M.Sc. Examination, 2017

Semester-IV
Chemistry (Elective)
Course: CH-1022
(Physical Chemistry)

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

Questions are of value as indicated in the margin.
Answer ***any four*** questions.

1. a) Prove that

   i) $I_{x'} = e^{-i\phi I_z} \quad I_x e^{i\phi I_z} = I_x \cos\phi + I_y \sin\phi$

   ii) $I_{y'} = e^{-i\phi I_z} \quad I_y e^{i\phi I_z} = -I_x \sin\phi + I_y \cos\phi$

   iii) $I_{z'} = e^{-i\phi I_z} \quad I_z e^{i\phi I_z} = I_z$

   (Symbols have their usual meanings)
   What is the meaning of these relations? 1+1+0.5+2.5

   b) Compare value of J_{max} and the transition frequencies involving the value of J_{max} for HCN (B = 44.136 GHz) and $N \equiv C - (C \equiv C)_2 - H$ (B = 1.313 GHz). 2.5

   c) Starting from an expression for rotational term values show that

   $$|\Delta\bar{\nu}| = (4B_0 - 6D_0)\left(J + \frac{3}{2}\right) - 8D_0\left(J + \frac{3}{2}\right)^3$$

   for rotational Raman transitions of a diatomic or linear polyatomic molecule. 2.5

2. a) According to quantum mechanics it has been shown that magnetic dipole moment of an electron having orbital angular momentum $\vec{L}$ follows the relation $\vec{\mu} = \frac{-e}{2m_e}\vec{L}$. (Symbols have their usual meaning).
   Could you account it based on classical loop model? Show that one can account diamagnetism phenomenon based on this loop model. 2+3

   b) Discuss Raman activity of different modes of vibrations of a C_{2v} molecule showing its polarizability and plots of variation of the polarizability during vibration. 3

   c) What is rule of mutual exclusion? What is its significance? 1+1

3. a) Describe a principle to determine the number density of charge carriers in a metallic conductor. 3

   b) Using the Hall effect one can measure directly the drift speed v_d of the charge carriers – comment on the statement. 2

   c) Express Maxwell's equation of electromagnetic radiation in terms of $\vec{k}$ and ω and then show that both $\vec{E}$ and $\vec{H}$ are perpendicular to the propagation direction and also $\vec{E}$ and $\vec{H}$ are perpendicular to each other. (Symbols have their usual meaning). 4

   d) Show that electrostatic energy density of radiation is equal to the magnetic energy density. 1

4. a) Using the rotating co-ordinate system calculate the duration of the 90 degree pulse in terms of amplitude of the applied alternating magnetic field. 5

   b) Show that the fundamental basis for spectroscopic transition is the interaction of the momenta of charged particles with the vector potential of radiation. 5

P.T.O.

5. a) Write the Schrödinger equation in the laboratory co-ordinate system for the motion of a magnetic moment in the presence of a rotating magnetic field,

$$H = iH_1 \cos\omega_z t + jH_1 \sin\omega_z t + kH_o.$$

What it would be in the rotating coordinate system with angular velocity, $\vec{\omega} = k\omega_z$. Solve the Schrödinger equation in rotating coordinate system. Using the solution at resonance condition show that the z component of the magnetic moment oscillates with time. 1+1.5+0.5+2

b) Derive the energy level expression for vibration of a diatomic molecule assuming it a harmonic oscillator. 5

6. a) Write the Block equation which account the dynamics of magnetism in the presence of a static magnetic field and an environment. Write the meaning of each term which appears in the equation of motion. Could you suggest a possible mechanism of the Bloch's postulate? 1+1.5+2.5

b) Find selection rule for rotational transition of a rigid diatomic molecule. 5

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