Birla Institute of Technology & Science, Pilani, Rajasthan - 333 031
First Semester, 2023-2024

CHEM G553 Advanced Physicsl Chemistry

Mid-Sem Time: 90 mins. Date: 12.10.2023 [60 M]

Useful information: R_H = 109680 cm^{-1}; 1 eV = 1.602×10^{-19} J; h = 6.626×10^{-34}; me = 9.11 ×10^{-31} kg;

Q1. (a) (i) The work function for Na metal is 1.82 eV. Calculate ν_0 for Na? **[2]**
(ii) Using Balmer's formula, calculate the wavelengths of the first two lines of the visible region of the hydrogen atom spectrum. **[3]**
(b) An electron is confined in a square box of length L. **(i)** What would be the form of the wavefunction in the first four energy levels? **(ii)** Are there any degenerate states within the first four energy levels? **(iii)** What is the energy difference between the second and fourth energy levels with the side of the square box of 1 Å? **(iv)** What would be the form of the time-dependent wavefunction of the electron in the ground state? **[10]**

Q2. (a) (i) Write down the Schrödinger equation for a simple harmonic oscillator in one-dimension. **(ii)** Confirm that the wavefunction, $\Psi = N_0\, exp^{(-x^2/2\alpha^2)}$ (where, $\alpha = \left\{\frac{\hbar^2}{mk_f}\right\}^{1/4}$) is a solution of the Schrödinger equation. All parameters are having the usual meaning. **(iii)** Determine the energy of the state that is represented by the above wavefunction. **[7]**
(b) Consider an electron in the $2p_y$ orbital of H-atom. What would be the outcome of: (i) Energy operator ($\widehat{H}$), (ii) Angular momentum operator ($\widehat{L}$), (iii) Z-Component of the angular momentum operator ($\widehat{L_Z}$), and (iv) Z-component of the spin operator ($\widehat{S_Z}$). **[5]**
(c) Write down all possible spin functions for $1s_2$ electronic configuration. Determine the ground state spin function for the same electronic configuration. **[3]**

Q3. (a) Normalize the molecular orbital, φ = ψ_1 + λψ_2 in terms of the parameter λ and the overlap integral S. **[2]**
(b) Show that the linear combinations h_1 = s + p_x + p_y +p_z and h_2 = s − p_x − p_y + p_z are mutually orthogonal. **[3]**
(c) What is the speed of a photoelectron ejected from a molecule with radiation energy of 21 eV and known to come from an orbital of ionisation energy of 12 eV? **[3]**
(d) Which of the following has a higher dissociation energy? (i) F_2 and (ii) F_2^+. **[2]**
(e) How will you distinguish between C_6H_5-CH_2-NH_2 and C_6H_5-CO-NH_2 using IR spectroscopy? State roughly the region of the IR spectrum (in cm^{-1}) where the characteristic absorption for the distinguishing peak will occur. What would be the expected peak position of the same vibration mode in C_6H_5-CO-ND_2? Justify your answer in brief. **[3]**
(f) In general, emission spectrum is red-shifted compared to the excitation spectrum. Comment using an energy level diagram. **[2]**

Q4. (a) (i) 1,4-dihydroxy benzene may exist in three different conformers depending on the dihedral angle (d_θ = ∠H-O-O-H). Dihedral angle of those three conformers are d_θ = 0° (Conformer-I), d_θ = 90° (Conformer-II), and d_θ = 180° (Conformer-III). Comment on rotational activity of each of the conformers with proper justification. **(ii)** Determine the number of stretching mode of vibrations for 1,4-dihydroxy benzene molecule. **(iii)** Which conformer(s) may exhibit both vibrational and vibrational Raman transitions? Proper justification is mandatory. **[8]**
(b) Consider an electronic transition from the ground state (wavefunction, Ψ) to the excited state (wavefunction, Ψ'). Derive the expressions for **(i)** Orbital section rule, **(ii)** spin selection rule, and **(iii)** Franck-Condon factor. **[7]**

**********END**********