The simplest ground-state VB wave function of a diatomic molecule like HCl is written as $\Psi = \Psi_H (1s, 1) \Psi_{Cl} (3p_z, 2) + B$ where B stands for—

(a) $\Psi_H (3p_z, 2) \Psi_{Cl} (1s, 1)$ (b) $\Psi_H (1s, 2) \Psi_{Cl} (3p_z, 1)$

(c) $\Psi_{Cl} (1s, 2) \Psi_{Cl} (3p_z, 1)$ (d) $\Psi_{Cl} (1s, 2) \Psi_H (3p_z, 1)$

Ans. HCl is a covalent molecule. Thus, both the electrons cannot reside only in Cl atom. Thus, option (C) is wrong. In option (A) and (D) for H-atom, 3p orbital is not present (H → 1s; Cl = $3s^2 3p^5$).

Correct option is (b).

Q. A molecular orbital of a diatomic molecule changes sign when it is rotated by 180° around the molecular axis. This orbital is—

(a) σ (b) π (c) δ (d) ϕ

Ans. In diatomic molecule only σ and π-bond is possible

σ (gerade) spherical $\xrightarrow{180°}$ No change occur.

π (ungerade) $\xrightarrow{180°}$ change in sign occur.

Correct option is (b).

Q. IR active normal modes of methane belong to the irreducible representation—

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	
A_1	1	1	1	1	1	$x^2 + y^2 + z^2$
A_2	1	1	1	-1	-1	
E	2	-1	2	0	0	$2z^2 - x^2 - y^2$, $x^2 - y^2$
T_1	3	0	-1	1	-1	R_x, R_y, R_z
T_2	3	0	-1	-1	1	x, y, z, xy, yz, zx
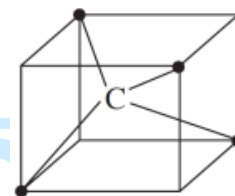
(a) $E + A_1$ (B) $E + A_2$ (C) T_1 (D) T_2

Ans.

$h = 24$	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
No. of unshifted atom	5	2	1	1	3
Contribution per atom	3	0	-1	-1	1
Reducible representation	15	0	-1	-1	3

$n A_1 = 1$, $n A_2 = 0$, $n E = 1$, $n T_1 = 1$, $n T_2 = 3$.

So reducible representation: $A_1 + E + T_1 + 3T_2$

Translational: T_2

Rotational: T_1

Vibrational: $A_1 + E + 2T_2$

Since IR activity is count by x, y, z coordinate so T_2 mode is IR active by using character table.

Correct option is (d).

Q. Which of the following statements is INCORRECT?

(a) A Slater determinant is an antisymmetrized wavefunction

(b) Electronic wavefunction should be represented by Slater determinants

(c) A Slater determinant always corresponds to a particular spin state

(d) A Slater determinant obeys the Pauli Exclusion Principle

Ans. A slater determinent always corresponds to a particular spin state. Slater determinate changes by changing sign upon exchange of 2 electrons.

Correct option is (c).

Q. 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 and Δ_3 for the three cases is—

(a) $\Delta_1 > \Delta_2 > \Delta_3$ (b) $\Delta_1 = \Delta_2 = \Delta_3$ (c) $\Delta_3 > \Delta_2 > \Delta_1$ (d) $\Delta_3 > \Delta_1 > \Delta_2$

Ans.

	1-D	2-D	3-D
Energy:	$\dfrac{n_x^2 h^2}{8ml_x^2}$	$\dfrac{h^2}{8m}\left(\dfrac{n_x^2}{l_x^2} + \dfrac{n_y^2}{l_y^2}\right)$	$\dfrac{h^2}{8m}\left(\dfrac{n_x^2}{l_x^2} + \dfrac{n_y^2}{l_y^2} + \dfrac{n_z^2}{l_z^2}\right)$
Ground State:	$n=1$	$n_x = 1,\ n_y = 1$	$n_x = 1,\ n_y = 1,$ $n_z = 1$
Excited State:	$n=2$	$n_x = 2,\ n_y = 1$	$n_x = 2,\ n_y = 1,$ $n_z = 1$
Energy difference:	$\dfrac{3h^2}{8ml_x^2}$	$\dfrac{3h^2}{8ml_x^2}$	$\dfrac{3h^2}{8ml_x^2}$

So, $\Delta_1 = \Delta_2 = \Delta_3$

Correct option is (b)

Q. 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 $\langle p \rangle = 0$

Ans. For 1-d harmonic oscillator wave function,

$$\psi_{0(x)} = \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\beta x^2/2}$$

$$\langle x \rangle = \int_{-\infty}^{+\infty} \psi^* x \psi \, dx = \int_{-\infty}^{+\infty} \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\beta x^2/2} x \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\beta x^2/2} dx$$

$$= \left(\frac{\beta}{\pi}\right)^{1/2} \int_{-\infty}^{+\infty} x e^{-\beta x^2} dx \quad .....(i)$$

Now for $\int_{-\infty}^{+\infty} x^n e^{-ax^2} dx$; if n= odd, integral will be 0,

In equation (i), n=1,

Therefore, $\langle x \rangle = 0$

$$\langle p_x \rangle = \int_{-\infty}^{+\infty} \psi^* \langle p_x \rangle \psi \, dx = \int_{-\infty}^{+\infty} \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\beta x^2/2} \left(-i\hbar \frac{\partial}{\partial x}\right) \left(\frac{\beta}{\pi}\right)^{1/4} e^{-\beta x^2/2} dx$$

$$= \left(\frac{\beta}{\pi}\right)^{1/2} (-i\hbar) \int_{-\infty}^{+\infty} e^{-\beta x^2/2} \left\{\frac{\partial}{\partial x}\left(e^{-\beta x^2/2}\right)\right\} dx$$

$$= \left(\frac{\beta}{\pi}\right)^{1/2} (-i\hbar) \int_{-\infty}^{+\infty} e^{-\beta x^2/2} \left(\frac{-2\beta x}{2}\right) e^{-\beta x^2/2} dx$$

$$= (-\beta) \left(\frac{\beta}{\pi}\right)^{1/2} (-i\hbar) \int_{-\infty}^{+\infty} x e^{-\beta x^2} dx \qquad \text{[Now for, } \int_{-\infty}^{+\infty} x^n e^{-ax^2} dx; \text{ if n= odd, integral will be 0]}$$

$$= (-\beta) \left(\frac{\beta}{\pi}\right)^{1/2} (-i\hbar) \times 0 = 0, \textbf{ Correct option is (c).}$$

Q. The value of the commutator $[x, [x, p_x]]$ is—

(a) $i\hbar x$ (b) $-i\hbar$ (c) $i\hbar$ (d) 0

Ans. Let the wave function is ψ.

So, $[x, p_x]\psi = x p_x \psi - p_x x \psi = x\left(-i\hbar \frac{\partial}{\partial x}\right)\psi - \left(-i\hbar \frac{\partial}{\partial x}\right)x\psi$

$$= -i\hbar x\left(\frac{\partial \psi}{\partial x}\right) + i\hbar\left[x\frac{\partial \psi}{\partial x} + \psi\right]$$

$$= -xi\hbar \frac{\partial \psi}{\partial x} + i\hbar x \frac{\partial \psi}{\partial x} + i\hbar\psi = i\hbar\psi$$

So, we have $[x, p_x] = i\hbar$

Now, $[x, [x, p_x]]\psi = 0$

Correct option is (d).

NET DEC 2015

Q. Two different non-zero operators $\hat{A}$ and $\hat{B}$ $(\hat{A} \neq \hat{B})$ satisfy the relation$(\hat{A} + \hat{B})(\hat{A} - \hat{B}) = \hat{A}^2 - \hat{B}^2$

(a) $\hat{A}\hat{B} = \hat{A}^2$ and $\hat{B}\hat{A} = \hat{B}^2$ (b) $\hat{A}\hat{B} + \hat{B}\hat{A} = 0$

(c) $\hat{A}$ and $\hat{B}$ are arbitrary   (d) $\hat{A}\hat{B} - \hat{B}\hat{A} = 0$

Ans. $(\hat{A} + \hat{B})(\hat{A} - \hat{B}) = \hat{A}(\hat{A} - \hat{B}) + \hat{B}(\hat{A} - \hat{B})$

$$= \hat{A}^2 - \hat{A}\hat{A} + \hat{B}\hat{A} - \hat{B}^2$$

$$= \hat{A}^2 - \hat{B}^2 \text{ only if } \hat{A}\hat{B} = \hat{B}\hat{A}$$

Correct option is (d).

Q. The degeneracy of an excited state of a particle in 3-dimensional cubic box with energy 3 times its ground state energy is

(a) 3   (b) 2   (c) 1   (d) 4

Ans. Given, energy $= 3 \times E_0 = 3 \times \dfrac{3h^2}{8ml^2} = \dfrac{9h^2}{8ml^2}$

So, possibility of energy states is (2,2,1), (2,1,2), (1,2,2)

Therefore, degeneracy = 3.

Correct option is (a).

Q. Possible term symbol(s) of the excited states of atom with the electronic configuration $[1s^2\, 2s^2\, 2p^6\, 3p^1]$ is/are

(a) $^2S_{1/2}$ (b) $^2P_{3/2}$ and $^2P_{1/2}$ (c) $^1S_0$ and $^1P_1$ (d) $^3P_0$ and $^3P_1$

Ans. For $[1s^2\, 2s^2\, 2p^6\, 3p^1]$

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

$2s+1 = 2$

$J = |l+s|\ldots\ldots|l-s|$

$\quad = 3/2 \ldots\ldots 1/2$

Term symbol is $^2P_{3/2}$ and $^2P_{1/2}$

Correct option is (b).

Q. A certain 2-level system has stationary state energies E_1 and E_2 ($E_1 < E_2$) with normalized wave functions ψ_1 and ψ_2 respectively. In the presence of a perturbation V, the second-order correction to the energy for the first state (ψ_1) will be

(a) $\dfrac{\langle \psi_1|V|\psi_2 \rangle}{E_1 - E_2}$ 　　　　(b) $\dfrac{\langle \psi_1|V|\psi_2 \rangle}{E_2 - E_1}$ 　　　　(c) $\dfrac{|\langle \psi_1|V|\psi_2 \rangle|^2}{E_1 - E_2}$ 　　　　(d)

$\dfrac{|\langle \psi_1|V|\psi_2 \rangle|^2}{E_2 - E_1}$

Ans. The second order correction to n^{th} state

$$E_n^{(2)} = \sum_{m \neq n} \frac{|\langle \psi_m|V|\psi_n \rangle|^2}{E_n - E_m}$$

Hence, $E_1^{(2)} = \sum \dfrac{|\langle \psi_1|V|\psi_2 \rangle|^2}{E_1 - E_2}$

Correct option is (c).

Q. The molecule diborane belongs to the symmetry point group

(a) C_{2v} 　　　　(b) C_{2h} 　　　　(c) D_{2d} 　　　　(d) D_{2h}
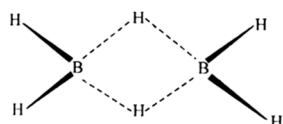
Ans. $C_2 + 2C_2 + 2\sigma_v + \sigma_h = D_{2h}$ **Correct option is (c).**

Q. The irreducible representations of C_{2h} are A_g, B_g, A_u and B_u. The Raman active modes of trans- 1,3-butadiene belong to the irreducible representations

(a) A_g and B_g 　　　(b) A_g and A_u 　　　(c) A_u and B_g 　　　(d) B_g and B_u

Ans. Generally, Raman active modes of vibrations are the quadratic function of x, y, and z and which are may be possible for A_g and B_g.

Correct option is (a).

Q. The symmetry-allowed atomic transition among the following is

(a) $^3F \rightarrow {}^1D$　　　(b) $^3F \rightarrow {}^3D$　　　(c) $^3F \rightarrow {}^1P$　　　(d) $^3F \rightarrow {}^3P$

Ans. As per selection rule we know that transition is allowed for which $\Delta S=0$, $\Delta L=0, \pm 1$

Only for $^3F \rightarrow {}^3D$ transition the selection rules are been obeyed.

Correct option is (b).

Q. The radial part of a hydrogenic wave function is given as $r(\alpha - r)e^{-\beta r}$ (α and ß are constants). This function is then identifiable as

(a) 2s　　　(b) 3p　　　(c) 4d　　　(d) 5f

Ans. In radial part of wave function highest power of r denote the value of l.

Correct option is (b).

Q. A normalized state Φ is constructed as a linear combination of the ground state (ψ_0) and the first excited state (ψ_1) of some harmonic oscillator with energies 1/2 and 3/2 units, respectively. If the average energy of the state Φ is 7/6, the probability of finding ψ_0 in ψ_1 will be

(a) 1/2　　　(b) 1/3　　　(c) 1/4　　　(d) 1/5

Ans. Let, $\Phi = c_1\psi_0 + c_2\psi_1$

Hence, $c_1^2 + c_2^2 = 1$……..(i) and $\dfrac{c_1^2}{2} + \dfrac{3c_2^2}{2} = \dfrac{7}{6}$………(ii)

Multiplying 3/2 to eqn. (i) we get

$\dfrac{3c_1^2}{2} + \dfrac{3c_2^2}{2} = \dfrac{3}{2}$………(iii)

Comparing eqn. (ii) and (iii) we get

$c_1^2 = \dfrac{1}{3}$

Correct option is (b).

NET JUNE 2016

Q. The simultaneous eigen functions of angular momentum operators L^2 and L_z are

(a) all of 2s, $2p_x$, $2p_y$ and $2p_z$ orbitals   (b) only 2s, $2p_x$ and $2p_y$ orbitals
(c) only 2s and $2p_z$ orbitals   (d) only $2p_z$ orbital

Ans. 2s and $2p_z$ orbitals are eigen functions of L^2 and L_z.

$L_z 2s = L_z \psi_{200} = 0 \psi_{200}$

$L_z 2p_z = L_z \psi_{210} = 0 \psi_{210}$

$L^2 2s = L^2 \psi_{200} = 0 \psi_{200}$

$L^2 2p_z = L^2 \psi_{210} = 2\hbar^2 \psi_{210}$

$L^2 2p_x = L^2 R_{21} \sqrt{\dfrac{3}{4\pi}} \sin\theta \cos\Phi$

$L^2 2p_y = L^2 R_{21} \sqrt{\dfrac{3}{4\pi}} \sin\theta \sin\Phi$

$L^2 2p_y = L_z R_{21} \sqrt{\dfrac{3}{4\pi}} \sin\theta \cos\Phi$ Not eigen function

As $L_z \to \dfrac{\partial}{\partial \Phi}$ will change $\cos\Phi$ to $-\sin\Phi$

$L_z 2p_y = L_z R_{21} \sqrt{\dfrac{3}{4\pi}} \sin\theta \sin\Phi$

Therefore not eigen functions,

$= 2\hbar^2 R_{21} \sqrt{\dfrac{3}{4\pi}} \sin\theta \cos\Phi$

$= 2\hbar^2 R_{21} \sqrt{\dfrac{3}{4\pi}} \sin\theta \sin\Phi$

Correct option is (c).

Q. The lowest energy term for the d^6 configuration is

(a) ^2D (b) ^5D (c) ^1P (d) ^1D

Ans. d^6 =

↑↓	↑	↑	↑	↑

L = $\sum M_L = 2 = D$

S= 2, 2S+1=5

Correct option is (b).

Q. The eigen functions of the Hamiltonian H (H = T + V) of a harmonic oscillator are (where T and V are kinetic energy and potential energy operators, respectively)

(a) eigen functions of T as well as V (b) eigen functions of T, but not of V

(c) eigen functions of V, but not of T (d) eigen functions of neither T nor V

Ans. We know if two operator commute this means that they have same sets of eigen functions.

Now, $T = \frac{p^2}{2m} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$, $V = \frac{1}{2}kx^2$, H = T + V

So, $[\hat{H}, \hat{T}] \neq 0$ & $[\hat{H}, \hat{V}] \neq 0$

Therefore, $[\hat{T}, \hat{V}] \neq 0$

Correct option is (d).

Q. The point group obtained by adding symmetry operation σ$_h$ to the point group C$_4$ is

(a) S$_4$ (b) C$_{4h}$ (c) D$_{2h}$ (d) D$_4$

Ans. C$_4$ + σ$_h$ = C$_{4h}$

Correct option is (b).

Q. For a particle of mass m confined in a rectangular box with sides $2a$ and a, the energy and degeneracy of the first excited state, respectively, are

(a) $\frac{h^2}{8m}\left(\frac{2}{a^2}\right), 1$ (b) $\frac{h^2}{8m}\left(\frac{17}{4a^2}\right), 2$ (c) $\frac{h^2}{8m}\left(\frac{5}{4a^2}\right), 1$ (d) $\frac{h^2}{8m}\left(\frac{5}{a^2}\right), 2$

Ans.

Degeneracy in 2-D box

$$E = \frac{h^2}{8m}\left[\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2}\right] = \frac{h^2}{8m}\left[\frac{n_x^2}{4a^2} + \frac{n_y^2}{a^2}\right] = \frac{h^2}{8m}\left[\frac{n_x^2 + 4n_y^2}{4a^2}\right]$$

Now, for first excited state, $n_x = 2$, $n_y = 1$

Hence, $E = \frac{h^2}{8m}\left[\frac{4+4}{4a^2}\right] = \frac{h^2}{8m}\left(\frac{2}{a^2}\right)$

Also for first excited state $n_x = 1$, $n_y = 2$

$$E = \frac{h^2}{8m}\left[\frac{n_x^2 + 4n_y^2}{4a^2}\right] = \frac{h^2}{8m}\left[\frac{1+16}{4a^2}\right] = \frac{h^2}{8m}\left(\frac{17}{4a^2}\right) = \frac{h^2}{8m}\left(\frac{4.25}{a^2}\right)$$

So, minimum energy $= \frac{h^2}{8m}\left(\frac{2}{a^2}\right)$, $g = 1$.

Correct option is (a).

Q. The ionization energy of hydrogen atom in its ground state is approximately 13.6 eV. The potential energy of He^+, in its ground state is approximately

(a) –54.4 eV   (b) –27.2 eV   (c) –13.6 eV   (d) –108.8 eV

Ans. $I. E_{He^+} = 13.6 \frac{Z^2}{n^2} = 13.6 \times 4$

As we know K.E + P.E = -54.4eV …………(i)

Now as per Virial Theorem,

$$2\langle T \rangle = -\langle V \rangle$$

Also, K.E $= -\frac{1}{2}$ P.E

Thereafter, from eqn. (i) $-\frac{1}{2}$ P.E + P.E $=-54.4$; P.E $= -108.8 \ eV$

Correct option is (d).

Q. The character table for the D_3 point group is provided below:

D_3	E	$2C_3$	$3C$		
A_1	1	1	1		$x^2 + y^2, z^2$
A_2	1	1	-1	z, R_z	
E	2	-1	0	$(x, y), (R_x, R_y)$	$(x^2 - y^2, xy), (xz, yz)$

For this point group, the correct statement among the following is:
(a) it is possible to have a totally symmetric normal mode of vibration which is IR-active
(b) all IR-active normal modes are necessarily Raman inactive
(c) all Raman-active normal modes are necessarily IR-active
(d) it is possible to have a pair of IR-active normal modes that are degenerate.
Ans. In front of 'E' irreducible representation, it is clear that there is a pair or IR active mode which is degenerate.

Correct option is (d).

Q. Suppose ψ_1, ψ_2, ψ_3....... are wavefunctions of an anharmonic oscillator and ϕ_0, ϕ_1, ϕ_2..... are wavefunctions of a harmonic oscillator with increasing order of energy. The subscripts denote vibrational quantum numbers in both the cases. Given

$\psi_0 = a_1\phi_0 + a_2\phi_2 + a_3\phi_4$

$\psi_1 = b_1\phi_0 + b_2\phi_6 + b_3\phi_6$

$\psi_2 = c_1\phi_1 + c_2\phi_4$

$\psi_3 = d_1\phi_3 + d_2\phi_5$

the FORBIDDEN electric dipole (assuming the dipole operator is linear in normal coordinates) transition among the following is

(a) $\psi_0 \rightarrow \psi_1$ (b) $\psi_0 \rightarrow \psi_2$ (c) $\psi_0 \rightarrow \psi_3$ (d) $\psi_1 \rightarrow \psi_2$

Ans. ϕ_0, ϕ_1, ϕ_2..... are wavefunctions of a harmonic oscillator in ground state, first excited state, second excited state respectively.

We know that for a harmonic oscillator ϕ_0, ϕ_2, ϕ_4, ϕ_6..... will have even parity and ϕ_1, ϕ_3, ϕ_5, ϕ_7..... will have odd parity.

So, $\psi_{0[EVEN\ PARITY]} = a_1\phi_{0[EVEN\ PARITY]} + a_2\phi_{2[EVEN\ PARITY]} + a_3\phi_{4[EVEN\ PARITY]}$

$\psi_{1[EVEN\ PARITY]} = b_1\phi_{0[EVEN\ PARITY]} + b_2\phi_{6[EVEN\ PARITY]} + b_3\phi_{6[EVEN\ PARITY]}$

$\psi_{2[MIXED\ PARITY]} = c_1\phi_{1[ODD\ PARITY]} + c_2\phi_{4[EVEN\ PARITY]}$

$\psi_{3[ODD\ PARITY]} = d_1\phi_{3[ODD\ PARITY]} + d_2\phi_{5[ODD\ PARITY]}$

Since the dipole moment operator is linear, therefore electric dipole transition is forbidden if the initial and final states have same parity.

Since, ψ_0 and ψ_1 have same parity, so, the transition $\psi_0 \rightarrow \psi_1$ is forbidden.

Correct option is (a).

Q. The character table of C_{3v} point group is provided below, along with an additional reducible representation, Γ

	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
Γ	6	0	2

Γ is given by

(a) $A_1 + A_2 + 2E$ (b) $2A_1 + 2E$ (c) $2A_2 + 2E$ (d) $2A_1 + 2A_2 + E$

Ans. $n_{A_1} = 2,\ n_{A_2} = 2$

Correct option is (b).

Q. Average value of momentum for the ground state of a particle in a 1-d box is zero because

(a) $[p, H] = 0$ (b) V (potential) $= 0$

(c) H is hermitian   (d) the state is bound and stationary

Ans. For any bound state particle has equal and opposite value of moment.

Correct option is (d).

Q. Choosing some Hamiltonian H and an orthonormal basis, a linear variation is carried out to get approximately energies $\overline{E_j}$. With 2 basis functions, one obtains $\overline{E_1}(2) \leq \overline{E_2}(2)$. Taking 3 basis functions, similarly three ordered energies $\overline{E_1}(3) \leq \overline{E_2}(3) \leq \overline{E_3}(3)$ are found. The relation which holds from the following is?

(a) $\overline{E_1}(2) \leq \overline{E_1}(3);$ $\qquad\qquad$ $\overline{E_2}(2) \leq \overline{E_2}(3)$

(b) $\overline{E_1}(3) \leq \overline{E_1}(2);$ $\qquad\qquad$ $\overline{E_2}(2) \leq \overline{E_2}(3)$

(c) $\overline{E_1}(2) \leq \overline{E_1}(3);$ $\qquad\qquad$ $\overline{E_2}(3) \leq \overline{E_2}(2)$

(d) $\overline{E_1}(3) \leq \overline{E_1}(2);$ $\qquad\qquad$ $\overline{E_2}(3) \leq \overline{E_2}(2)$

Ans. Correct option is (d).

Q. For a hermitian operator A, which does NOT commute with the Hamiltonian H, let ψ1 be an eigenfunction of A and ψ_2 be an eigenfunction of H. The correct statement regarding the average value of the commutator of A with H([A,H]) is

(a) both $\langle\psi_1|[A,H]|\psi_1\rangle$ and $\langle\psi_2|[A,H]|\psi_2\rangle$ are non-zero

(b) only $\langle\psi_1|[A,H]|\psi_1\rangle$ is zero, but $\langle\psi_2|[A,H]|\psi_2\rangle$ is non-zero

(c) only $\langle\psi_2|[A,H]|\psi_2\rangle$ is zero, but $\langle\psi_1|[A,H]|\psi_1\rangle$ is non-zero

(d) both $\langle\psi_1|[A,H]|\psi_1\rangle$ and $\langle\psi_2|[A,H]|\psi_2\rangle$ are zero

Ans. $A|\psi_1> = a|\psi_1>$ and $H|\psi_2> = b|\psi_2>$, $<\psi_2|H = b<\psi_2|$

Here, 'a' is eigen value.

$\langle\psi_1|A = A|\psi_1\rangle^\dagger = a|\psi_1>^\dagger = a^* <\psi_1| = a <\psi_1|$ [as a is real number]

Now, $\langle\psi_1|[A,H]|\psi_1\rangle = \langle\psi_1|AH - HA|\psi_1\rangle = \langle\psi_1|AH|\psi_1\rangle - \langle\psi_1|H|a\psi_1\rangle$

$$= a[\langle\psi_1|H|\psi_1\rangle - \langle\psi_1|H|\psi_1\rangle] = 0$$

Similarly, $\langle\psi_2|[A,H]|\psi_2\rangle = 0$; **Correct option is (d).**

Q. In simple molecular orbital theory of hydrogen molecule, bonding σ_g and anti-bonding σ_u molecular orbitals are constructed as linear combinations of atomic orbitals of two hydrogen atoms. The spatial part of a purely covalent singlet wavefunction is obtained by

(a) $\sigma_g^2 + \sigma_u^2$ (b) σ_g^2 (c) $\sigma_g^2 - \sigma_u^2$ (d) $\sigma_g^2 + \frac{1}{2}\sigma_u^2$

Ans. Correct option is (c).

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Q. Covariance is defined by the relation $\mathrm{Cov}(x,y) = \langle xy \rangle - \langle x \rangle \langle y \rangle$. Given the arbitrary constants A, B and C, $\mathrm{Cov}(x,y)$ will be zero only when

(a) $y = Ax^2$ (b) $y = Ax^2 + B$ (c) $y = Ax + B$ (d) $y = Ax^2 + Bx + C$

Ans. Covariance has the tendency for the linear relationship between the variables

If $y = f(x) \propto x^n$ (where n>1), then $\mathrm{cov}(x, y) = +ve$

If $y = f(x) \propto x^n$ (where n<0), then $\mathrm{cov}(x, y) = -ve$

If $y = f(x) \propto x$, then $\mathrm{cov}(x, y) = 0$

Correct option is (c).

Q. The correct normalized wavefunction for one of the sp^2 hybrid orbitals is

(a) $\frac{1}{3}\psi_{2s} + \frac{1}{3}\psi_{2p_x} + \frac{1}{3}\psi_{2p_y}$ (b) $\frac{1}{\sqrt{3}}\psi_{2s} + \frac{2}{\sqrt{3}}\psi_{2p_x} + \frac{1}{\sqrt{6}}\psi_{2p_y}$

(c) $\frac{1}{\sqrt{3}}\psi_{2s} + \frac{2}{\sqrt{3}}\psi_{2p_x} + \frac{1}{\sqrt{6}}\psi_{2p_y}$ (d) $\frac{1}{\sqrt{3}}\psi_{2s} + \frac{1}{2\sqrt{3}}\psi_{2p_x} + \frac{1}{\sqrt{6}}\psi_{2p_y}$

Ans. For normalized wave function, $c_1^2 + c_2^2 + c_3^2 = 1$

$\frac{1}{3} + \frac{1}{2} + \frac{1}{6} = 1$

Correct option is (c).

Q. The transition that belongs to the Lyman series in the hydrogen-atom spectrum is

(a) $1s \leftarrow 4s$ (b) $1s \leftarrow 4p$ (c) $2s \leftarrow 4s$ (d) $2s \leftarrow 4p$

Ans. As we know for any allowed transition $\Delta l = \pm 1$ and for Lyman series transition is from the higher level to n =1.

Correct option is (b).

Q. Vibrations of diatomic molecules are usually modelled by a harmonic potential. If the potential is given by x^2, the correct statement is

(a) force is 2x and force constant is 2 (b) force is –2x and force constant is 2

(c) force is 2x and force constant is –1 (d) force is –2x and force constant is –1

Ans. Given, $V = x^2$

Now force, $-\frac{\partial v}{\partial x} = -\frac{\partial}{\partial x}(x^2) = -2x$

Now, $V = \frac{1}{2}kx^2 = x^2$ (given)

So, k = 2.

Correct option is (b).

Q. The orbital degeneracy of the level of a one-electron atomic system with Z = 5 and energy ≈ -13.6 eV, is

(a) 1 (b) 5 (c) 25 (d) 36

Ans. We know that, $E_n = -13.6\frac{Z^2}{n^2}$; $-13.6\frac{25}{n^2} = -13.6$, n=5

Correct option is (b).

Q. If we write a normalized wavefunction $\psi = \widehat{A}\phi$, then ϕ is also normalized when

(a) $\widehat{A}$ is hermitian   (b) $\widehat{A}$ is anti-hermitian

(c) $\widehat{A}$ is unitary   (d) $\widehat{A}$ is any linear operator

Ans. $\psi = \widehat{A}\phi$ is normalized.

$$\int \left(\widehat{A}\phi\right)^{\dagger}\left(\widehat{A}\phi\right)d\tau = 1$$

i.e., $\int \phi^{\dagger}A^{\dagger}A\phi \, d\tau = 1$, i.e., $\int \phi^{\dagger}\phi \, d\tau = 1$

Therefore, ϕ will be normalized if $A^{\dagger}A = 1$ i.e., A is unitary.

Correct option is (c).

124. The ground state of a certain system with energy ϵ_0 is subjected to a perturbation V, yielding a first order correction ϵ_1. If E_0 is the true ground-state energy of the perturbed system, the inequality that always holds is

(a) $\epsilon_1 \geq 0$ (b) $\epsilon_1 \geq E_0$ (c) $\epsilon_0 + \epsilon_1 \leq E_0$ (d) $\epsilon_0 + \epsilon_1 \geq E_0$

Ans. As per perturbation theory, "The energy of perturbed system is equal or greater than the standard system".

Correct option is (d).

Q. The spatial part of an excited state b $^3\Sigma_u^+$ of hydrogen molecule is proportional to $[1\sigma_g(1)1\sigma_u(2) - 1\sigma_g(2)1\sigma_u(1)]$. Using LCAO–MO expansion of $1\sigma_g$ and $1\sigma_u$ in terms of 1s-atomic orbitals, one can infer that this wavefunction has

(a) only ionic parts

(b) only covalent parts

(c) both ionic and covalent parts

(d) neither ionic nor covalent parts

Ans. $1\sigma_g(1)1\sigma_u(2) - 1\sigma_g(2)1\sigma_u(1)$

$$= \left[\left(\psi_{1s(H_a)}(1) + \psi_{1s(H_b)}(1)\right)\left(\psi_{1s(H_a)}(2) - \psi_{1s(H_b)}(2)\right)\right]$$

$$= \left[\left(\psi_{1s(H_a)}(2) + \psi_{1s(H_b)}(2)\right)\left(\psi_{1s(H_a)}(1) - \psi_{1s(H_b)}(1)\right)\right]$$

$$= 2\left[\psi_{1s(H_a)}(2)\psi_{1s(H_b)}(1) - \psi_{1s(H_a)}(1)\psi_{1s(H_b)}(2)\right]$$

Correct option is (b).

Q. The highest molecular orbitals for an excited electronic configuration of the oxygen molecule are $[1\pi_g]^1[3\sigma_u]^1$. A possible molecular term symbol for oxygen with this electronic configuration is

(a) $^1\pi$ (b) $^3\Sigma$ (c) $^1\Delta$ (d) $^1\Sigma$

Ans. The arrangement for $[1\pi_g]^1[3\sigma_u]^1$ configuration are

(I) m_L $\uparrow$ σ_u
      0
     $\uparrow$
   $\overline{\pi_g}$ $\overline{\pi_g}$
m_L +1   -1

$S = 1, 2S + 1 = 3$
$L = 1 \rightarrow \pi$ Term

Spectroscopic Term $= {}^3\pi$

(II) m_L $\downarrow$ σ_u
      0
     $\uparrow$
   $\overline{\pi_g}$ $\overline{\pi_g}$
m_L +1   -1

$L = 1 \rightarrow \pi$ Term
$S = 0, 2S + 1 = 1$

Spectroscopic Term $\rightarrow {}^1S$

Thus only one possible molecular term symbol is $^1\pi$.

Correct option is (a).

Q. For H_2O molecule, the electronic transition from the ground state to an excited state of B_1 symmetry is

C_{2v}	E	C_2	σ_v	σ_v'	
A_1	1	1	1	1	z, z^2, x^2, y^2
A_2	1	1	-1	-1	xy
B_1	1	-1	1	-1	x, xz
B_2	1	-1	-1	1	y, yz

(a) not allowed

(b) allowed with x polarization

(c) allowed with y polarisation

(d) allowed with z polarisation

Ans. We have $A_1 \times B_1 = 1 \quad -1 \quad 1 \quad -1$, i.e., X-polarised.

Correct option is (b).

Q. The pair of symmetry points groups that are associated with only polar molecules is

(a) C_{2v}, $D_{\infty h}$ (b) C_{3v}, C_{2h} (c) D_{2h}, T_d (d) C_{2v}, $C_{\infty v}$

Ans. The polar point groups are C_{nv}, C_n, C_l, C_s.

Correct option is (d).

Q. Two bound stationary states, 1 and 2, of a one-electron atom, with $E_2 > E_1$ (E is the total energy) obey the following statement about their kinetic energy (T) and potential energy (V)

(a) $T_2 > T_1$; $V_2 > V_1$

(b) $T_2 > T_1$; $V_2 < V_1$

(c) $T_2 < T_1$; $V_2 > V_1$

(d) $T_2 = T_1$; $V_2 > V_1$

Ans. $T_1 = \frac{1}{2} V_1$; $T_2 = -\frac{1}{2} V_2$

$E_2 > E_1$; $T_1 + T_2 < V_1 + V_2$

Correct option is (c).

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Q. Consider a particle in its ground state confined to a one-dimensional box in the interval (0, 8). The probability of finding it between $4.0 - \frac{\delta}{2}$ and $4.0 + \frac{\delta}{2}$ is close to (δ is sufficiently small so that the wavefunction can be taken as a constant in this interval.

(a) $\frac{\delta}{4}$ (b) $\frac{\delta}{3}$ (c) $\frac{\delta}{2}$ (d) δ

Ans. Probability of finding electron is a particular region,

$$P_r = |\psi|^2 dx = \left[\sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l} \sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l} \right] \delta$$

$$= \frac{1}{4} \sin^2 \left(\frac{\pi}{2} \right) \delta = \frac{\delta}{4}.$$

Correct option is (a)

Q. Which of the functions below is a common eigenfunction of $\frac{d}{dx}$ and $\frac{d^2}{dx^2}$ operators?

(a) $\cos x$ (b) kx (c) e^{ix} (d) $e{-x^2}$

Ans. $\frac{d}{dx} e^{ix} = i e^{ix}$; eigen function

$\frac{d^2}{dx^2} e^{ix} = i^2 e^{ix}$; eigen function

Correct option is (c).

Q. For the electronic configuration $1s^22s^22p^4$, two of the possible term symbols are ^1S and ^3p. The remaining term is

(a) ^1D (b) ^1F (c) ^3D (d) ^3F

Ans. The number of possible microstate for $p^4 = \frac{6!}{4!(6-4)!} = 15$

$^1S=1\times1=1$; $^3p=3\times3=9$

Therefore the remaining microstates are 5 which comes from $^1D = 1\times5=5$

Correct option is (a)

Q. The correct relation involving symmetry operations

(a) $S_4^2 = S_2$ (b) $\sigma(xz)\sigma(yz) = C_2(s)$

(c) $S_4^3 = C_4^3$ (d) $S_6^3 = S_2$

Ans. $S_6^3 = C_6^3 \times \sigma^3 = C_2' \times a = S_2$

Correct option is (d)

Q. For a point group, an incomplete character table is given below with one irreducible representation missing

	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
-	-	-	-
E	2	-1	0

The Mulliken symbol and characters of the missing representation are

(a) A_1' 1 -1 1 (b) B_1 1 -1 1

(c) A_2 1 1 -1 (d) B_2 1 -1 1

Ans. For a C_{3v} point group the complete character table is

	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

Correct option is (c).

Q. Given below is a specific vibrational mode of BCl_3 with $\oplus$ and $\varnothing$ denoting movements of the respective atoms above and below the plane of the molecule respectively. The irreducible representation of the vibrational mode and its IR / Raman activity are

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1	1	1	1	1	1	1		x^2+y^2, z^2
A_2	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	x, y	x^2-y^2, xy
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	R_x, R_y	xz, yz
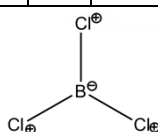
(a) A_2'; neither IR nor Raman active   (b) E' both IR and Raman active

(c) A_1; Raman active   (d) A_2'; IR active

Ans. As per the given character table, the vibrational node is not symmetric with respect to σ_h.

Correct option is (d).

Q. The two limiting wavefunctions of the ground state of H_2^+ molecular ion, as the internuclear separation R goes to (i) (infinity) and (ii) 0 (zero) are ($1s_a$,$1s_b$ are 1s-orbital wave functions of hydrogen atoms a and b in H_2^+ , and He 1s is the wave function of the 1s orbital of He^+)

(a) (i) $1s_a(r)$; (ii) $1s_b(r)$ (b) (i) $1s_b(r)$; (ii) $1s_a(r)$

(c) (i) $1s_a(r_1)$ $1s_b(r_2)$; (ii) $1s_{He}(r_1)$ $1s_{He}(r_2)$ (d) (i) $1s_a(r)+1s_b(r)$; (ii) $1s_{He}(r)$

Ans.
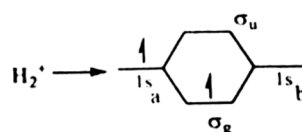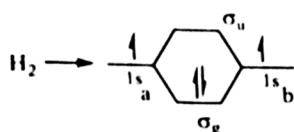
$_2He = 1s^2$;

$He^+ = 1s^1$

$H_2^+ = r\rightarrow\infty = 1s_a(r)+1s_b(r)$

$He^+ = r\rightarrow 0 = 1s_{He}(r)$; **Correct option is (d).**

Q. The un-normalized radial wave function of a certain hydrogen atom eigenstate is (6r-r2)exp(-r/3). A possible angular part of the eigenstate is

(a) $5cos^3\theta - 3cos\theta$ (b) $3cos^2\theta - 1$ (c) $cos\theta$ (d) 1

Ans. In the given eigen state equation the maximum power of r is 1 i.e., l=1 i.e., possible angular part is $cos\theta$.

Correct option is (c).

Q. Given a trial wave function $\psi_t = C_1\phi_1 + C_2\phi_2$, and the Hamiltonian matrix elements, $\int \phi_1^* H\phi_1 dv = 0$, $\int \phi_1^* H\phi_1 dv = 2.5$, $\int \phi_1^* H\phi_1 dv = 12.0$, the variationally determined ground state energy is

(a) -0.52   (b) -0.50   (c) 12.50   (d) 12.52

Ans. $\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{21} - ES_{21} & H_{22} - ES_{22} \end{vmatrix} = 0$

$\begin{vmatrix} 0 - E & 2.5 \\ 2.5 & 12 - E \end{vmatrix} = 0$

$E = -0.50$

Correct option is (b).

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Q. The number of degenerate spatial orbital's of a hydrogen- like atom with principal quantum Number n=6 is

(a) 12   (b) 6   (c) 72   (d) 36

Ans. As we know orbital degeneracy $= n^2 = 6^2 = 36$

Correct option is (d).

Q. If $[\hat{A}, \hat{B}] = 0$ and $[\hat{A}, \hat{C}] = 0$, then which of the following **necessarily** holds: $[\hat{A}, \hat{B}$ & $\hat{C}$ are operators]

(a) $[\hat{B}, \hat{C}] = 0$ (b) $[\hat{A}, \widehat{BC}] = 0$ (c) $[\hat{B}, \widehat{AC}] = 0$ (d) $[\hat{C}, \widehat{AB}] = 0$

Ans. $[\hat{A}, \widehat{BC}] = [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}] = 0$

Correct option is (b).

Q. The correct statement among the following is ($\hat{A}$ is a hermitian operator)

1. The eigenvalues of $\widehat{A^2}$ can be negative.

2. The eigenvalues of $\widehat{A^2}$ are always positive.

3. No eigenfunction of $\hat{A}$ is an eigenfunction of $\widehat{A^2}$.

4. The eigenvalues of $\widehat{A^2}$ can be complex.

Ans. Assuming $\hat{A} = \widehat{p_x}$ and $\psi = e^{-ikx}$

Therefore, $\hat{A}\psi = \hat{A}e^{-ikx} = (-\hbar k)\psi$; $\widehat{A^2}\psi = \widehat{A^2}e^{-ikx} = (\hbar k)^2\psi$, i.e., +ve

Correct option is (b).

Q. The correct statement about the symmetry of the eigenfunctions of a quantum of 1-D harmonic oscillator is

(a) All the eigenfunctions are only even functions, because the potential is an even function.

(b) All the eigenfunctions are only odd functions, although the potential is an even function.

(c) The eigenfunctions have no odd-even symmetry.

(d) All the eigenfunction are either odd or even functions, because the potential is an even function.

Ans. Eigen functions are even for even values of vibrational quantum number and odd for odd values vibrational quantum number.

Correct option is (d)

Q. The correct statement about the difference of second and first excited state energies (ΔE) of a particle in 1-D, 2-D square and 3-D cubic boxes with same length for each, is

(a) ΔE (1-D box) = ΔE (2-D box) = ΔE (3-D box)

(b) ΔE (1-D box) > ΔE (2-D box) ΔE (3-D box)

(c) ΔE (1-D box) > ΔE (2-D box) = ΔE (3-D box)

(d) ΔE (1-D box) < ΔE (2-D box) < ΔE (3-D box)

Ans. In 1-D box, $\Delta E = 5\left(\frac{h^2}{8ml^2}\right)$, for 2-D box, $\Delta E = 3\left(\frac{h^2}{8ml^2}\right)$ and for 3-D box, $\Delta E = 3\left(\frac{h^2}{8ml^2}\right)$.
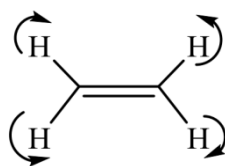
Correct option is (c).

103. A one-dimensional quantum harmonic oscillator is perturbed by a potential λx^2. The first order correction to the energy for the ground state $[\Delta E^{(1)}]$ is,

(a) $\Delta E^{(1)} > 0$ but < 1 (b) $\Delta E^{(1)} < 0$ (c) $\Delta E^{(1)} = 0$ (d) $\Delta E^{(1)} > 2$

Ans. For odd power of perturbed potential, $\Delta E^{(1)} = 0$

Correct option is (c).

Q. The normal mode of ethylene represented, by the figure below, is

(a) Only IR active   (b) Only Raman active

(c) Both IR and Raman active   (d) Neither IR nor Raman active

Ans. Correct option is (b)

Q. A part of the character table of a point group (of order 4) is given below.

	E	X_1	X_2	X_3
Γ_1	1	1	1	1
Γ_2	1	-1	1	-1
Γ_3	1	-1	-1	1
Γ_4	?	?	?	?

The four characters of Γ_4 are, respectively

(a) l, l, −l, −l   (b) 2, − 0, 0, 1   (c) 1, i, i, 1   (d) 1, − i, i, − 1

Ans. According to the Great Orthogonal Theorem, any two IR must be orthogonal to each other.

Correct option is (a).

Q. The electronic transition energy from $\pi_1 \rightarrow \pi_2$ in propenyl radical is 4.8 eV. Within the frame work of Huckel theory, the transitions energy from $\pi_1 \rightarrow \pi_3$ would be

(a) 2.4 eV   (b) 4.8 eV   (c) 9.6 eV   (d) 14.4 eV

Ans.

$\begin{array}{l} \underline{\quad\quad} \pi_3 = \alpha - 2\sqrt{\beta} \\ \underline{\quad\quad} \pi_2 = \alpha \\ \underline{\quad\quad} \pi_1 = \alpha + 2\sqrt{\beta} \end{array}$ $E_{\pi_1 \rightarrow \pi_3} = 2E_{\pi_1 \rightarrow \pi_2} = 2 \times 4.8 = 9.6$
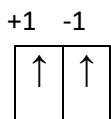
Correct option is (c).

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Q. The term symbol for the ground state of B_2 is

(a) $^1\Sigma_g^+$　　　　　(b) $^1\Sigma_g^-$　　　　　(c) $^3\Sigma_g^-$　　　　　(d) $^3\Sigma_g^+$

Ans. For B_2, $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_y^2\ ^1\pi_y = ^1\pi_y\ 3\sigma_g^2$

```
   +1   -1
  ┌──┬──┐
  │ ↑│ ↑│
  └──┴──┘
```

$S = \dfrac{1}{2} + \dfrac{1}{2} = 1$

$2S+1 = 3$

$\Delta\Lambda = 0, \pm 1$

$\Lambda = +1, -1, 0$ i.e., Σ

Thus, $^3\Sigma_g$

Correct option is (c).

Q. A Gaussian distribution has the functional form $f(x) = \dfrac{2}{\sqrt{2a^2\pi}} e^{-\frac{(x-b)^2}{2a^2}}$. The variance of such distribution is

(a) a　　　　　(b) a^2　　　　　(c) b　　　　　(d) b^2

Ans. $f(x) = \dfrac{2}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-x_e)^2}{2a^2}}$ compare with $f(x) = \dfrac{2}{\sqrt{2a^2\pi}} e^{-\frac{(x-b)^2}{2a^2}}$

Variance $= \sigma^2$; Variance $= a^2$

Correct option is (b)

Q. The lowest energy state of a *$1s^1 2s^1$* electronic configuration, according to hund's rule, is

(a) $^3S_0$ (b) $^1S_0$ (c) $^3S_1$ (d) $^1S_1$

Ans. $S = \frac{1}{2} + \frac{1}{2} = 1$

$2S+1 = 3$

i.e., l=0, S(term); $^3S_1$

Correct option is (c).

Q. The commutator of $\hat{x}$ with the Hamiltonian, $\hat{H}$, $[\hat{x}, \hat{H}]$ is

(a) 0   (b) $i\hbar$ (c) $-\frac{\hbar^2}{2m}\hat{p}_x$ (d) $\frac{i\hbar}{m}\hat{p}_x$

Ans. $[\hat{x}, \hat{H}] = [\hat{x}, \frac{p^2}{2m}] + [\hat{x}, V(x)] = \frac{1}{2m}[\hat{x}, \frac{p^2}{2m}] = \frac{i\hbar}{m}p$

Correct option is (d).

Q. Which of these is not a suitable unnormalized wave function for the excited 1s '2s' electron configuration of the helium atom?

(a) $[1s(1)2s(2)-2s(1)1s(2)][\beta(1)\beta(2)]$

(b) $[1s(1)2s(2)+2s(1)1s(2)][\alpha(1)\beta(2)-\beta(1)\alpha(2)]$

(c) $[1s(1)2s(2)-2s(1)1s(2)][\alpha(1)\beta(2)+\beta(1)\alpha(2)]$

(d) $[1s(1)2s(2)+2s(1)1s(2)][\alpha(1)\alpha(2)]$

Ans. $\psi_{total} = \psi_{space}\,\psi_{spin} = \left.\begin{array}{c}[1s(1)2s(2) + 1s(2)2s(1)]\\ [1s(1)2s(2) - 1s(2)2s(1)]\end{array}\right\}$ spatial part

$\alpha(1)\,\alpha(2)$; $\beta(1)\beta(2)$ = spin part

$\frac{1}{\sqrt{2}}(\alpha(1)\beta(2) + \beta(1)\alpha(2))$ i.e., $\frac{1}{\sqrt{2}}(\alpha(1)\beta(2) - \beta(1)\alpha(2))$ spin part
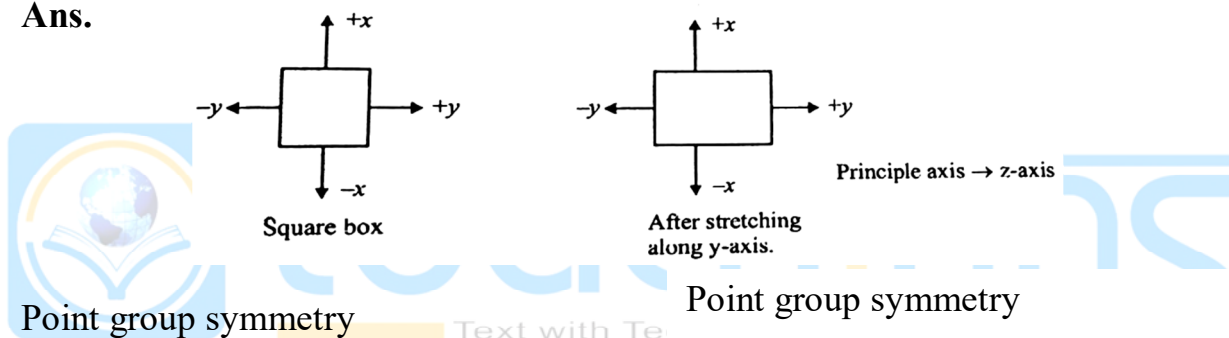
Correct option is (d).

Q. Two opposite sides (in the y – direction) of a square box of side L are slightly stretched. Consider the following four statements:

A. The point group changes from D_{4h} to D_{2h}.

B. The (1,2) and (2,1) energy levels remain doubly degenerate

C. Both the energy levels are lowered and the energy of the (1,2) level higher than that of the (2,1) level.

D. Both the energy levels are lowered and the energy of the (1,2) level lower than that of the (2,1) level. The two correct statements are:

(a) A and B   (b) A and C   (c) B and C   (d) A and D

Ans.

Square box

After stretching along y-axis.

Principle axis → z-axis

Point group symmetry

C_4 → along principle axis

$4C_2$ → perpendicular to principle axis

σ_h → along molecular plane

$C_4 \perp 4C_2 = D_4$

Hence D_{4h}

Point group symmetry

C_2 → along principle axis

$2C_2$ → perpendicular to principle axis

σ_h → along molecular plane

$C_4 \perp 4C_2 = D_4$

Hence D_{4h}

In above rectangle $L_y > L_x$

Energy of particle in rectangular box is given by

$$E_{xy} = \frac{h^2}{8m^2}\left[\frac{n_x^2}{l_x^2} + \frac{n_y^2}{l_y^2}\right]$$

Hence, $E_{12} = \frac{h^2}{8m^2}\left[\frac{1}{l_x^2} + \frac{4}{l_y^2}\right] = \frac{h^2}{8m^2}\left[\frac{l_x^2 + 4l_y^2}{l_x^2 \cdot l_y^2}\right]$

and $E_{21} = \frac{h^2}{8m^2}\left[\frac{4}{l_x^2} + \frac{1}{l_y^2}\right] = \frac{h^2}{8m^2}\left[\frac{4l_x^2 + l_y^2}{l_x^2 \cdot l_y^2}\right]$

As $L_y > L_x$

Hence $E_{21} > E_{12}$. **Correct option is (d).**

Q. Consider a model system of five non – interacting fermions in a single 3 – dimensional harmonic oscillator. The Hamiltonian of a single particle is

$$\hat{H} = \frac{1}{2m}\left(\hat{p}_x^{\,2} + \hat{p}_y^{\,2} + \hat{p}_z^{\,2}\right) + \frac{1}{2}m\omega^2(x^2 + y^2 + z^2)$$

where m is the mass of the particle, ω is the angular frequency, $\hat{p}_x$, $\hat{p}_y$ and $\hat{p}_z$ are the momentum operators. The ground state energy of the system of non – interacting fermions is
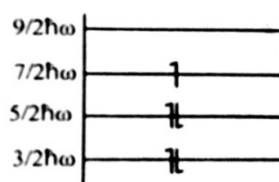
(a) $\frac{21}{2}\hbar\omega$ (b) $\frac{15}{2}\hbar\omega$ (c) $\frac{5}{2}\hbar\omega$ (d) $\frac{25}{2}\hbar\omega$

Ans. $E = \left(n_x + n_y + n_z + \frac{3}{2}\right)\hbar\omega$

Hence $E = \frac{21}{2}\hbar\omega$

Correct option is (a).

Q. A particle is in a state $\phi = \psi_1 + 3\psi_2$ where ψ_1 and ψ_2 are eigen functions of the Hamiltonian of the particle with eigen values E_1 and E_2, respectively. The average energy of the particle in the state ϕ is

(a) $(E_1 + 9E_2)/10$

(b) $(E_1 + 3E_2)$

(c) $(E_1 + 9E_2)/4$

(d) $(E_1 + 3E_2)/10$

Ans. $\phi = \psi_1 + 3\psi_2$

So, $\hat{H}\psi_1 = E_1\psi_1$ and $\hat{H}\psi_2 = E_2\psi_2$

For average energy,

$$\langle E \rangle = \frac{\langle \phi^* | \hat{H} | \phi \rangle}{\langle \phi^* \phi \rangle} = \frac{\langle (\psi_1 + 3\psi_2) | \hat{H} | (\psi_1 + 3\psi_2) \rangle}{\langle (\psi_1 + 3\psi_2).(\psi_1 + 3\psi_2) \rangle}$$

$$= \frac{\langle \psi_1 | \hat{H} | \psi_1 \rangle + 3\langle \psi_1 | \hat{H} | \psi_2 \rangle + 3\langle \psi_2 | \hat{H} | \psi_1 \rangle + 9\langle \psi_2 | \hat{H} | \psi_2 \rangle}{\langle \psi_1 \psi_2 \rangle + 3\langle \psi_1 \psi_2 \rangle + 3\langle \psi_2 \psi_1 \rangle + 9\langle \psi_2 \psi_2 \rangle}$$

$$= \frac{E_1\langle \psi_1 \psi_2 \rangle + 3E_2\langle \psi_1 \psi_2 \rangle + 3E_1\langle \psi_2 \psi_1 \rangle + 9E_2\langle \psi_2 \psi_2 \rangle}{\langle \psi_1 \psi_2 \rangle + 3\langle \psi_1 \psi_2 \rangle + 3\langle \psi_2 \psi_1 \rangle + 9\langle \psi_2 \psi_2 \rangle}$$

$$= \frac{E_1 + 9E_2}{1 + 9} = \frac{(E_1 + 9E_2)}{10};$$

Correct option is (a).

Q. Which of the following statements on ground state perturbation theory, involving the zeroth order energy $E_0^{(0)}$, first order energy correction $E_0^{(1)}$ and second order energy correction $E_0^{(2)}$, is false ?

(a) $E_0^{(1)}$ is the average value of perturbation operator with respect to the ground state of the zeroth order Hamiltonian.

(b) $E_0^{(1)}$ is necessarily negative.

(c) $E_0^{(2)}$ is necessarily negative.

(d) $E_0^{(0)} + E_0^{(1)}$ is an upper bound to the exact ground state energy.

Ans. First order energy correction is

$$E_0' = \int_{-\infty}^{\infty}(\psi^0|\hat{H}^0 + \hat{H}'|\psi^0)dy = E_0^0 + \Delta E$$

Hence, $E_0' \geq E_0^0$

Correct option is (a).

Q. The allowed electronic transition in fluorine molecule is

(a) $\Sigma_g^+ \to \Sigma_g^+$ (b) $\Sigma_g^+ \to \Sigma_g^-$ (c) $\Sigma_g^+ \to \Pi_u$ (d) $\Sigma_g^+ \to \Delta_u$

Ans. As per selection rule, $\Delta\Lambda = 0, \pm 1$

And g→g forbidden

Correct option is (c).

Q. One of the correct normalized sp^2 hybrid orbitals is

(a) $\frac{1}{3}\Phi_{2s} + \frac{1}{3}\Phi_{2p_x} + \frac{1}{3}\Phi_{2p_y}$

(b) $\frac{1}{2}\Phi_{2s} + \frac{\sqrt{3}}{\sqrt{8}}\Phi_{2p_x} + \frac{\sqrt{3}}{\sqrt{8}}\Phi_{2p_y}$

(c) $\frac{1}{\sqrt{3}}\Phi_{2s} + \frac{\sqrt{2}}{\sqrt{3}}\Phi_{2p_x}$

(d) $\frac{1}{\sqrt{3}}\Phi_{2s} + \frac{2}{3}\Phi_{2p_x}$

Ans. For normalized molecular orbital must follow the total probability condition

$$\psi_{sp^2} = \frac{1}{\sqrt{3}}\Phi_{2s} + \frac{\sqrt{2}}{\sqrt{3}}\Phi_{2p_x}$$

Now $\psi_{sp^2} = C_1\Phi_{2s} + C_2\Phi_{2p_x}$

Here, $C_1^2 + C_2^2 = 1$

$$\left(\frac{1}{\sqrt{3}}\right)^2 + \left(\frac{\sqrt{2}}{\sqrt{3}}\right)^2 = 1$$

If we assume ψ_1 to point towards x-axis, then the contribution of p_y orbital will be zero i.e., $C_1 = 0$

Applying normalization condition for $\psi1$ we get $a_1^2 + b_1^2 = 1$

Hence $b_1 = \frac{\sqrt{2}}{\sqrt{3}}$ as $a_1 = \frac{1}{\sqrt{3}}$

So, $\psi_1 = \psi_{sp^2} = \frac{1}{\sqrt{3}}\Phi_{2s} + \frac{\sqrt{2}}{\sqrt{3}}\Phi_{2p_x}$

Let us assume the three sp^2 orbitals are

$$\psi_1 = a_1\Phi_s + b_1\Phi_{2p_x} + c_1\Phi_{2p_y}$$

$$\psi_2 = a_2\Phi_s + b_2\Phi_{2p_x} + c_2\Phi_{2p_y}$$

$$\psi_3 = a_3\Phi_s + b_3\Phi_{2p_x} + c_3\Phi_{2p_y}$$

For which $a_1^2 + a_2^2 + a_3^2 = 1$ $\begin{bmatrix} \text{As we know s} - \text{orbital is spherically} \\ \text{symmetrical so } a_1 = a_2 = a_3 \end{bmatrix}$

$a_1 = a_2 = a_3 = \frac{1}{\sqrt{3}}$

So, in sp^2 hybridization, the % of s character is 33.33%

Correct option is (c).