M.Sc.Examination, 2018

Semester-I

Chemistry

Course: CH-705

(Physical Chemistry)

Time: Three Hours **Full Marks: 40**

Questions are of value as indicated in the margin.

Answer***any four***questions.

1. a) Consider the states $|\psi\rangle = 3i|\phi_1\rangle - 7i|\phi_2\rangle$ and $|\chi\rangle = -|\phi_1\rangle + 2i|\phi_2\rangle$ where $|\phi_1\rangle$ and $|\phi_2\rangle$ are orthonormal.
   i) Calculate $\langle\psi|\chi\rangle$ and $\langle\chi|\psi\rangle$. Are they equal?
   ii) Show that the states $|\psi\rangle$ and $|\chi\rangle$ satisfy the Schwartz inequality. 3

   b) State and prove 'Turn overrule'. 4

   c) If two operators $\hat{A}$ and $\hat{B}$ commute then one can always select a common complete set of eigenfunctions of both $\hat{A}$ and $\hat{B}$ – Comment on the statement. 3

2. a) Derive an equation for the time evolution of average value of any observable, the operator of which is say $\hat{A}$. In this connection what do you understand by constant of motion. 3

   b) Show that $\frac{d\langle p_x\rangle}{dt} = -\left\langle \frac{dv(x)}{dx} \right\rangle$. What is the essential content of this equation? 3

   c) Consider a state which is given in terms of three orthonormal vectors $|\phi_1\rangle, |\phi_2\rangle$ and $|\phi_3\rangle$ as follows:

   $|\psi\rangle = \frac{1}{\sqrt{15}}|\phi_1\rangle + \frac{1}{\sqrt{3}}|\phi_2\rangle + \frac{1}{\sqrt{5}}|\phi_3\rangle$; where $|\phi_n\rangle$ are eigenstates to an operator A such that $\hat{A}|\phi_n\rangle = (3n^2 - 1)|\phi_n\rangle$ with $n = 1,2,3$.

   i) Find the norm of the state $|\psi\rangle$.
   ii) If the property corresponding to the operator $\hat{A}$ is measured on a large number of identical systems that are all initially in the same state $|\psi\rangle$, what values would one obtain with what probabilities?
   iii) Find the expectation value of A for the state $|\psi\rangle$. 4

3. a) Test whether the following operators are hermitian or not: 2
   (i) $\hat{x}\hat{p}_x$ (ii) $\hat{p}_x\hat{x}$ (iii) $\hat{x}\hat{p}_x + \hat{p}_x\hat{x}$ (iv) $\hat{x}\hat{p}_x - \hat{p}_x\hat{x}$

   b) Consider a one-dimensional particle which moves along the x axis $(-\infty$ to $+\infty)$ and whose Hamiltonian is H and $\hat{H} = -\varepsilon\frac{d^2}{dx^2} + 16\varepsilon x^2$; where ε is a real constant having the dimension of energy. (Given $\int_{-\infty}^{+\infty} e^{-4x^2}dx = \sqrt{\pi}/2$)

   i) Let consider a wave function $\psi(x) = A \cdot e^{-2x^2}$; where 'A' is normalization constant. Find A.
   ii) Test whether the $\psi(x)$ is an eigen function of the operator $\hat{H}$. If it is then find the eigen values. 3

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c) Two normalized 1s atomic orbitals ($1s_A$ and $1s_B$) are located on nearby nuclei A and B. These orbitals overlap each other enough so that $\langle 1s_A | 1s_B \rangle = 0.50$. Construct a function from these two that is orthogonal to $1s_A$ and is normalized. 2

d) Show that the momentum uncertainty of a perticle in 1-d box for the ground state is not zero. Hence calculate the zero point energy of the particle. 3

4. a) Consider the 2nd excited state of a particle in 1-d box. Hence calculate the position of the nodal and the antinodal points. What are the probabilities of finding the particles at antinodal points? Comment on your result. 3

b) Show that the length of the box in a particle in a 1-d box model is an integral multiple of $\frac{\lambda}{2}$; where λ is the wavelength associated with the wave. 2

c) An electron in a 3-d rectangular box with dimension of $5A^\circ, 3A^\circ$ and $6A^\circ$, makes a radiative transition from the lowest excited state to the ground state. Calculate the frequency of the photon emitted. ($m_e = 9.11 \times 10^{-31}$ kg) 3

d) The tunneling probability of a particle of mass 'm' is given by

$$T_p = \frac{16k^2k''^2}{\left(k''^2 - k^2\right)^2\left(e^{-k''a} - e^{k''a}\right)^2 + 4k^2k''^2\left(e^{-k''a} + e^{k''a}\right)^2}$$ (symbols have their usual meaning)

Find the conditions at which the tunneling probability are maximum. 2

5. a) For 1-d Harmonic oscillator model define raising (r_-) and lowering operators (r_+). Using the properties of raising operator obtain a general expression for ψ_n of the Harmonic Oscillator in terms of ψ_0. 4

b) Find out the selection rule for vibrational transition using Harmonic Oscillator as a model for molecular vibration. 2

c) The power series expansion of Hermite polynomial is given as

$H_n(\xi) = a_0 + a_1\xi + a_2\xi^2 + \ldots$. Substituting this into the Hermite differential equation

$$\frac{d^2H_n(\xi)}{d\xi^2} - 2\xi\frac{dH_n(\xi)}{d\xi} + \left(\frac{\lambda}{\alpha} - 1\right)H_n(\xi) = 0.$$

Show that $(n+1)(n+2)a_{n+2} + \left(\frac{\lambda}{\alpha} - 1 - 2n\right)a_n = 0.$ 4

6. a) For the ground state of one-dimensional Harmonic Oscillator, find the average value of the kinetic energy and of the potential energy. What conclusion one can draw from this result? 5

b) Using the appropriate recursion relation find the average value of the position of 1-d Harmonic oscillator model. 3

c) What do you mean by classical turning point? Find it for the ground state of the 1-d Harmonic oscillator. 2