POSTGRADUATE FOURTH SEMESTER EXAMINATION, 2022
CHEMISTRY

Course Code: CHEM 401E **Course ID: 41451**

Physical Chemistry Special

Time: 2 Hours **Full Marks: 40**

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

1. Answer *any five* of the following questions: 2×5 = 10

   a) The threshold wavelength for photoelectric emission in tungsten is 2300 Å. What wavelength of light must be used in order to eject electrons with a maximum energy of 1.5 eV?

   b) If Φ_1 and Φ_2 are two degenerate eigenfunctions of the linear operator, $\widehat{H}$, show that $\psi = C_1\Phi_1+C_2\Phi_2$ is an eigenfunction of $\widehat{H}$ with the same eigenvalue as that for Φ_1 and Φ_2.

   c) Consider an electron in a one dimensional box of 20 Å lengths. What is the zero point energy of the electron?

   d) A wavefunction is given as $\psi = \sin(x)$. Is it normalized? Explain.

   e) Mention the linear and non-linear operators from the following equations, (i) $\hat{A}\phi = \lambda\phi$, (ii) $\hat{C}\phi = \phi^2$

   f) If $\hat{A} = 3x^2$ and $\hat{C} = d/dx$, then show that $\hat{A}$ and $\hat{C}$ commute.

   g) What do you mean by a well behaved function?

2. Answer *any four* of the following questions: 5×4 = 20

   a) A particle of mass 'm' is confined in a one-dimensional box of length 'a'. Calculate the probability of finding the particle in the following region: (i) $0 \leq x \leq a/3$. 5

b) Consider a particle of mass 'm' confined in a two-dimensional box of edge lengths 'a' and 'b'. Find the energy and wavefunctions by solving the Schrödinger equation. The potential energy,

V (x, y) = 0 for $0 \le x \le a$ and $0 \le x \le b$

= ∞ elsewhere 5

c) If $\psi(x) = \frac{1}{\pi^{1/4}} e^{-x^2/2}$ and $g(x) = \frac{2^{1/2}}{\pi^{1/4}} x e^{-x^2/2}$ then using these two functions show that $\hat{P}_x$ is a Hermitian operator over the range $-\infty \le x \le \infty$. 5

d) The normalized wave function of the hydrogen atom for the 1s state is $\psi_{1S} = (\pi a_0^3)^{-1/2} e^{-r/a_0}$

Show that in such a state the most probable distance from the proton to the electron is a_0. 5

e) Show that the angle θ between L_z and L is minimum when m_l is maximum. For l = 1, find θ between L_z and L. 5

f) Show that, $[\widehat{L^2}, \widehat{L_z}] = 0$. 5

3. Answer *any one* of the following question: 10×1 = 10

a) i) Consider a trial function, ψ = x(a-x) for a particle in a one-dimensional box of length a. Show that this function satisfies the boundary conditions. Apply the variation method to get an upper bound to the ground state energy of the particle, and compare the result with true value given $E = \frac{h^2}{8ma^2}$. 5

ii) A particle is confined in a box such that V = 0 outside the box and V = k (1 – x/a) inside the box. Calculate the ground state energy of the particle using the first order the perturbation theory.

Given that, $\int_0^a \sin^2 \frac{n\pi x}{a} dx = \frac{a}{2}$, $\int_0^a x \sin^2 \frac{n\pi x}{a} dx = \frac{a^2}{4}$ and $H^{(1)} = k(1 - x/a)$, $0 \le x \le a$.

Where, k is a constant. The unperturbed eigenfunction and eigenvalue for the particle in a box are, $\psi_n^{(0)} = (2/a)^{1/2} Sin \frac{n\pi x}{a}$, $0 \le x \le a$ and, $E_n^{(0)} = \frac{n^2 h^2}{8ma^2}$. 5

b) i) The Hamiltonian for hydrogen atom and 1s wave function in atomic units are,

$$\hat{H} = -\tfrac{1}{2}\nabla^2 - \tfrac{1}{r} \qquad\qquad \psi_{1s} = \tfrac{1}{\sqrt{\pi}} e^{-r}$$

Calculate the ground state energy of hydrogen atom in S.I. units and also electron volts. 5

ii) Calculate the average value of $\bar{x}$ for the 1s electron in H-atom. Is it the same as $\bar{r}$? Explain. 5
