Name: **Enrolment No:**	

UPES

End Semester Examination, December 2024

Course: Quantum Chemistry **Semester: I**

Program: M.Sc. Chemistry **Time: 03 hrs.**

Course Code: CHEM7062 **Max. Marks: 100**

Instructions:

- Do not write anything else on the question paper except your name and roll number.
- Use of scientific calculator is allowed.
- Attempt all the parts of a question at one place only. Internal choice is given in Q8 & Q10
- CO1, CO2, & CO3 in the last column stand for course outcomes and are for official use only.

SECTION A
(5Qx4M=20Marks)

S. No.		Marks	CO
Q 1	Which of the following are eigenfunctions of d/dx? (a) Ae^{-ax}, (b) x^2, (c) B cos nx, (d) cosx + sinx	**4**	**CO1**
Q 2	State whether true or false with justification: (a) the lowest energy state of a particle in a three-dimensional cubic box is triply degenerate. (b) x cos x is an even function	**4**	**CO1**
Q 3	Derive the commutator of the following (a) $[x, p_x^2]$ (b) $[x^2, d/dx]$	**4**	**CO1**
Q 4	What are linear and Hermitian operators?	**4**	**CO1**
Q 5	State and explain Born-Oppenheimer approximation. Discuss its significance.	**4**	**CO2**

SECTION B
(4Qx10M= 40 Marks)

Q 6	The wave function for a quantum mechanical particle in a one-dimensional box of length 'a' is given by $\psi = B \sin\frac{2\pi x}{a}$. Find the normalization constant B and then calculate the value of B for a box of length 100 nm? **OR** Derive the expression of wavefunction and energy for particle confined in a 3D box.	**10**	**CO3**
Q 7	Find the ground state energy of a particle confined to one dimensional box of length 'a' using variation theorem. Use the trial function φ=x(a-x).	**10**	**CO2**

Q 8	(a) State and explain the postulates of quantum mechanics. (b) Consider a diatomic molecule as a rigid rotor. Describe the rotational energy levels and the transitions observed in the rotational spectra. Draw the energy levels and indicate the rotational spectral lines.	**10**	**CO3**
Q 9	(a) Apply HMO method to find the π-molecular orbitals and their energy values for allyl cation. Also calculate the π-bond energy. (b) State the Schrödinger equation for a hydrogen atom in Cartesian and spherical polar coordinates. Write down the general forms of the radial and angular wavefunctions.	**10**	**CO2**
SECTION-C (2Qx20M=40 Marks)			
Q 10	(a) A one-dimensional anharmonic oscillator is treated by perturbation theory. The harmonic oscillator is used as the unperturbed system and the perturbation is λx^3 (λ is constant). Using only the first order perturbation correction, determine the total ground state energy of the anharmonic oscillator. **OR** If $\Psi = 0.7\varphi_A + 0.5\varphi_B$ is a normalized molecular orbital of a diatomic molecule AB, constructed from φ_A and φ_B which are also normalized. Calculate the overlap between φ_A and φ_B. (b) Apply HMO theory to find the wave functions of π -molecular orbitals and their energy values for ethylene molecule. **OR** Derive the expression of wave function correction due to the first order perturbation.	**10+10**	**CO2** **CO3**
Q 11	(a) Write the Hamiltonian operator for H_2^+. Derive the expression of energy and wavefunction of bonding and antibonding molecular orbitals of H^{2+} using LCAO-MO treatment. (b) The vibration of $^1H^{127}I$ molecule can be considered as simple harmonic oscillation. The force constant is 300 Nm^{-1}. Calculate the fundamental vibration frequency and the zero point energy of this molecule.	**10+10**	**CO2** **CO3**