PAPER-16 **Marks: 150**

PHYSICAL: QUANTUM CHEMISTRY, PHOTOCHEMISTRY & SURFACE CHEMISTRY

THEORY

Unit I: Quantum Chemistry

Postulates of quantum mechanics, quantum mechanical operators, Schrödinger equation and its application to free particle and "particle-in-a-box" (rigorous treatment), quantization of energy levels, zero-point energy and Heisenberg Uncertainty principle; wave functions, probability distribution functions, nodal properties, Extension to two and three dimensional boxes, separation of variables, degeneracy. Qualitative treatment of simple harmonic oscillator model of vibrational motion: Setting up of Schrödinger equation and discussion of solution and wave functions. Vibrational energy of diatomic molecules and zero-point energy.

Rigid rotator model of rotation of diatomic molecule.

Qualitative treatment of hydrogen atom and hydrogen-like ions: setting up of Schrödinger equation in spherical polar coordinates, radial part, quantization of energy (only final energy expression), radial distribution functions of 1*s*, 2*s*, 2*p*, 3*s*, 3*p* and 3*d* orbitals. Average and most probable distances of electron from nucleus.

Setting up of Schrödinger equation for many-electron atoms (He, Li). Need for approximation methods. Statement of variation theorem and application to simple systems (particle-in-a-box, harmonic oscillator, hydrogen atom).

Chemical bonding: Covalent bonding, valence bond and molecular orbital approaches, LCAO-MO treatment of H_2^+. Bonding and antibonding orbitals. Qualitative extension to H_2. Comparison of LCAO-MO and VB treatments of H_2 (only wave functions, detailed solution not required) and their limitations. Refinements of the two approaches (Configuration Interaction for MO, ionic terms in VB, only wave functions, detailed solution not required).

Qualitative description of LCAO-MO treatment of second row homonuclear and heteronuclear diatomic molecules (HF, LiH, NO, CO). Qualitative MO theory and its application to AH_2 type molecules. Simple Hückel Molecular Orbital (HMO) theory and its application to simple polyenes (ethene, butadiene).

Introduction to molecular modelling and geometry optimization (elementary ideas).

Unit II: Photochemistry

Characteristics of electromagnetic radiation, Lambert-Beer's law and its limitations, physical significance of absorption coefficients. Laws of photochemistry, quantum yield, actinometry, examples of low and high quantum yields, photochemical equilibrium and the differential rate of photochemical reactions, photosensitized reactions, quenching.

Role of photochemical reactions in biochemical processes, photostationary states, chemiluminescence.

Unit III: Surface chemistry

Physical adsorption, chemisorption. Freundlich adsorption isotherm, Langmuir adsorption equation, BET isotherms. Determination of surface area of adsorbent. Gibbs adsorption equation.

Recommended texts:

1. Chandra, A. K. *Introductory Quantum Chemistry*, Tata McGraw-Hill 2001.
2. House, J. E. *Fundamentals of Quantum Chemistry 2nd Ed*., Elsevier: USA 2004.
3. Lowe, J. P. & Peterson, K., *Quantum Chemistry*, Academic Press 2005.
4. Atkins, P. W. & Paula, J. de *Atkin's Physical Chemistry 8th Ed.,* Oxford University Press 2006.
5. Ball, D. W. *Physical Chemistry*, Cengage, India 2012.
6. Castellan, G. W. *Physical Chemistry 4th Ed.,* Narosa 2004.
7. Laidler, K. J. *Chemical Kinetics*, Pearson Education: New Delhi 2004.

PRACTICAL

PHYSICAL: MOLECULAR MODELLING

i. Compare the optimized C-C bond lengths in ethane, ethene, ethyne and benzene. Visualize the molecular orbitals of the ethane σ bonds and ethene, ethyne, benzene and pyridine π bonds.

ii. (a) Perform a conformational analysis of butane. (b) Determine the enthalpy of isomerization of *cis* and *trans* 2-butene.

iii. Visualize the electron density and electrostatic potential maps for LiH, HF, N_2, NO and CO and comment. Relate to the dipole moments. Animate the vibrations of these molecules.

iv. (a) Relate the charge on the hydrogen atom in hydrogen halides with their acid character. (b) Compare the basicities of the nitrogen atoms in ammonia, methylamine, dimethylamine and trimethylamine.

v. (a) Compare the shapes of the molecules: 1-butanol, 2-butanol, 2-methyl-1-propanol, and 2-methyl-2-propanol. Note the dipole moment of each molecule. (b) Show how the shapes affect the trend in boiling points: (118 ºC, 100 ºC, 108 ºC, 82 ºC, respectively).

vi. Build and minimize organic compounds of your choice containing the following functional groups. Note the dipole moment of each compound: (a) alkyl halide (b) aldehyde (c) ketone (d) amine (e) ether (f) nitrile (g) thiol (h) carboxylic acid (i) ester (j) amide.

vii. (a) Determine the heat of hydration of ethylene. (b) Compute the resonance energy of benzene by comparison of its enthalpy of hydrogenation with that of cyclohexene.

viii. Arrange 1-hexene, 2-methyl-2-pentene, (*E*)-3-methyl-2-pentene, (*Z*)-3-methyl-2-pentene, and 2,3-dimethyl-2-butene in order of increasing stability.

ix. (a) Compare the optimized bond angles H_2O, H_2S, H_2Se. (b) Compare the HAH bond angles for the second row dihydrides and compare with the results from qualitative MO theory.

Note: Software: ChemSketch, ArgusLab (www.planaria-software.com), TINKER 6.2 (dasher.wustl.edu/ffe), WebLab Viewer or any similar software.

Recommended Texts:

1. Lewars, E. G. *Computational Chemistry 2nd Ed.,* Springer (India) Pvt. Ltd. 2011, Ch. 1 & 2.
2. Engel, T. & Reid, P. *Physical Chemistry 3rd Ed.,* Prentice-Hall 2012, Ch. 26.
3. Rogers, D. W. *Computational chemistry using PC 3rd Ed.,* John Wiley & Sons.