

1. (a) A particle of mass  $m$ , in a one-dimensional box of length  $a$  can be represented by the function,  $\psi(x) = \sin \frac{n\pi x}{a}$  ( $n=1,2,3\dots$ ). Normalize the given function  $\psi(x)$  and find whether it is an eigen function of (i)  $p_x$  (ii)  $p_x^2$ .

• **Normalization of the wave function  $\psi(x)$ :**

- For a normalized wave function, the integral of  $|\psi(x)|^2$  over all space must be equal to 1.
- $\int_0^a \psi^*(x)\psi(x)dx = 1$
- $\int_0^a \left(\sin \frac{n\pi x}{a}\right) \left(\sin \frac{n\pi x}{a}\right) dx = 1$
- $\int_0^a \sin^2 \frac{n\pi x}{a} dx = 1$
- Using the identity  $\sin^2 \theta = \frac{1-\cos 2\theta}{2}$ :
- $\int_0^a \frac{1-\cos \frac{2n\pi x}{a}}{2} dx = 1$
- $\frac{1}{2} \left[ x - \frac{a}{2n\pi} \sin \frac{2n\pi x}{a} \right]_0^a = 1$
- $\frac{1}{2} \left[ \left( a - \frac{a}{2n\pi} \sin(2n\pi) \right) - \left( 0 - \frac{a}{2n\pi} \sin(0) \right) \right] = 1$
- Since  $\sin(2n\pi) = 0$  and  $\sin(0) = 0$ :
- $\frac{1}{2} [a - 0] = 1$
- $\frac{a}{2} = 1$
- This result shows that the given function is not normalized. To normalize it, we introduce a normalization constant  $N$ :
- Let  $\psi_{normalized}(x) = N \sin \frac{n\pi x}{a}$
- $\int_0^a N^2 \sin^2 \frac{n\pi x}{a} dx = 1$

- $N^2 \frac{a}{2} = 1$
- $N^2 = \frac{2}{a}$
- $N = \sqrt{\frac{2}{a}}$
- Therefore, the normalized wave function is  $\psi(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$ .
- **Eigenfunction of (i)  $p_x$ :**
  - The momentum operator in the x-direction is  $p_x = -i\hbar \frac{d}{dx}$ .
  - Apply the operator to the wave function  $\psi(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$ :
  - $p_x \psi(x) = -i\hbar \frac{d}{dx} \left( \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} \right)$
  - $p_x \psi(x) = -i\hbar \sqrt{\frac{2}{a}} \frac{n\pi}{a} \cos \frac{n\pi x}{a}$
  - For  $\psi(x)$  to be an eigenfunction of  $p_x$ , the result must be a constant (eigenvalue) multiplied by the original function  $\psi(x)$ .
  - Since  $\cos \frac{n\pi x}{a}$  is not a constant multiple of  $\sin \frac{n\pi x}{a}$ ,  $\psi(x)$  is **not** an eigenfunction of  $p_x$ .
- **Eigenfunction of (ii)  $p_x^2$ :**
  - The operator  $p_x^2$  is  $(-i\hbar \frac{d}{dx})^2 = -\hbar^2 \frac{d^2}{dx^2}$ .
  - Apply the operator to the wave function  $\psi(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$ :
  - $p_x^2 \psi(x) = -\hbar^2 \frac{d^2}{dx^2} \left( \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} \right)$

- First derivative:  $\frac{d}{dx} \left( \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} \right) = \sqrt{\frac{2}{a}} \frac{n\pi}{a} \cos \frac{n\pi x}{a}$
  - Second derivative:  $\frac{d^2}{dx^2} \left( \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} \right) = \sqrt{\frac{2}{a}} \frac{n\pi}{a} \left( -\frac{n\pi}{a} \sin \frac{n\pi x}{a} \right)$
  - $\frac{d^2}{dx^2} \left( \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} \right) = - \left( \frac{n\pi}{a} \right)^2 \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$
  - Now, apply  $p_x^2$ :
  - $p_x^2 \psi(x) = -\hbar^2 \left[ - \left( \frac{n\pi}{a} \right)^2 \psi(x) \right]$
  - $p_x^2 \psi(x) = \left( \frac{n^2 \pi^2 \hbar^2}{a^2} \right) \psi(x)$
  - Since the result is a constant  $\left( \frac{n^2 \pi^2 \hbar^2}{a^2} \right)$  multiplied by the original function  $\psi(x)$ ,  $\psi(x)$  is an eigenfunction of  $p_x^2$ . The eigenvalue is  $\frac{n^2 \pi^2 \hbar^2}{a^2}$ .
2. (b) Write four properties of a function to make it acceptable as a solution of Schrodinger equation. Determine whether the following functions are acceptable or not acceptable as state functions over the interval indicated, giving appropriate reasons.
- **Four properties of a function to be acceptable as a solution of Schrodinger equation:**
    - **Single-valued:** The function must have only one value for each point in space. This ensures that the probability of finding a particle at a given point is uniquely defined.
    - **Finite:** The function must be finite everywhere (not go to infinity). This is required so that the probability of finding the particle within a finite region of space is also finite and normalizable.

- **Continuous:** The function and its first derivative must be continuous everywhere. This ensures that the momentum of the particle is well-defined and that there are no abrupt changes in the wave function.
- **Square-integrable:** The integral of the square of the absolute value of the function over all space must be finite ( $\int |\psi|^2 d\tau < \infty$ ). This allows the wave function to be normalized, meaning the total probability of finding the particle somewhere in space is 1.
- **Determine whether the following functions are acceptable or not acceptable as state functions over the interval indicated:**

Function	Interval	Acceptability	Reasons
$(1 - x^2)^{-1}$	$(-1, +1)$	Not acceptable	At $x = \pm 1$ , the function becomes $\frac{1}{0}$ , which tends to infinity. Therefore, it is not finite at the boundaries of the given interval, violating the finiteness condition.
$\exp(-x)$	$(0, \infty)$	Not acceptable	For $x \rightarrow 0$ , the function approaches $\exp(0) = 1$ . For $x \rightarrow \infty$ , the function approaches $\exp(-\infty) = 0$ . It is single-valued, finite, and continuous. However, we need to check if it is square-integrable: $\int_0^\infty \exp(-2x) dx$

3. (c) Evaluate the commutator  $[L_x, L_y]$  where  $L_x$  and  $L_y$ , are the angular momentum operators along the x and y-direction respectively.

- **Commutator  $[L_x, L_y]$ :**
  - The angular momentum operators are defined as:

$$\blacksquare L_x = -i\hbar \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$$

$$\blacksquare L_y = -i\hbar \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right)$$

- The commutator is defined as  $[A, B] = AB - BA$ .
- $[L_x, L_y] = L_x L_y - L_y L_x$
- Let's apply the commutator to an arbitrary function  $f$ :
- $L_x L_y f = \left( -i\hbar \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \right) \left( -i\hbar \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \right) f$
- $L_x L_y f = -\hbar^2 \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \left( z \frac{\partial f}{\partial x} - x \frac{\partial f}{\partial z} \right)$
- Using the product rule  $(uv)' = u'v + uv'$ :
- $\frac{\partial}{\partial z} \left( z \frac{\partial f}{\partial x} - x \frac{\partial f}{\partial z} \right) = \left( 1 \cdot \frac{\partial f}{\partial x} + z \frac{\partial^2 f}{\partial z \partial x} \right) - \left( 0 \cdot \frac{\partial f}{\partial z} + x \frac{\partial^2 f}{\partial z^2} \right) = \frac{\partial f}{\partial x} + z \frac{\partial^2 f}{\partial z \partial x} - x \frac{\partial^2 f}{\partial z^2}$
- $\frac{\partial}{\partial y} \left( z \frac{\partial f}{\partial x} - x \frac{\partial f}{\partial z} \right) = z \frac{\partial^2 f}{\partial y \partial x} - x \frac{\partial^2 f}{\partial y \partial z}$
- So,  $L_x L_y f = -\hbar^2 \left[ y \left( \frac{\partial f}{\partial x} + z \frac{\partial^2 f}{\partial z \partial x} - x \frac{\partial^2 f}{\partial z^2} \right) - z \left( z \frac{\partial^2 f}{\partial y \partial x} - x \frac{\partial^2 f}{\partial y \partial z} \right) \right]$
- $L_x L_y f = -\hbar^2 \left[ y \frac{\partial f}{\partial x} + yz \frac{\partial^2 f}{\partial z \partial x} - yx \frac{\partial^2 f}{\partial z^2} - z^2 \frac{\partial^2 f}{\partial y \partial x} + zx \frac{\partial^2 f}{\partial y \partial z} \right]$
- Now, calculate  $L_y L_x f$ :
- $L_y L_x f = \left( -i\hbar \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \right) \left( -i\hbar \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \right) f$
- $L_y L_x f = -\hbar^2 \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \left( y \frac{\partial f}{\partial z} - z \frac{\partial f}{\partial y} \right)$
- $\frac{\partial}{\partial x} \left( y \frac{\partial f}{\partial z} - z \frac{\partial f}{\partial y} \right) = y \frac{\partial^2 f}{\partial x \partial z} - z \frac{\partial^2 f}{\partial x \partial y}$
- $\frac{\partial}{\partial z} \left( y \frac{\partial f}{\partial z} - z \frac{\partial f}{\partial y} \right) = \left( y \frac{\partial^2 f}{\partial z^2} \right) - \left( 1 \cdot \frac{\partial f}{\partial y} + z \frac{\partial^2 f}{\partial z \partial y} \right) = y \frac{\partial^2 f}{\partial z^2} - \frac{\partial f}{\partial y} - z \frac{\partial^2 f}{\partial z \partial y}$

- So,  $L_y L_x f = -\hbar^2 \left[ z \left( y \frac{\partial^2 f}{\partial x \partial z} - z \frac{\partial^2 f}{\partial x \partial y} \right) - x \left( y \frac{\partial^2 f}{\partial z^2} - \frac{\partial f}{\partial y} - z \frac{\partial^2 f}{\partial z \partial y} \right) \right]$
- $L_y L_x f = -\hbar^2 \left[ zy \frac{\partial^2 f}{\partial x \partial z} - z^2 \frac{\partial^2 f}{\partial x \partial y} - xy \frac{\partial^2 f}{\partial z^2} + x \frac{\partial f}{\partial y} + xz \frac{\partial^2 f}{\partial z \partial y} \right]$
- Now, subtract  $L_y L_x f$  from  $L_x L_y f$ :
- $[L_x, L_y]f = L_x L_y f - L_y L_x f$
- Notice that the second-order partial derivatives cancel out due to equality of mixed partials (e.g.,  $\frac{\partial^2 f}{\partial z \partial x} = \frac{\partial^2 f}{\partial x \partial z}$ ), except for the  $yx \frac{\partial^2 f}{\partial z^2}$  terms which become  $-yx \frac{\partial^2 f}{\partial z^2} - (-xy \frac{\partial^2 f}{\partial z^2}) = 0$ .
- The terms that remain are:
- $[L_x, L_y]f = -\hbar^2 \left[ y \frac{\partial f}{\partial x} - x \frac{\partial f}{\partial y} \right]$
- $[L_x, L_y]f = i^2 \hbar^2 \left[ y \frac{\partial f}{\partial x} - x \frac{\partial f}{\partial y} \right]$  (This step is incorrect,  $i^2 = -1$ , so  $-\hbar^2$  is correct).
- Let's rewrite the expression for  $L_z$ :
- $L_z = -i\hbar \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$
- We have  $-\hbar^2 \left[ y \frac{\partial f}{\partial x} - x \frac{\partial f}{\partial y} \right] = i\hbar \left( -i\hbar \left[ y \frac{\partial}{\partial x} - x \frac{\partial}{\partial y} \right] \right) f$
- This is incorrect. Let's re-examine the terms that don't cancel:
- From  $L_x L_y f$ :  $-\hbar^2 \left[ y \frac{\partial f}{\partial x} \right]$
- From  $L_y L_x f$ :  $-\hbar^2 \left[ x \frac{\partial f}{\partial y} \right]$
- So,  $[L_x, L_y]f = -\hbar^2 \left[ y \frac{\partial f}{\partial x} \right] - \left( -\hbar^2 \left[ x \frac{\partial f}{\partial y} \right] \right)$
- $[L_x, L_y]f = -\hbar^2 \left[ y \frac{\partial f}{\partial x} - x \frac{\partial f}{\partial y} \right]$

- We know  $L_z = -i\hbar \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right) = i\hbar \left( y \frac{\partial}{\partial x} - x \frac{\partial}{\partial y} \right)$
  - Therefore,  $iL_z = i \left( i\hbar \left( y \frac{\partial}{\partial x} - x \frac{\partial}{\partial y} \right) \right) = -\hbar \left( y \frac{\partial}{\partial x} - x \frac{\partial}{\partial y} \right)$
  - This means  $\hbar \left( y \frac{\partial}{\partial x} - x \frac{\partial}{\partial y} \right) = -iL_z$ .
  - So,  $-\hbar^2 \left[ y \frac{\partial f}{\partial x} - x \frac{\partial f}{\partial y} \right] = -i\hbar \left( -i\hbar \left[ y \frac{\partial}{\partial x} - x \frac{\partial}{\partial y} \right] \right) f$
  - $= -i\hbar L_z f$
  - Thus,  $[L_x, L_y] = i\hbar L_z$ .
2. (a) Are the following functions eigen functions of the operator  $\frac{d^2}{dx^2}$ ? If so, give the eigen value.

- **Operator:**  $\hat{A} = \frac{d^2}{dx^2}$
- **(i)  $f(x) = \exp\left(-\frac{x^2}{2}\right)$** 
  - First derivative:  $\frac{df}{dx} = \frac{d}{dx} \left( e^{-x^2/2} \right) = e^{-x^2/2} \cdot (-x) = -xe^{-x^2/2}$
  - Second derivative:  $\frac{d^2f}{dx^2} = \frac{d}{dx} \left( -xe^{-x^2/2} \right)$
  - Using the product rule  $(uv)' = u'v + uv'$ :
  - $\frac{d^2f}{dx^2} = (-1)e^{-x^2/2} + (-x)(-xe^{-x^2/2})$
  - $\frac{d^2f}{dx^2} = -e^{-x^2/2} + x^2e^{-x^2/2}$
  - $\frac{d^2f}{dx^2} = (x^2 - 1)e^{-x^2/2}$
  - For  $f(x)$  to be an eigenfunction,  $\frac{d^2f}{dx^2}$  must be equal to a constant multiplied by  $f(x)$ .

- Since  $(x^2 - 1)$  is not a constant,  $f(x) = \exp\left(-\frac{x^2}{2}\right)$  is **not** an eigenfunction of  $\frac{d^2}{dx^2}$ .

- **(ii)  $\cos 2x$**

- First derivative:  $\frac{d}{dx}(\cos 2x) = -2\sin 2x$
- Second derivative:  $\frac{d^2}{dx^2}(\cos 2x) = \frac{d}{dx}(-2\sin 2x) = -2(2\cos 2x) = -4\cos 2x$
- Here,  $\frac{d^2}{dx^2}(\cos 2x) = -4(\cos 2x)$ .
- The result is a constant  $(-4)$  multiplied by the original function  $(\cos 2x)$ .
- Therefore,  $\cos 2x$  **is** an eigenfunction of  $\frac{d^2}{dx^2}$ , and the eigenvalue is **-4**.

3. (b) Consider a particle of mass 'm' in a cubic box of edge length 'L'. What is the degeneracy of the level that has energy three times the lowest energy? Write the mathematical expressions for the degenerate wavefunctions.

- **Energy of a particle in a 3D cubic box:**

- $E = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2)$ , where  $n_x, n_y, n_z$  are positive integers (1, 2, 3, ...).

- **Lowest energy level (ground state):**

- For the lowest energy,  $n_x = 1, n_y = 1, n_z = 1$ .
- $E_{111} = \frac{h^2}{8mL^2}(1^2 + 1^2 + 1^2) = \frac{3h^2}{8mL^2}$ .

- **Energy level three times the lowest energy:**

- We are looking for an energy level  $E'$  such that  $E' = 3 \times E_{111}$ .



- $E' = 3 \times \frac{3h^2}{8mL^2} = \frac{9h^2}{8mL^2}$ .
- So, we need to find combinations of  $(n_x, n_y, n_z)$  such that  $n_x^2 + n_y^2 + n_z^2 = 9$ .
- **Possible combinations of  $(n_x, n_y, n_z)$  (positive integers):**
  - $(1^2 + 2^2 + 2^2) = 1 + 4 + 4 = 9$
  - Possible permutations of (1, 2, 2) are:
    - (1, 2, 2)
    - (2, 1, 2)
    - (2, 2, 1)
  - Are there any other combinations?
    - (3, 0, 0) is not allowed as quantum numbers must be positive integers.
    - The next possible set of numbers would involve values larger than 2, but  $3^2 = 9$ , so any other number would exceed 9 immediately. Thus, (1,2,2) and its permutations are the only possibilities.
- **Degeneracy:**
  - The degeneracy of this energy level is the number of distinct sets of quantum numbers that give the same energy.
  - In this case, the degeneracy is **3**.
- **Mathematical expressions for the degenerate wavefunctions:**
  - The general form of the wavefunction for a particle in a 3D cubic box is:

$$\psi_{n_x, n_y, n_z}(x, y, z) = \sqrt{\frac{8}{L^3}} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right)$$

- The three degenerate wavefunctions are:

$$\psi_{1,2,2}(x, y, z) = \sqrt{\frac{8}{L^3}} \sin\left(\frac{1\pi x}{L}\right) \sin\left(\frac{2\pi y}{L}\right) \sin\left(\frac{2\pi z}{L}\right)$$

$$\psi_{2,1,2}(x, y, z) = \sqrt{\frac{8}{L^3}} \sin\left(\frac{2\pi x}{L}\right) \sin\left(\frac{1\pi y}{L}\right) \sin\left(\frac{2\pi z}{L}\right)$$

$$\psi_{2,2,1}(x, y, z) = \sqrt{\frac{8}{L^3}} \sin\left(\frac{2\pi x}{L}\right) \sin\left(\frac{2\pi y}{L}\right) \sin\left(\frac{1\pi z}{L}\right)$$

4. (c) If A and B are two atoms bonding along the z-axis predict, giving reasons, which of the following atomic orbitals can combine:

- **Principle of Orbital Combination (LCAO-MO theory):**

- Atomic orbitals can combine to form molecular orbitals if they satisfy three conditions:
  - Proper Symmetry:** The atomic orbitals must have the correct symmetry with respect to the internuclear axis (here, the z-axis). Their overlap integral must be non-zero.
  - Comparable Energy:** The atomic orbitals must have comparable energies. Orbitals with very different energies will not combine effectively.
  - Maximum Overlap:** The atomic orbitals must overlap significantly. The greater the overlap, the stronger the bond formed.

- **Predicting orbital combination along the z-axis:**

- (i)  $\varphi_{2s}^A$  and  $\varphi_{2pz}^B$ 
  - $\varphi_{2s}^A$ : This is a spherical orbital, so it has spherical symmetry around atom A.

- $\varphi_{2pz}^B$ : This orbital has a lobe along the z-axis (positive on one side, negative on the other, with a node in the xy-plane).
- **Reason:** When  $\varphi_{2s}^A$  and  $\varphi_{2pz}^B$  approach along the z-axis, the positive lobe of  $2p_z$  will overlap with the  $2s$  orbital (which has a positive phase). The negative lobe of  $2p_z$  will also overlap with the  $2s$  orbital, but this overlap will be destructive. However, the overall overlap integral is non-zero. For  $\sigma$  bond formation, a head-on overlap is required. The  $2s$  orbital has spherical symmetry, and the  $2p_z$  orbital is aligned along the z-axis. They can form a  $\sigma$  bond through head-on overlap.
- **Can combine.** (They can combine to form a  $\sigma$  molecular orbital, provided their energies are comparable, which they generally are for  $2s$  and  $2p_z$  from different atoms.)
- (ii)  $\varphi_{1s}^A$  and  $\varphi_{2s}^B$ 
  - $\varphi_{1s}^A$ : This is a spherical orbital.
  - $\varphi_{2s}^B$ : This is also a spherical orbital (though with a radial node).
  - **Reason:** Both are spherical orbitals, so they have the correct symmetry for head-on overlap along the z-axis (or any axis for that matter). They will form a  $\sigma$  bond. However, the crucial factor here is the **comparability of energy**.  $1s$  orbitals are significantly lower in energy than  $2s$  orbitals.
  - **Cannot combine effectively.** (While they have correct symmetry and can overlap, the energy difference between a  $1s$  orbital of one atom and a  $2s$  orbital of another atom is usually too large for effective combination.)

○ (iii)  $\varphi_{2px}^A$  and  $\varphi_{2pz}^B$

- $\varphi_{2px}^A$ : This orbital has lobes along the x-axis.
- $\varphi_{2pz}^B$ : This orbital has lobes along the z-axis.
- **Reason:** The bonding occurs along the z-axis. For  $\varphi_{2px}^A$  and  $\varphi_{2pz}^B$  to combine, they must have proper symmetry with respect to the z-axis. The  $2p_x$  orbital is perpendicular to the z-axis (internuclear axis). Its positive and negative lobes will overlap equally and oppositely with the  $2p_z$  orbital, leading to zero net overlap (due to symmetry mismatch). There will be no net constructive or destructive interference.
- **Cannot combine.** (They have inappropriate symmetry for combination along the z-axis, as their overlap integral would be zero.)

3. (a) Write the expression for the Hamiltonian operator for the helium atom explaining briefly all the terms involved. Simplify this expression using the Born Oppenheimer approximation. Write the expression for the corresponding Schrodinger's equation.

• **Hamiltonian operator for the helium atom:**

- The Hamiltonian operator (denoted as  $\hat{H}$ ) represents the total energy of the system. For the helium atom, it consists of kinetic energy terms for the nucleus and electrons, and potential energy terms for electron-nucleus attraction and electron-electron repulsion.
- Let the nucleus be denoted by N, and the two electrons by 1 and 2.
- Let  $M$  be the mass of the nucleus,  $m_e$  be the mass of an electron.

- Let  $R$  be the position vector of the nucleus,  $r_1$  and  $r_2$  be the position vectors of electron 1 and electron 2, respectively.
- The nuclear charge is  $Z = +2$ .
- The distance between the nucleus and electron 1 is  $|r_1 - R|$ .
- The distance between the nucleus and electron 2 is  $|r_2 - R|$ .
- The distance between electron 1 and electron 2 is  $|r_1 - r_2|$ .
- $$\hat{H} = -\frac{\hbar^2}{2M} \nabla_N^2 - \frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0|r_1-R|} - \frac{Ze^2}{4\pi\epsilon_0|r_2-R|} + \frac{e^2}{4\pi\epsilon_0|r_1-r_2|}$$
- **Explanation of terms:**

- $-\frac{\hbar^2}{2M} \nabla_N^2$ : This is the **kinetic energy operator for the nucleus**.  $\nabla_N^2$  is the Laplacian operator for the nucleus.
- $-\frac{\hbar^2}{2m_e} \nabla_1^2$ : This is the **kinetic energy operator for electron 1**.  $\nabla_1^2$  is the Laplacian operator for electron 1.
- $-\frac{\hbar^2}{2m_e} \nabla_2^2$ : This is the **kinetic energy operator for electron 2**.  $\nabla_2^2$  is the Laplacian operator for electron 2.
- $-\frac{Ze^2}{4\pi\epsilon_0|r_1-R|}$ : This term represents the **attractive potential energy between the nucleus and electron 1**.  $Z$  is the nuclear charge (2 for helium),  $e$  is the elementary charge,  $\epsilon_0$  is the permittivity of free space.
- $-\frac{Ze^2}{4\pi\epsilon_0|r_2-R|}$ : This term represents the **attractive potential energy between the nucleus and electron 2**.
- $+\frac{e^2}{4\pi\epsilon_0|r_1-r_2|}$ : This term represents the **repulsive potential energy between electron 1 and electron 2**.

- **Simplification using the Born-Oppenheimer Approximation:**

- The Born-Oppenheimer approximation is based on the significant difference in mass between the nucleus and electrons ( $M \gg m_e$ ). Due to this mass difference, electrons move much faster than the nucleus.
- The approximation assumes that the nuclei are essentially stationary compared to the electrons. This allows us to decouple the electronic and nuclear motions.
- **Simplification:**
  - The kinetic energy term of the nucleus ( $-\frac{\hbar^2}{2M} \nabla_N^2$ ) is set to zero or treated as a constant, effectively considering the nucleus as fixed in space.
  - The nuclear coordinates (R) are treated as parameters rather than variables. We can set the nucleus at the origin (R=0) for convenience.
- **Simplified Hamiltonian for the electronic motion:**
  - With the nucleus fixed at the origin,  $|r_1 - R| = r_1$  and  $|r_2 - R| = r_2$ .
  - $$\hat{H}_{elec} = -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 |r_1 - r_2|}$$

• **Corresponding Schrodinger's Equation:**

- The time-independent Schrodinger equation is given by  $\hat{H}\Psi = E\Psi$ .
- For the electronic part of the helium atom under Born-Oppenheimer approximation:
- $$\left( -\frac{\hbar^2}{2m_e} \nabla_1^2 - \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 |r_1 - r_2|} \right) \psi_{elec}(r_1, r_2) = E_{elec} \psi_{elec}(r_1, r_2)$$

- Here,  $\psi_{elec}(r_1, r_2)$  is the electronic wavefunction which depends only on the coordinates of the two electrons, and  $E_{elec}$  is the electronic energy.
4. (b) Evaluate the expectation value of the radius,  $\langle r \rangle$ , at which the electron in the ground state of Hydrogen atom ( $Z=1$ ) is found. Given the wave function for this state is  $\psi_{1,0,0} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{3/2} \exp\left(-\frac{Zr}{a_0}\right)$  where  $a_0$  is the Bohr radius and  $\int_0^\infty r^n \exp(-ar) dr = \frac{n!}{a^{(n+1)}}$ .

• **Expectation Value of an Operator:**

- The expectation value of an observable (represented by an operator  $\hat{A}$ ) for a normalized wavefunction  $\psi$  is given by  $\langle A \rangle = \int \psi^* \hat{A} \psi d\tau$ .
- Here, we want to find  $\langle r \rangle$ , so the operator is simply  $r$ .
- The given wavefunction is for the ground state of the Hydrogen atom ( $Z = 1$ ):

$$\psi_{1,0,0} = \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \exp\left(-\frac{r}{a_0}\right)$$

- Since this is a radial function, the volume element  $d\tau$  in spherical coordinates is  $r^2 \sin\theta dr d\theta d\phi$ . The integration over angular parts for a purely radial function is  $4\pi$ .
- So,  $\langle r \rangle = \int_0^\infty \psi_{1,0,0}^* r \psi_{1,0,0} (4\pi r^2) dr$
- $\langle r \rangle = \int_0^\infty \left(\frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \exp\left(-\frac{r}{a_0}\right)\right) r \left(\frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \exp\left(-\frac{r}{a_0}\right)\right) (4\pi r^2) dr$
- $\langle r \rangle = \frac{1}{\pi} \left(\frac{1}{a_0}\right)^3 \int_0^\infty r \exp\left(-\frac{2r}{a_0}\right) (4\pi r^2) dr$
- $\langle r \rangle = \frac{4\pi}{\pi a_0^3} \int_0^\infty r^3 \exp\left(-\frac{2r}{a_0}\right) dr$

- $\langle r \rangle = \frac{4}{a_0^3} \int_0^\infty r^3 \exp\left(-\frac{2r}{a_0}\right) dr$
  - **Using the given integral formula:**
    - $\int_0^\infty r^n \exp(-ar) dr = \frac{n!}{a^{(n+1)}}$
    - In our case,  $n = 3$  and  $a = \frac{2}{a_0}$ .
    - So,  $\int_0^\infty r^3 \exp\left(-\frac{2r}{a_0}\right) dr = \frac{3!}{\left(\frac{2}{a_0}\right)^{(3+1)}} = \frac{6}{\left(\frac{2}{a_0}\right)^4} = \frac{6}{\frac{16}{a_0^4}} = \frac{6a_0^4}{16} = \frac{3a_0^4}{8}$
  - **Substitute back into the expression for  $\langle r \rangle$ :**
    - $\langle r \rangle = \frac{4}{a_0^3} \times \frac{3a_0^4}{8}$
    - $\langle r \rangle = \frac{12a_0^4}{8a_0^3}$
    - $\langle r \rangle = \frac{3}{2}a_0$
    - Therefore, the expectation value of the radius for an electron in the ground state of the Hydrogen atom is  $\frac{3}{2}a_0$ .
5. (c) Write the electronic configuration of  $H_2$ ,  $H_2^+$  and hypothetical  $H_2^-$  species using molecular orbital theory. Explain why  $He_2^+$  exist whereas  $He_2$  does not.
- **Electronic Configuration using Molecular Orbital Theory:**
    - **$H_2$  (Hydrogen Molecule):**
      - Number of electrons: Each H atom has 1 electron, so  $H_2$  has a total of 2 electrons.
      - Atomic orbitals involved:  $1s$  from each H atom.
      - Molecular orbitals formed:  $\sigma_{1s}$  (bonding) and  $\sigma_{1s}^*$  (antibonding).



- Electronic configuration:  $(\sigma_{1s})^2$
- Bond order =  $\frac{1}{2}$  (Number of bonding electrons - Number of antibonding electrons) =  $\frac{1}{2}(2 - 0) = 1$ . This indicates a stable single bond.
- **H<sub>2</sub><sup>+</sup> (Hydrogen Molecular Ion):**
  - Number of electrons: One H atom contributes 1 electron, the other is H<sup>+</sup> (0 electrons), so H<sub>2</sub><sup>+</sup> has a total of 1 electron.
  - Atomic orbitals involved: 1s from each H atom.
  - Molecular orbitals formed:  $\sigma_{1s}$  and  $\sigma_{1s}^*$ .
  - Electronic configuration:  $(\sigma_{1s})^1$
  - Bond order =  $\frac{1}{2}(1 - 0) = \frac{1}{2}$ . This indicates a half-bond, which is stable enough to exist.
- **H<sub>2</sub><sup>-</sup> (Hypothetical Hydrogen Molecular Anion):**
  - Number of electrons: Each H atom has 1 electron, plus one extra electron for the negative charge, so H<sub>2</sub><sup>-</sup> has a total of 3 electrons.
  - Atomic orbitals involved: 1s from each H atom.
  - Molecular orbitals formed:  $\sigma_{1s}$  and  $\sigma_{1s}^*$ .
  - Electronic configuration:  $(\sigma_{1s})^2(\sigma_{1s}^*)^1$
  - Bond order =  $\frac{1}{2}(2 - 1) = \frac{1}{2}$ . This also indicates a half-bond, suggesting it could exist, although it would be less stable than H<sub>2</sub>.
- **Explanation for He<sub>2</sub><sup>+</sup> existence and He<sub>2</sub> non-existence:**
  - **He<sub>2</sub> (Helium Molecule):**

- Number of electrons: Each He atom has 2 electrons, so  $\text{He}_2$  has a total of 4 electrons.
  - Atomic orbitals involved:  $1s$  from each He atom.
  - Molecular orbitals formed:  $\sigma_{1s}$  (bonding) and  $\sigma_{1s}^*$  (antibonding).
  - Electronic configuration:  $(\sigma_{1s})^2(\sigma_{1s}^*)^2$
  - Bond order =  $\frac{1}{2}(2 - 2) = 0$ .
  - **Reason for non-existence:** A bond order of zero means that there is no net bonding interaction between the two helium atoms. The attractive forces from the bonding electrons are exactly cancelled by the repulsive forces from the antibonding electrons. Therefore, the  $\text{He}_2$  molecule is not stable and does not exist under normal conditions.
- **$\text{He}_2^+$  (Helium Molecular Ion):**
- Number of electrons: One He atom has 2 electrons, the other is  $\text{He}^+$  (1 electron), so  $\text{He}_2^+$  has a total of 3 electrons.
  - Atomic orbitals involved:  $1s$  from each He atom.
  - Molecular orbitals formed:  $\sigma_{1s}$  and  $\sigma_{1s}^*$ .
  - Electronic configuration:  $(\sigma_{1s})^2(\sigma_{1s}^*)^1$
  - Bond order =  $\frac{1}{2}(2 - 1) = \frac{1}{2}$ .
  - **Reason for existence:** A bond order of  $\frac{1}{2}$  indicates that there is a net bonding interaction (a half-bond) between the two helium atoms. Although it is less stable than a full bond, this positive bond order is sufficient for the  $\text{He}_2^+$  molecular ion to exist as a stable species.

4. (a) A diatomic molecule can be treated as a simple quantum mechanical oscillator. How is the simple Schrodinger Wave Equation (SWE) modified for this system? Show that (i)  $\exp(-\beta x^2)$  is a solution to this SWE and (ii)  $E = \frac{1}{4\pi} \sqrt{\frac{k}{\mu}}$ , here  $k$  is the force constant and  $\mu$  is the reduced mass).

• **Modification of the Schrodinger Wave Equation (SWE) for a Diatomic Molecule as a Simple Harmonic Oscillator (SHO):**

- For a single particle in 1D, the SWE is  $-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$ .
- For a diatomic molecule, we consider the relative motion of the two atoms. The "mass" in the kinetic energy term is replaced by the **reduced mass** ( $\mu$ ) of the two atoms, defined as  $\mu = \frac{m_1 m_2}{m_1 + m_2}$ , where  $m_1$  and  $m_2$  are the masses of the two atoms.
- The potential energy  $V(x)$  for a simple harmonic oscillator is given by  $V(x) = \frac{1}{2} k x^2$ , where  $k$  is the force constant of the bond and  $x$  is the displacement from the equilibrium bond length.
- So, the modified Schrodinger Wave Equation for a diatomic molecule as an SHO in one dimension is:

$$\blacksquare \quad -\frac{\hbar^2}{2\mu} \frac{d^2\psi}{dx^2} + \frac{1}{2} k x^2 \psi = E\psi$$

• **(i) Show that  $\exp(-\beta x^2)$  is a solution to this SWE:**

- Let  $\psi(x) = \exp(-\beta x^2)$ .
- First derivative:  $\frac{d\psi}{dx} = \exp(-\beta x^2)(-2\beta x) = -2\beta x \exp(-\beta x^2)$
- Second derivative:  $\frac{d^2\psi}{dx^2} = \frac{d}{dx}(-2\beta x \exp(-\beta x^2))$
- Using product rule:  $\frac{d^2\psi}{dx^2} = (-2\beta) \exp(-\beta x^2) + (-2\beta x)(-2\beta x \exp(-\beta x^2))$

- $\frac{d^2\psi}{dx^2} = -2\beta\exp(-\beta x^2) + 4\beta^2 x^2 \exp(-\beta x^2)$
- $\frac{d^2\psi}{dx^2} = (4\beta^2 x^2 - 2\beta)\exp(-\beta x^2)$
- Substitute this into the SWE:
- $-\frac{\hbar^2}{2\mu}(4\beta^2 x^2 - 2\beta)\exp(-\beta x^2) + \frac{1}{2}kx^2 \exp(-\beta x^2) = E\exp(-\beta x^2)$
- Divide by  $\exp(-\beta x^2)$  (since it's never zero):
- $-\frac{\hbar^2}{2\mu}(4\beta^2 x^2 - 2\beta) + \frac{1}{2}kx^2 = E$
- $-\frac{2\hbar^2\beta^2}{\mu}x^2 + \frac{\hbar^2\beta}{\mu} + \frac{1}{2}kx^2 = E$
- Rearrange terms based on  $x^2$  and constant terms:
- $\left(\frac{1}{2}k - \frac{2\hbar^2\beta^2}{\mu}\right)x^2 + \frac{\hbar^2\beta}{\mu} = E$
- For this equation to hold for all values of  $x$ , the coefficient of  $x^2$  must be zero, and the constant term must be equal to  $E$ .
- From the coefficient of  $x^2$ :
  - $\frac{1}{2}k - \frac{2\hbar^2\beta^2}{\mu} = 0$
  - $\frac{1}{2}k = \frac{2\hbar^2\beta^2}{\mu}$
  - $\beta^2 = \frac{k\mu}{4\hbar^2}$
  - $\beta = \sqrt{\frac{k\mu}{4\hbar^2}} = \frac{1}{2\hbar}\sqrt{k\mu}$
- From the constant term:
  - $E = \frac{\hbar^2\beta}{\mu}$

- Substitute the value of  $\beta$ :
  - $E = \frac{\hbar^2}{\mu} \left( \frac{1}{2\hbar} \sqrt{k\mu} \right)$
  - $E = \frac{\hbar}{2\mu} \sqrt{k\mu} = \frac{\hbar}{2} \sqrt{\frac{k\mu}{\mu^2}} = \frac{\hbar}{2} \sqrt{\frac{k}{\mu}}$
  - This shows that  $\exp(-\beta x^2)$  is a solution if  $\beta = \frac{1}{2\hbar} \sqrt{k\mu}$  and the energy is  $E = \frac{\hbar}{2} \sqrt{\frac{k}{\mu}}$ . This is the ground state energy of the SHO.
  - (ii) Show that  $E = \frac{1}{4\pi} \sqrt{\frac{k}{\mu}}$ :
    - From the derivation above, we found  $E = \frac{\hbar}{2} \sqrt{\frac{k}{\mu}}$ .
    - We know that  $\hbar = \frac{h}{2\pi}$ .
    - Substitute  $\hbar$ :
    - $E = \frac{h/2\pi}{2} \sqrt{\frac{k}{\mu}}$
    - $E = \frac{h}{4\pi} \sqrt{\frac{k}{\mu}}$
    - This shows that  $E = \frac{h}{4\pi} \sqrt{\frac{k}{\mu}}$ , which is also commonly written as  $E = \frac{1}{2} h\nu$ , where  $\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$  is the classical oscillation frequency.
- The question asks for  $E = \frac{1}{4\pi} \sqrt{\frac{k}{\mu}}$ . This seems to be missing an 'h'. If 'h' is implicitly assumed to be part of the constant  $\frac{1}{4\pi}$ , it would be  $\frac{h}{4\pi}$ . Assuming the question intends to include  $h$ , then  $E = \frac{h}{4\pi} \sqrt{\frac{k}{\mu}}$ . If it is literally  $\frac{1}{4\pi} \sqrt{\frac{k}{\mu}}$ , then the units do not match.

Quantum mechanical energy expressions always involve  $\hbar$  or  $h$ . It's highly probable the  $h$  is missing in the question's formula.

Assuming it's  $E = \frac{h}{4\pi} \sqrt{\frac{k}{\mu}}$ , then the derivation above proves it.

5. (b) What is the degeneracy of each of the following energy levels of H atom?

• **Energy levels of Hydrogen atom:**

- The energy of an electron in a hydrogen atom depends only on the principal quantum number  $n$ :  $E_n = -\frac{Z^2 e^2}{8\pi\epsilon_0 a_0 n^2}$ . For hydrogen,

$$Z = 1, \text{ so } E_n = -\frac{e^2}{8\pi\epsilon_0 a_0 n^2}.$$

- The degeneracy of an energy level  $E_n$  for the hydrogen atom (excluding spin degeneracy) is  $n^2$ . Including spin degeneracy, it's  $2n^2$ . Typically, for "degeneracy", unless spin is explicitly mentioned, we refer to orbital degeneracy. Let's provide both.

• (i)  $\frac{-e^2}{72\pi\epsilon_0 a_0}$

- We compare this to the general formula  $E_n = -\frac{e^2}{8\pi\epsilon_0 a_0 n^2}$ .

- So,  $\frac{1}{n^2} = \frac{1}{9}$  (because  $72 = 8 \times 9$ )

- $n^2 = 9$

- $n = 3$  (since  $n$  must be a positive integer).

- **Orbital degeneracy:**  $n^2 = 3^2 = 9$ .

- **Total degeneracy (including spin):**  $2n^2 = 2 \times 9 = 18$ .

• (ii)  $\frac{-e^2}{128\pi\epsilon_0 a_0}$

- We compare this to  $E_n = -\frac{e^2}{8\pi\epsilon_0 a_0 n^2}$ .

- So,  $\frac{1}{n^2} = \frac{1}{16}$  (because  $128 = 8 \times 16$ )
  - $n^2 = 16$
  - $n = 4$  (since  $n$  must be a positive integer).
  - **Orbital degeneracy:**  $n^2 = 4^2 = 16$ .
  - **Total degeneracy (including spin):**  $2n^2 = 2 \times 16 = 32$ .
6. (c) Explain and calculate zero point energy (ZPE) of an electron in a one dimensional box of infinite height and 1 Å length. State the Bohr's - Correspondence principle.
- **Zero Point Energy (ZPE) of an electron in a one-dimensional box of infinite height and 1 Å length:**
    - **Explanation of ZPE:**
      - Zero Point Energy (ZPE) is the minimum possible energy that a quantum mechanical system can possess.
      - According to the Heisenberg Uncertainty Principle, it is impossible to simultaneously know both the exact position and momentum of a particle.
      - If a particle were to have exactly zero energy, it would imply that its momentum is precisely zero, and its position is precisely known (as it would be perfectly stationary at the bottom of a potential well). This would violate the uncertainty principle.
      - Therefore, even at absolute zero temperature (0 K), a quantum mechanical system retains a minimum amount of vibrational or translational energy, known as its zero-point energy. This energy prevents the particle from being perfectly localized and having zero momentum.
      - For a particle in a box, the existence of ZPE means the particle is never truly at rest and its energy is never zero.

○ **Calculation of ZPE:**

- The energy levels for a particle in a one-dimensional box of length  $L$  are given by:  $E_n = \frac{n^2 h^2}{8mL^2}$ , where  $n = 1, 2, 3, \dots$
- The lowest energy level corresponds to  $n = 1$ . This is the zero-point energy.
- Given:
  - Mass of electron,  $m = 9.109 \times 10^{-31}$  kg
  - Length of the box,  $L = 1 \text{ \AA} = 1 \times 10^{-10}$  m
  - Planck's constant,  $h = 6.626 \times 10^{-34}$  J s
- For  $n = 1$ :

$$\bullet \text{ } ZPE = E_1 = \frac{1^2 \cdot h^2}{8mL^2} = \frac{h^2}{8mL^2}$$

$$\bullet \text{ } ZPE = \frac{(6.626 \times 10^{-34} \text{ J s})^2}{8 \times (9.109 \times 10^{-31} \text{ kg}) \times (1 \times 10^{-10} \text{ m})^2}$$

$$\bullet \text{ } ZPE = \frac{43.904 \times 10^{-68} \text{ J}^2 \text{ s}^2}{8 \times 9.109 \times 10^{-31} \text{ kg} \times 1 \times 10^{-20} \text{ m}^2}$$

$$\bullet \text{ } ZPE = \frac{43.904 \times 10^{-68}}{72.872 \times 10^{-51}} \text{ J}$$

$$\bullet \text{ } ZPE \approx 0.6025 \times 10^{-17} \text{ J}$$

$$\bullet \text{ } ZPE \approx 6.025 \times 10^{-18} \text{ J}$$

• **Bohr's Correspondence Principle:**

- Bohr's Correspondence Principle states that in the limit of large quantum numbers, the predictions of quantum mechanics must agree with the predictions of classical mechanics.
- In simpler terms, as a system moves from the quantum realm to the classical realm (e.g., as its size or energy becomes large),



the quantum mechanical description should smoothly transition into the classical description.

- This principle acts as a bridge between quantum theory and classical theory, suggesting that classical physics is a limiting case of quantum physics.
  - **Example for particle in a box:** As  $n$  (the quantum number) becomes very large, the energy levels become very closely spaced, and the discrete nature of energy becomes less apparent. The quantum mechanical probability distribution for finding the particle approaches the classical uniform probability distribution.
5. (a) Show that the wave functions describing the 1s atomic orbital and the 2s atomic orbital for the hydrogen atom are orthogonal. Given that

- $\psi_{1s} = (\pi a_0^3)^{-1/2} \exp(-r/a_0)$  and
- $\psi_{2s} = \frac{1}{4\sqrt{2}\pi} \left(\frac{1}{a_0}\right)^{3/2} (2 - (r/a_0)) \exp\left(\frac{-r}{2a_0}\right)$
- where  $a_0$  is Bohr's radius and  $\int_0^\infty r^n \exp(-ar) dr = n!/a^{(n+1)}$ .

• **Orthogonality Condition:**

- Two wave functions  $\psi_i$  and  $\psi_j$  are orthogonal if their overlap integral is zero:  $\int \psi_i^* \psi_j d\tau = 0$ .
- For hydrogenic orbitals, which are real functions,  $\psi^* = \psi$ .
- The volume element in spherical coordinates is  $d\tau = r^2 \sin\theta dr d\theta d\phi$ . Since both 1s and 2s are spherically symmetric functions (only depend on  $r$ ), the angular integrals  $(\int_0^\pi \sin\theta d\theta \int_0^{2\pi} d\phi = 2 \times 2\pi = 4\pi)$  can be factored out.
- So, we need to show that  $\int_0^\infty \psi_{1s} \psi_{2s} (4\pi r^2) dr = 0$ .

• **Evaluate the integral:**

- $\psi_{1s} = \frac{1}{\sqrt{\pi a_0^3}} \exp\left(-\frac{r}{a_0}\right)$
- $\psi_{2s} = \frac{1}{4\sqrt{2}\pi a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) \exp\left(-\frac{r}{2a_0}\right)$
- $\int_0^\infty \psi_{1s} \psi_{2s} (4\pi r^2) dr = \int_0^\infty \frac{1}{\sqrt{\pi a_0^3}} \exp\left(-\frac{r}{a_0}\right) \frac{1}{4\sqrt{2}\pi a_0^{3/2}} \left(2 - \frac{r}{a_0}\right) \exp\left(-\frac{r}{2a_0}\right) (4\pi r^2) dr$
- Combine constants:
  - Constant Factor =  $\frac{1}{\sqrt{\pi a_0^3}} \cdot \frac{1}{4\sqrt{2}\pi a_0^{3/2}} \cdot 4\pi = \frac{4\pi}{4\sqrt{2}\pi^{3/2} a_0^3} = \frac{1}{\sqrt{2}\pi^{1/2} a_0^3}$
- The integral becomes:
  - $\frac{1}{\sqrt{2}\pi a_0^3} \int_0^\infty r^2 \left(2 - \frac{r}{a_0}\right) \exp\left(-\frac{r}{a_0} - \frac{r}{2a_0}\right) dr$
  - Combine exponents:  $-\frac{r}{a_0} - \frac{r}{2a_0} = -\frac{2r}{2a_0} - \frac{r}{2a_0} = -\frac{3r}{2a_0}$
  - $\frac{1}{\sqrt{2}\pi a_0^3} \int_0^\infty r^2 \left(2 - \frac{r}{a_0}\right) \exp\left(-\frac{3r}{2a_0}\right) dr$
  - Split the integral into two parts:
  - $\frac{1}{\sqrt{2}\pi a_0^3} \left[ \int_0^\infty 2r^2 \exp\left(-\frac{3r}{2a_0}\right) dr - \int_0^\infty \frac{r^3}{a_0} \exp\left(-\frac{3r}{2a_0}\right) dr \right]$
- Evaluate each integral using the formula  $\int_0^\infty r^n \exp(-ar) dr = \frac{n!}{a^{(n+1)}}$ :
  - First integral:  $2 \int_0^\infty r^2 \exp\left(-\frac{3r}{2a_0}\right) dr$ 
    - Here,  $n = 2$  and  $a = \frac{3}{2a_0}$ .
    - $2 \times \frac{2!}{\left(\frac{3}{2a_0}\right)^{2+1}} = 2 \times \frac{2}{\left(\frac{3}{2a_0}\right)^3} = 4 \times \frac{8a_0^3}{27} = \frac{32a_0^3}{27}$

○ **Second integral:**  $-\frac{1}{a_0} \int_0^\infty r^3 \exp\left(-\frac{3r}{2a_0}\right) dr$

▪ Here,  $n = 3$  and  $a = \frac{3}{2a_0}$ .

▪ 
$$-\frac{1}{a_0} \times \frac{3!}{\left(\frac{3}{2a_0}\right)^{3+1}} = -\frac{1}{a_0} \times \frac{6}{\left(\frac{3}{2a_0}\right)^4} = -\frac{1}{a_0} \times \frac{6}{\frac{81}{16a_0^4}} = -\frac{1}{a_0} \times \frac{6 \times 16a_0^4}{81} = -\frac{96a_0^3}{81} = -\frac{32a_0^3}{27}$$

• **Sum the two parts:**

○  $\frac{32a_0^3}{27} - \frac{32a_0^3}{27} = 0$

• **Conclusion:**

- Since the integral evaluates to zero, the 1s and 2s atomic orbitals for the hydrogen atom are **orthogonal**.

6. (b) Set up the Hamiltonian operator for a particle oscillating about a mean position (a simple harmonic oscillator). Explain the significance of zero-point energy of a simple harmonic oscillator.

• **Hamiltonian Operator for a Simple Harmonic Oscillator (SHO):**

- The Hamiltonian operator,  $\hat{H}$ , represents the total energy of a system. For a particle oscillating about a mean position, it consists of two parts: the kinetic energy operator and the potential energy operator.

○ **Kinetic Energy Operator ( $\hat{T}$ ):**

- For a particle of mass  $m$  moving in one dimension ( $x$ ), the classical kinetic energy is  $T = \frac{p_x^2}{2m}$ .
- In quantum mechanics, the momentum operator is  $\hat{p}_x = -i\hbar \frac{d}{dx}$ .

- So, the kinetic energy operator is  $\hat{T} = \frac{\hat{p}_x^2}{2m} = \frac{(-i\hbar \frac{d}{dx})^2}{2m} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$ .

○ **Potential Energy Operator ( $\hat{V}$ ):**

- For a simple harmonic oscillator, the restoring force is proportional to the displacement from the equilibrium position ( $F = -kx$ , where  $k$  is the force constant).
- The potential energy  $V(x)$  is given by the integral of the force with respect to displacement:  $V(x) = -\int F dx = -\int (-kx) dx = \frac{1}{2} kx^2$ .
- So, the potential energy operator is  $\hat{V} = \frac{1}{2} kx^2$ .

○ **Total Hamiltonian Operator ( $\hat{H}$ ):**

- $\hat{H} = \hat{T} + \hat{V}$
- $\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} kx^2$

• **Significance of Zero-Point Energy (ZPE) of a Simple Harmonic Oscillator:**

- The allowed energy levels for a simple harmonic oscillator are given by the formula:  $E_n = \left(n + \frac{1}{2}\right) \hbar\omega$ , where  $n = 0, 1, 2, \dots$  is the vibrational quantum number, and  $\omega = \sqrt{\frac{k}{m}}$  is the classical angular frequency of the oscillator.
- The lowest possible energy occurs when  $n = 0$ :
  - $E_0 = \left(0 + \frac{1}{2}\right) \hbar\omega = \frac{1}{2} \hbar\omega$
- This minimum energy,  $E_0$ , is the **zero-point energy (ZPE)**.
- **Significance:**

- **Violation of Classical Mechanics:** Classically, an oscillator at absolute zero temperature (0 K) would have zero energy and would be perfectly at rest at its equilibrium position. Quantum mechanically, however, the ZPE implies that even at 0 K, the oscillator is never perfectly at rest; it always has a minimum amount of vibrational energy.
  - **Heisenberg Uncertainty Principle:** The existence of ZPE is a direct consequence of the Heisenberg Uncertainty Principle ( $\Delta x \Delta p_x \geq \frac{\hbar}{2}$ ). If the oscillator had zero energy, its position and momentum would both be precisely known (position at equilibrium, zero momentum), which would violate the uncertainty principle. The ZPE ensures that there is always some uncertainty in both position and momentum.
  - **Stability of Matter:** ZPE plays a crucial role in the stability of matter. Without it, atoms could "collapse" or become perfectly static, which is not observed.
  - **Chemical Reactions:** In chemical kinetics, ZPE influences reaction rates and activation energies, as molecules retain vibrational energy even at very low temperatures.
  - **Spectroscopy:** The ZPE defines the lowest vibrational energy state, from which all other vibrational transitions originate.
7. (c) Why the quantum number 'n' cannot be assigned a zero value while solving for the particle in a 1-D box? Give the units of  $\psi^2$  for a particle in a 1-D box.
- **Why the quantum number 'n' cannot be assigned a zero value for a particle in a 1-D box:**

- The wave function for a particle in a 1-D box of length  $L$  is given

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

- The corresponding energy levels are  $E_n = \frac{n^2 h^2}{8mL^2}$ .

- If we assign  $n = 0$ :

- **Wave function:**  $\psi_0(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{0\pi x}{L}\right) = \sqrt{\frac{2}{L}} \sin(0) = 0$ .

- A wave function of  $\psi_0(x) = 0$  everywhere implies that the probability of finding the particle anywhere inside the box is zero ( $|\psi_0(x)|^2 = 0$ ). This contradicts the fundamental postulate that the particle must exist within the box. If the wave function is identically zero, it means there is no particle in the box, which is not the scenario we are trying to describe.

- **Energy:** If  $\psi_0(x) = 0$ , then  $E_0 = \frac{0^2 h^2}{8mL^2} = 0$ . This would mean the particle has zero energy and is at rest, which violates the Heisenberg Uncertainty Principle (a particle confined to a finite space must have some uncertainty in momentum, hence non-zero kinetic energy, thus non-zero total energy).

- Therefore,  $n$  must be a positive integer ( $n = 1, 2, 3, \dots$ ) to ensure a non-zero, physically meaningful wave function and a non-zero minimum energy (zero-point energy).

- **Units of  $\psi^2$  for a particle in a 1-D box:**

- The wave function  $\psi(x)$  itself has units such that  $|\psi(x)|^2 dx$  represents a probability (which is dimensionless).

- For a 1-D box, the normalization condition is  $\int_0^L |\psi(x)|^2 dx = 1$ .

- Since  $dx$  has units of length (m),  $|\psi(x)|^2$  must have units of  $\text{length}^{-1}$  to make the integral dimensionless.
  - So, the units of  $\psi^2$  (or  $|\psi|^2$ ) for a particle in a 1-D box are  $\text{m}^{-1}$  (**or  $\text{cm}^{-1}$  or  $\text{length}^{-1}$** ).
  - More precisely, for  $\psi(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$ , the unit of  $\sqrt{\frac{2}{L}}$  is  $\text{m}^{-1/2}$ .
  - Therefore, the unit of  $\psi^2$  is  $(\text{m}^{-1/2})^2 = \text{m}^{-1}$ .
6. (a) A particle of mass  $m$  exists in a one-dimensional box of length  $L$ . Using the trial wave function  $\Psi_{\text{trial}} = Nx(L-x)$  evaluate the energy associated with the lowest energy level and comment on whether this trial wave function is an acceptable function according to the variation theorem.
- **Evaluate the energy associated with the lowest energy level using the trial wave function:**
    - **Trial wave function:**  $\Psi_{\text{trial}}(x) = Nx(L-x) = N(Lx - x^2)$
    - **Hamiltonian for 1-D box:**  $\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$  (potential energy is 0 inside the box, infinite outside).
    - **According to the variation theorem, the expectation value of energy is given by:**

$$E_{\text{trial}} = \frac{\int \Psi_{\text{trial}}^* \hat{H} \Psi_{\text{trial}} dx}{\int \Psi_{\text{trial}}^* \Psi_{\text{trial}} dx}$$
    - Since  $\Psi_{\text{trial}}$  is a real function,  $\Psi_{\text{trial}}^* = \Psi_{\text{trial}}$ .
    - **Step 1: Normalize the trial function (find N).**
      - $\int_0^L N^2 (Lx - x^2)^2 dx = 1$
      - $N^2 \int_0^L (L^2 x^2 - 2Lx^3 + x^4) dx = 1$

$$\blacksquare N^2 \left[ \frac{L^2 x^3}{3} - \frac{2Lx^4}{4} + \frac{x^5}{5} \right]_0^L = 1$$

$$\blacksquare N^2 \left[ \frac{L^2 L^3}{3} - \frac{2LL^4}{4} + \frac{L^5}{5} \right] = 1$$

$$\blacksquare N^2 \left[ \frac{L^5}{3} - \frac{L^5}{2} + \frac{L^5}{5} \right] = 1$$

$$\blacksquare N^2 L^5 \left[ \frac{1}{3} - \frac{1}{2} + \frac{1}{5} \right] = 1$$

$$\blacksquare N^2 L^5 \left[ \frac{10-15+6}{30} \right] = 1$$

$$\blacksquare N^2 L^5 \left[ \frac{1}{30} \right] = 1$$

$$\blacksquare N^2 = \frac{30}{L^5} \Rightarrow N = \sqrt{\frac{30}{L^5}}$$

○ **Step 2: Calculate  $\hat{H}\Psi_{trial}$ .**

$$\blacksquare \Psi_{trial} = N(Lx - x^2)$$

$$\blacksquare \frac{d\Psi_{trial}}{dx} = N(L - 2x)$$

$$\blacksquare \frac{d^2\Psi_{trial}}{dx^2} = N(-2) = -2N$$

$$\blacksquare \hat{H}\Psi_{trial} = -\frac{\hbar^2}{2m}(-2N) = \frac{\hbar^2 N}{m}$$

○ **Step 3: Calculate the numerator  $\int \Psi_{trial}^* \hat{H}\Psi_{trial} dx$ .**

$$\blacksquare \int_0^L N(Lx - x^2) \left( \frac{\hbar^2 N}{m} \right) dx$$

$$\blacksquare = \frac{\hbar^2 N^2}{m} \int_0^L (Lx - x^2) dx$$

$$\blacksquare = \frac{\hbar^2 N^2}{m} \left[ \frac{Lx^2}{2} - \frac{x^3}{3} \right]_0^L$$

$$\blacksquare = \frac{\hbar^2 N^2}{m} \left[ \frac{L^3}{2} - \frac{L^3}{3} \right]$$



$$\blacksquare = \frac{\hbar^2 N^2}{m} \left[ \frac{3L^3 - 2L^3}{6} \right] = \frac{\hbar^2 N^2}{m} \frac{L^3}{6}$$

$$\blacksquare \text{ Substitute } N^2 = \frac{30}{L^5}:$$

$$\blacksquare = \frac{\hbar^2}{m} \frac{30}{L^5} \frac{L^3}{6} = \frac{5\hbar^2}{mL^2}$$

- **Step 4: Calculate the denominator**  $\int \Psi_{trial}^* \Psi_{trial} dx$ .

- This is the normalization integral, which we set to 1.

- **Step 5: Calculate**  $E_{trial}$ .

$$\blacksquare E_{trial} = \frac{5\hbar^2}{mL^2} = \frac{5(h/2\pi)^2}{mL^2} = \frac{5h^2}{4\pi^2 mL^2}$$

- **Compare with the exact ground state energy:**

- The exact ground state energy for a particle in a 1-D box is  $E_1 = \frac{h^2}{8mL^2}$ .

- Let's convert our  $E_{trial}$  to be in terms of  $h$ :

$$\blacksquare E_{trial} = \frac{5 \cdot (h/2\pi)^2}{mL^2} = \frac{5h^2}{4\pi^2 mL^2}$$

- Numerically,  $\frac{5}{4\pi^2} \approx \frac{5}{4 \times (3.14159)^2} \approx \frac{5}{4 \times 9.8696} \approx \frac{5}{39.478} \approx 0.1266 \frac{h^2}{mL^2}$ .

- The exact value is  $\frac{1}{8} = 0.125 \frac{h^2}{mL^2}$ .

- So,  $E_{trial} = \frac{5h^2}{4\pi^2 mL^2} \approx 1.013E_1$ . This is slightly higher than the true ground state energy.

- **Comment on whether this trial wave function is an acceptable function according to the variation theorem:**

- **Variation Theorem:** The variation theorem states that the energy calculated using any approximate (trial) wave function

will always be greater than or equal to the true ground state energy of the system ( $E_{trial} \geq E_{exact}$ ).

○ **Acceptability of the trial function:**

- The trial wave function  $\Psi_{trial}(x) = Nx(L - x)$  satisfies the boundary conditions of a particle in a box:
  - At  $x = 0$ ,  $\Psi_{trial}(0) = N(0)(L - 0) = 0$ .
  - At  $x = L$ ,  $\Psi_{trial}(L) = N(L)(L - L) = 0$ .
- It is also continuous, single-valued, and finite within the box. Its first and second derivatives are also continuous.
- Our calculated energy  $E_{trial} = \frac{5h^2}{4\pi^2mL^2}$  is indeed slightly greater than the exact ground state energy  $E_1 = \frac{h^2}{8mL^2}$ .
- Therefore, this trial wave function is an **acceptable** function according to the variation theorem, as it yields an energy value consistent with the theorem's statement. It provides a good approximation to the ground state energy.

7. (b) Show that operators, corresponding to  $\hat{x}$  and  $\hat{p}_x$  do not commute. Give the physical significance of your result.

• **Show that  $\hat{x}$  and  $\hat{p}_x$  do not commute:**

- The position operator is  $\hat{x} = x$ .
- The momentum operator in the x-direction is  $\hat{p}_x = -i\hbar \frac{d}{dx}$ .
- To check if they commute, we evaluate their commutator:  

$$[\hat{x}, \hat{p}_x] = \hat{x}\hat{p}_x - \hat{p}_x\hat{x}.$$
- We apply this to an arbitrary function  $f(x)$ :
- $$[\hat{x}, \hat{p}_x]f(x) = \left(x \left(-i\hbar \frac{d}{dx}\right)\right)f(x) - \left(\left(-i\hbar \frac{d}{dx}\right)x\right)f(x)$$

- $= -i\hbar x \frac{df}{dx} - (-i\hbar) \frac{d}{dx}(xf(x))$
- Using the product rule for the second term:  $\frac{d}{dx}(uv) = u'v + uv'$ .
- $\frac{d}{dx}(xf(x)) = (1)f(x) + x \frac{df}{dx}$
- So,  $[\hat{x}, \hat{p}_x]f(x) = -i\hbar x \frac{df}{dx} - (-i\hbar) \left( f(x) + x \frac{df}{dx} \right)$
- $= -i\hbar x \frac{df}{dx} + i\hbar f(x) + i\hbar x \frac{df}{dx}$
- The terms  $-i\hbar x \frac{df}{dx}$  and  $+i\hbar x \frac{df}{dx}$  cancel out.
- $[\hat{x}, \hat{p}_x]f(x) = i\hbar f(x)$
- Therefore, the commutator is  $[\hat{x}, \hat{p}_x] = i\hbar$ .
- Since the commutator is not zero (it is  $i\hbar$ ), the operators  $\hat{x}$  and  $\hat{p}_x$  **do not commute**.
- **Physical significance of the result:**
  - The fact that  $[\hat{x}, \hat{p}_x] \neq 0$  is a direct and fundamental statement of the **Heisenberg Uncertainty Principle**.
  - **Non-Commuting Operators and Uncertainty:** In quantum mechanics, if two operators do not commute, it means that the corresponding physical observables cannot be measured simultaneously with arbitrary precision. There is an inherent, fundamental limit to how accurately their values can be known at the same time.
  - **Position and Momentum:** For position ( $x$ ) and momentum ( $p_x$ ), their non-commutativity implies that if you precisely know the position of a particle, you will have a high uncertainty in its momentum, and vice-versa. You cannot precisely define both simultaneously.

- **Classical vs. Quantum:** Classically, one can simultaneously determine both the position and momentum of a particle with infinite precision. However, at the quantum level, this is not possible due to the wave-particle duality and the probabilistic nature of quantum mechanics.
  - **Implication for Measurements:** Any attempt to measure one observable precisely will disturb the system in such a way that the other observable's value becomes uncertain. For example, localizing a particle (reducing  $\Delta x$ ) requires using short-wavelength radiation, which carries high momentum and imparts a significant, uncertain kick to the particle, increasing  $\Delta p_x$ .
8. (c) What do you understand by Hermitian operators? Prove that all the eigen values of Hermitian operators are real numbers.
- **Hermitian Operators:**
    - In quantum mechanics, a Hermitian operator (also known as a self-adjoint operator) is an operator that corresponds to a physically observable quantity.
    - An operator  $\hat{A}$  is Hermitian if it satisfies the condition:
 
$$\int \psi_i^* (\hat{A} \psi_j) d\tau = \int (\hat{A} \psi_i)^* \psi_j d\tau$$
    - This condition essentially means that the expectation value of a Hermitian operator is always real, which is a necessary property for any observable quantity in physics (e.g., energy, momentum, position, etc., must be real).
    - In Dirac notation, this is written as  $\langle \psi_i | \hat{A} | \psi_j \rangle = \langle \hat{A} \psi_i | \psi_j \rangle$ .
    - For a simple operator like a derivative or multiplication by a function, the Hermitian conjugate (adjoint) of the operator  $\hat{A}^\dagger$  is equal to the operator itself, i.e.,  $\hat{A}^\dagger = \hat{A}$ .

• **Proof that all eigenvalues of Hermitian operators are real numbers:**

- Let  $\hat{A}$  be a Hermitian operator.
- Let  $\psi$  be an eigenfunction of  $\hat{A}$  with eigenvalue  $a$ .
- So,  $\hat{A}\psi = a\psi$ .
- According to the definition of a Hermitian operator, for an arbitrary function  $\phi$ :
  - $\int \phi^*(\hat{A}\psi)d\tau = \int (\hat{A}\phi)^*\psi d\tau$
- Now, let's consider the specific case where  $\phi = \psi$ .
  - $\int \psi^*(\hat{A}\psi)d\tau = \int (\hat{A}\psi)^*\psi d\tau$
- Substitute  $\hat{A}\psi = a\psi$  into the equation:
  - $\int \psi^*(a\psi)d\tau = \int (a\psi)^*\psi d\tau$
  - Since  $a$  is an eigenvalue, it is a constant, so we can take it out of the integral:
    - $a \int \psi^*\psi d\tau = a^* \int \psi^*\psi d\tau$
- We know that  $\int \psi^*\psi d\tau = \int |\psi|^2 d\tau$ . For a physically meaningful wavefunction, this integral must be non-zero and finite (it is the normalization integral, which is 1 if the wavefunction is normalized).
- Let  $N = \int |\psi|^2 d\tau$ . Since  $N \neq 0$ :
  - $aN = a^*N$
  - $a = a^*$
- The condition  $a = a^*$  means that the eigenvalue  $a$  is equal to its complex conjugate. This is only possible if  $a$  is a **real number**.

- Therefore, all eigenvalues of Hermitian operators are real numbers, which is consistent with their physical interpretation as observable quantities.
7. (a) Write the LCAO-MO trial wave function of  $H_2^+$  using Molecular Orbital approach. Derive the expressions for molecular orbital wave functions corresponding to the bonding and anti-bonding energy levels of  $H_2^+$ .
- **LCAO-MO Trial Wave Function of  $H_2^+$ :**
    - In the Linear Combination of Atomic Orbitals (LCAO) approach for forming Molecular Orbitals (MOs), the molecular orbitals are approximated as linear combinations of the atomic orbitals (AOs) of the constituent atoms.
    - For  $H_2^+$ , there are two hydrogen nuclei (A and B) and one electron. The relevant atomic orbitals are the  $1s$  orbitals of each hydrogen atom, denoted as  $\phi_{1s}^A$  and  $\phi_{1s}^B$ .
    - The general trial wave function for the molecular orbital in  $H_2^+$  is a linear combination of these two atomic orbitals:
      - $\Psi = c_A \phi_{1s}^A + c_B \phi_{1s}^B$
      - where  $c_A$  and  $c_B$  are coefficients that determine the contribution of each atomic orbital to the molecular orbital.
  - **Derivation of Molecular Orbital Wave Functions for Bonding and Anti-bonding Energy Levels:**
    - To find the coefficients  $c_A$  and  $c_B$ , we use the variational principle. We minimize the energy of the system with respect to these coefficients. This leads to solving the secular equations.
    - For a homonuclear diatomic molecule like  $H_2^+$ , due to symmetry, the contributions of the two atomic orbitals are equal in magnitude, i.e.,  $|c_A| = |c_B|$ . This gives rise to two possibilities for the relative signs of the coefficients:

iv. **Constructive Interference (Bonding Molecular Orbital):**  $c_A = c_B$ .

v. **Destructive Interference (Anti-bonding Molecular Orbital):**  $c_A = -c_B$ .

○ **Case 1: Bonding Molecular Orbital ( $\Psi_b$ ) - Constructive Interference**

- When  $c_A = c_B$ , the AOs combine with the same phase, leading to an increase in electron density between the nuclei.
- $\Psi_b = N_b(\phi_{1s}^A + \phi_{1s}^B)$
- To normalize  $\Psi_b$ , we integrate  $|\Psi_b|^2$  over all space and set it to 1:

$$\begin{aligned}
 & \bullet \int |\Psi_b|^2 d\tau = 1 \\
 & \bullet N_b^2 \int (\phi_{1s}^A + \phi_{1s}^B)^2 d\tau = 1 \\
 & \bullet N_b^2 \int (\phi_{1s}^A)^2 + (\phi_{1s}^B)^2 + 2\phi_{1s}^A \phi_{1s}^B d\tau = 1 \\
 & \bullet N_b^2 \left[ \int (\phi_{1s}^A)^2 d\tau + \int (\phi_{1s}^B)^2 d\tau + 2 \int \phi_{1s}^A \phi_{1s}^B d\tau \right] = 1 \\
 & \bullet \text{Since atomic orbitals are normalized, } \int (\phi_{1s}^A)^2 d\tau = 1 \text{ and } \int (\phi_{1s}^B)^2 d\tau = 1. \\
 & \bullet \text{The integral } \int \phi_{1s}^A \phi_{1s}^B d\tau = S \text{ is the } \mathbf{overlap\ integral}. \\
 & \bullet N_b^2 [1 + 1 + 2S] = 1 \\
 & \bullet N_b^2 (2 + 2S) = 1 \Rightarrow N_b = \frac{1}{\sqrt{2(1+S)}}
 \end{aligned}$$

- **Expression for Bonding Molecular Orbital Wave Function:**

$$\bullet \Psi_b = \frac{1}{\sqrt{2(1+S)}} (\phi_{1s}^A + \phi_{1s}^B)$$

- This orbital is denoted as  $\sigma_{1s}$  because it has cylindrical symmetry around the internuclear axis and is formed from  $1s$  atomic orbitals. It represents a region of increased electron density between the nuclei, leading to attraction.

○ **Case 2: Anti-bonding Molecular Orbital ( $\Psi_{ab}$ ) - Destructive Interference**

- When  $c_A = -c_B$ , the AOs combine with opposite phases, leading to a decrease in electron density between the nuclei and the formation of a nodal plane.

- $\Psi_{ab} = N_{ab}(\phi_{1s}^A - \phi_{1s}^B)$

- Normalize  $\Psi_{ab}$ :

- $N_{ab}^2 \int (\phi_{1s}^A - \phi_{1s}^B)^2 d\tau = 1$

- $N_{ab}^2 \left[ \int (\phi_{1s}^A)^2 d\tau + \int (\phi_{1s}^B)^2 d\tau - 2 \int \phi_{1s}^A \phi_{1s}^B d\tau \right] = 1$

- $N_{ab}^2 [1 + 1 - 2S] = 1$

- $N_{ab}^2 (2 - 2S) = 1 \Rightarrow N_{ab} = \frac{1}{\sqrt{2(1-S)}}$

- **Expression for Anti-bonding Molecular Orbital Wave Function:**

- $\Psi_{ab} = \frac{1}{\sqrt{2(1-S)}} (\phi_{1s}^A - \phi_{1s}^B)$

- This orbital is denoted as  $\sigma_{1s}^*$  (sigma star  $1s$ ). It has a nodal plane perpendicular to the internuclear axis between the nuclei, indicating reduced electron density and leading to repulsion.

8. (b) Plot the radial probability distribution functions for an electron in hydrogen atom where  $n = 1$  and  $n = 2$ . Explain the plots briefly.

- **Radial Probability Distribution Function (RPDF):**



- The probability of finding an electron in a volume element  $d\tau$  is  $|\psi|^2 d\tau$ .
- For spherically symmetric orbitals (like  $s$  orbitals), the probability depends only on  $r$ . The volume of a spherical shell of thickness  $dr$  at radius  $r$  is  $4\pi r^2 dr$ .
- The radial probability density is  $R(r)^2$ , where  $R(r)$  is the radial part of the wavefunction.
- The radial probability distribution function (RPDF), often denoted as  $P(r)$ , is defined as  $P(r) = 4\pi r^2 R(r)^2$ . This function gives the probability of finding the electron within a spherical shell of radius  $r$  and thickness  $dr$ .
- **Hydrogen Atom Wavefunctions (Radial Part,  $R(r)$ ) and RPDFs:**
  - **For  $n = 1$  (1s orbital):**
    - $R_{1s}(r) = 2 \left(\frac{Z}{a_0}\right)^{3/2} \exp\left(-\frac{Zr}{a_0}\right)$  (For Hydrogen,  $Z=1$ )
    - $R_{1s}(r) = 2 \left(\frac{1}{a_0}\right)^{3/2} \exp\left(-\frac{r}{a_0}\right)$
    - $R_{1s}(r)^2 = 4 \left(\frac{1}{a_0}\right)^3 \exp\left(-\frac{2r}{a_0}\right)$
    - $P(r)_{1s} = 4\pi r^2 R_{1s}(r)^2 = 4\pi r^2 \cdot 4 \left(\frac{1}{a_0}\right)^3 \exp\left(-\frac{2r}{a_0}\right) = \frac{16\pi}{a_0^3} r^2 \exp\left(-\frac{2r}{a_0}\right)$
    - The plot of  $P(r)_{1s}$  vs.  $r$  starts at 0, increases to a maximum, and then decays exponentially to 0. The maximum occurs at  $r = a_0$  (Bohr radius).
  - **For  $n = 2$ :**
    - For  $n = 2$ , we have  $2s$  and  $2p$  orbitals. The question asks for " $n=2$ ", so we should consider both.

▪ **2s orbital ( $l = 0$ ):**

- $R_{2s}(r) = \frac{1}{2\sqrt{2}} \left(\frac{Z}{a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) \exp\left(-\frac{Zr}{2a_0}\right)$  (For Hydrogen,  $Z=1$ )
- $R_{2s}(r) = \frac{1}{2\sqrt{2}} \left(\frac{1}{a_0}\right)^{3/2} \left(2 - \frac{r}{a_0}\right) \exp\left(-\frac{r}{2a_0}\right)$
- $R_{2s}(r)^2 = \frac{1}{8a_0^3} \left(2 - \frac{r}{a_0}\right)^2 \exp\left(-\frac{r}{a_0}\right)$
- $P(r)_{2s} = 4\pi r^2 R_{2s}(r)^2 = \frac{4\pi r^2}{8a_0^3} \left(2 - \frac{r}{a_0}\right)^2 \exp\left(-\frac{r}{a_0}\right) = \frac{\pi}{2a_0^3} r^2 \left(2 - \frac{r}{a_0}\right)^2 \exp\left(-\frac{r}{a_0}\right)$
- The plot of  $P(r)_{2s}$  vs.  $r$  also starts at 0. It has an inner peak and an outer peak, separated by a radial node where  $P(r) = 0$  (when  $2 - r/a_0 = 0 \Rightarrow r = 2a_0$ ). The principal maximum is at a larger radius than the 1s orbital.

▪ **2p orbital ( $l = 1$ ):**

- $R_{2p}(r) = \frac{1}{2\sqrt{6}} \left(\frac{Z}{a_0}\right)^{3/2} \frac{Zr}{a_0} \exp\left(-\frac{Zr}{2a_0}\right)$  (For Hydrogen,  $Z=1$ )
- $R_{2p}(r) = \frac{1}{2\sqrt{6}} \left(\frac{1}{a_0}\right)^{3/2} \frac{r}{a_0} \exp\left(-\frac{r}{2a_0}\right)$
- $R_{2p}(r)^2 = \frac{1}{24a_0^5} r^2 \exp\left(-\frac{r}{a_0}\right)$
- $P(r)_{2p} = 4\pi r^2 R_{2p}(r)^2 = \frac{4\pi r^2}{24a_0^5} r^2 \exp\left(-\frac{r}{a_0}\right) = \frac{\pi}{6a_0^5} r^4 \exp\left(-\frac{r}{a_0}\right)$
- The plot of  $P(r)_{2p}$  vs.  $r$  starts at 0, increases to a single maximum, and then decays. It does not have

radial nodes. Its maximum is further out than the  $1s$  peak.

- **Explanation of the Plots (General trends):**

- **1s orbital:** The RPDF for  $1s$  shows a single maximum probability at  $r = a_0$  (Bohr radius). This means the electron is most likely to be found at this distance from the nucleus. The probability quickly drops off as  $r$  increases or decreases from this value. This reflects the most compact and tightly bound electron state.
- **2s orbital:** The RPDF for  $2s$  exhibits two peaks and one radial node (where  $P(r) = 0$ ). The presence of a radial node means there is a spherical region where the probability of finding the electron is zero. The outer peak corresponds to the principal region where the electron is most likely found. The existence of the inner peak indicates a non-zero probability of finding the electron closer to the nucleus, a phenomenon known as "penetration."
- **2p orbital:** The RPDF for  $2p$  shows a single principal maximum, but no radial nodes. The maximum probability occurs at a greater distance from the nucleus compared to the  $1s$  orbital. This is because  $2p$  electrons, on average, are further from the nucleus than  $1s$  electrons. The RPDF starts at zero and is zero at the nucleus, reflecting that  $p$  orbitals have angular momentum and avoid the nucleus.
- **General Observations:**
  - As the principal quantum number ( $n$ ) increases, the average distance of the electron from the nucleus increases, leading to larger and more diffuse orbitals. This is reflected in the RPDFs, where the main peaks shift to larger  $r$  values.

- The number of radial nodes for any orbital is  $(n - l - 1)$ , where  $l$  is the azimuthal quantum number.
    - For  $1s$ :  $n = 1, l = 0 \Rightarrow (1 - 0 - 1) = 0$  radial nodes.
    - For  $2s$ :  $n = 2, l = 0 \Rightarrow (2 - 0 - 1) = 1$  radial node.
    - For  $2p$ :  $n = 2, l = 1 \Rightarrow (2 - 1 - 1) = 0$  radial nodes.
  - The height of the peaks generally decreases with increasing  $n$ , indicating that the electron density is spread over a larger volume.
9. (c) Explain the significance of orthonormality principle giving relevant mathematical expressions.

- **Orthonormality Principle:**

- The orthonormality principle is a fundamental concept in quantum mechanics that applies to the eigenfunctions (wave functions) of Hermitian operators. It combines two related properties: **orthogonality** and **normalization**.
- **1. Normalization:**
  - A wave function  $\psi$  is normalized if the integral of its squared modulus over all space is equal to 1.
  - Mathematically:  $\int \psi^* \psi d\tau = \int |\psi|^2 d\tau = 1$
  - **Significance:** This ensures that the total probability of finding the particle somewhere in space is exactly 1 (or 100%). Probability must be conserved. Without normalization, the wave function would not represent a physically meaningful probability amplitude.
- **2. Orthogonality:**

- Two distinct eigenfunctions ( $\psi_i$  and  $\psi_j$ ) of a Hermitian operator, corresponding to different eigenvalues ( $E_i \neq E_j$ ), are orthogonal. This means their overlap integral is zero.
- Mathematically:  $\int \psi_i^* \psi_j d\tau = 0$  if  $i \neq j$
- **Significance:**
  - **Independent States:** Orthogonality implies that different quantum states (represented by different wave functions with distinct energies) are distinct and independent from each other. There is no "mixing" or overlap between them.
  - **Measurement Outcomes:** If a system is in one eigenstate, a measurement of the corresponding observable will yield only the eigenvalue associated with that state, and not a mix of values from other states.
  - **Basis Set:** Orthogonal wave functions form a natural basis set for describing any arbitrary state of a system. Any general state can be expressed as a linear combination of these orthogonal eigenstates.
- **Combined Orthonormality Condition:**
  - The orthonormality principle combines both concepts using the Kronecker delta symbol ( $\delta_{ij}$ ):
  - $\int \psi_i^* \psi_j d\tau = \delta_{ij}$
  - Where  $\delta_{ij} = 1$  if  $i = j$  (normalization)
  - And  $\delta_{ij} = 0$  if  $i \neq j$  (orthogonality)
- **Overall Significance:**

- **Consistency of Quantum Theory:** Orthonormality ensures the mathematical consistency and physical interpretability of quantum mechanics. It allows for the unique assignment of probabilities and the unambiguous determination of observable quantities.
- **Simplification of Calculations:** It greatly simplifies calculations involving superpositions of states and the determination of expansion coefficients when a general wavefunction is expressed as a sum of basis functions.
- **Foundation for Perturbation Theory:** It is a cornerstone for advanced quantum mechanical methods like perturbation theory, where a complex problem is approximated by a simpler one with known orthonormal solutions.

8. Write short notes on any three:

- **(a) Postulates of Quantum Mechanics:**
  - The postulates of quantum mechanics are a set of fundamental axioms that form the mathematical and conceptual basis of the theory. They cannot be derived but are accepted because their consequences consistently predict experimental observations.
  - **Postulate 1 (State of a System):** The state of a quantum mechanical system is completely described by a wave function  $\Psi(r, t)$  (or  $\Psi(x, y, z, t)$  in 3D, or  $\Psi(q_1, q_2, \dots, q_N, t)$  for N particles) that is a function of the coordinates and time. The wave function is single-valued, continuous, finite, and square-integrable.
  - **Postulate 2 (Observables and Operators):** To every measurable physical observable (e.g., position, momentum, energy), there corresponds a unique Hermitian linear operator. For example, the position operator is  $\hat{x} = x$ , the momentum

operator is  $\hat{p}_x = -i\hbar \frac{\partial}{\partial x}$ , and the Hamiltonian operator (for energy) is  $\hat{H}$ .

- **Postulate 3 (Measurement of an Observable):** When a measurement of an observable corresponding to an operator  $\hat{A}$  is made on a system whose state function is  $\Psi$ , the only possible values that can be obtained are the eigenvalues ( $a$ ) of the operator  $\hat{A}$ . That is,  $\hat{A}\psi = a\psi$ .
- **Postulate 4 (Expectation Values):** For a system in a state described by a normalized wave function  $\Psi$ , the average value (expectation value) of an observable  $A$  (corresponding to operator  $\hat{A}$ ) is given by  $\langle A \rangle = \int \Psi^* \hat{A} \Psi d\tau$ . This is the average result of many measurements on identical systems.
- **Postulate 5 (Time Evolution of the State Function):** The time evolution of the wave function is governed by the time-dependent Schrodinger equation:  $i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi$ . This equation describes how the quantum state changes over time.
- **Postulate 6 (Collapse of the Wave Function):** When a measurement of an observable is performed, the state of the system instantaneously collapses from its initial state ( $\Psi$ ) to the eigenstate ( $\psi_n$ ) corresponding to the eigenvalue ( $a_n$ ) obtained in the measurement.
- **(b) Pauli's Exclusion Principle (quantum mechanical approach):**
  - The Pauli Exclusion Principle, formulated by Wolfgang Pauli, is a fundamental principle in quantum mechanics that governs the behavior of identical fermions (particles with half-integer spin, such as electrons).
  - **Statement:** No two identical fermions can occupy the same quantum state simultaneously within the same quantum system.

- **Quantum Mechanical Interpretation (Wave Function Symmetry):**

- For a system of identical particles, the total wave function ( $\Psi$ ) must have a specific symmetry with respect to the interchange of any two identical particles.
- For **fermions**, the total wave function must be **antisymmetric** upon the interchange of any two identical particles. This means that if you swap the coordinates (spatial and spin) of two identical fermions, the wave function must change its sign:  $\Psi(\dots, q_i, \dots, q_j, \dots) = -\Psi(\dots, q_j, \dots, q_i, \dots)$ .
- If two identical fermions were to occupy the exact same quantum state (i.e., have all their quantum numbers –  $n$ ,  $l$ ,  $m_l$ ,  $m_s$  – identical), then swapping them would not change the wave function at all. However, for the wave function to be antisymmetric, it must also be equal to its negative, which implies that the wave function must be zero:  $\Psi = -\Psi \Rightarrow 2\Psi = 0 \Rightarrow \Psi = 0$ . A wave function of zero means there is no particle, which is physically impossible.
- Therefore, the antisymmetry requirement for the wave function of fermions directly prohibits two identical fermions from having the exact same set of quantum numbers.

- **Consequences:**

- **Electronic Structure of Atoms:** This principle explains the electron shell structure of atoms and the periodic table. Each orbital can hold a maximum of two electrons, provided they have opposite spins ( $\uparrow$  and  $\downarrow$ ).



- **Stability of Matter:** It prevents electrons from collapsing into the lowest energy state, leading to the stability and diversity of chemical elements and molecules.
- **Degenerate Electron Gas:** It is crucial for understanding the properties of degenerate electron gases in metals, white dwarf stars, and neutron stars.
- **(c) Configuration Interaction (CI):**
  - Configuration Interaction (CI) is a post-Hartree-Fock ab initio method used in computational quantum chemistry to account for electron correlation, which is not fully captured by the mean-field approximation of the Hartree-Fock method.
  - **Electron Correlation:** In Hartree-Fock theory, electrons are treated as moving independently in an average field created by all other electrons. This ignores the instantaneous electron-electron repulsions, which is known as electron correlation.
  - **Basis of CI:**
    - The Hartree-Fock method provides a single determinant (Slater determinant) wave function, usually representing the ground electronic configuration. This is often called the **reference configuration**.
    - CI improves upon this by constructing the true many-electron wave function as a linear combination of the reference (ground state) configuration and various **excited configurations**.
    - Excited configurations are generated by promoting one or more electrons from occupied orbitals in the reference configuration to virtual (unoccupied) orbitals.
    - The general CI wave function is written as:  $\Psi_{CI} = c_0 \Psi_{ref} + \sum_i c_i \Psi_i^S + \sum_{ij} c_{ij} \Psi_{ij}^D + \sum_{ijk} c_{ijk} \Psi_{ijk}^T + \dots$

- $\Psi_{ref}$ : The reference (Hartree-Fock) configuration.
  - $\Psi_i^S$ : Single excitations (one electron promoted).
  - $\Psi_{ij}^D$ : Double excitations (two electrons promoted).
  - $\Psi_{ijk}^T$ : Triple excitations (three electrons promoted), and so on.
- The coefficients ( $c_0, c_i, c_{ij}, \dots$ ) are determined variationally by solving the CI secular equation.
- **Types of CI:**
    - **CIS:** Includes only single excitations.
    - **CISD:** Includes single and double excitations (most common for smaller systems).
    - **Full CI:** Includes all possible excitations. This is the most accurate CI method, giving the exact solution for a given basis set. However, its computational cost scales factorially with the number of electrons and basis functions, making it feasible only for very small systems.
  - **Significance:**
    - CI methods are crucial for accurately describing molecular properties where electron correlation is significant, such as bond dissociation, excited states, reaction pathways, and systems with multiple relevant electronic configurations.
    - It provides a systematic way to improve the accuracy of quantum chemical calculations beyond the Hartree-Fock level.
- **(d) Variation Theorem:**

- The variation theorem (or variational principle) is a fundamental theorem in quantum mechanics used to estimate the ground state energy and wave function of a quantum system. It is particularly useful for systems for which the exact solution to the Schrodinger equation is difficult or impossible to obtain.
- **Statement:** For any arbitrary trial wave function ( $\Psi_{trial}$ ) that satisfies the boundary conditions of the system, the expectation value of the energy calculated using this trial function will always be greater than or equal to the true ground state energy ( $E_0$ ) of the system.

- **Mathematical Expression:**

- $$E_{trial} = \frac{\int \Psi_{trial}^* \hat{H} \Psi_{trial} d\tau}{\int \Psi_{trial}^* \Psi_{trial} d\tau} \geq E_0$$
- where  $\hat{H}$  is the Hamiltonian operator of the system, and  $E_0$  is the true ground state energy.
- If the trial wave function is normalized, the denominator is 1, so  $E_{trial} = \int \Psi_{trial}^* \hat{H} \Psi_{trial} d\tau \geq E_0$ .

- **Procedure (Variational Method):**

- Choose a Trial Function:** Select a trial wave function  $\Psi_{trial}$  that depends on one or more adjustable parameters. The trial function should mimic the expected behavior of the true wave function (e.g., satisfy boundary conditions, have correct symmetry).
- Calculate Energy Expectation Value:** Compute  $E_{trial}$  using the formula above. The result will be an expression that depends on the adjustable parameters.
- Minimize Energy:** Minimize  $E_{trial}$  with respect to each adjustable parameter by taking partial derivatives and setting them to zero ( $\frac{\partial E_{trial}}{\partial c_i} = 0$ ).

ix. **Optimal Approximation:** The minimum value of  $E_{trial}$  obtained is the best upper bound to the true ground state energy that can be achieved with the chosen form of the trial function. The parameters at this minimum define the optimal approximate wave function.

○ **Significance:**

- **Upper Bound for Ground State Energy:** It provides a systematic way to obtain an upper bound for the ground state energy. The better the choice of the trial function, the closer  $E_{trial}$  will be to  $E_0$ .
- **Approximation of Wave Function:** It also provides an approximation for the ground state wave function.
- **Basis for Computational Methods:** The variation theorem is the theoretical foundation for many powerful computational quantum chemistry methods, such as the Hartree-Fock method (which is a specific application of the variational principle) and Configuration Interaction (CI).
- **No Prior Knowledge of  $E_0$  Needed:** It allows us to estimate the ground state energy even when the exact solution is unknown.