

MAY 2011

P/ID 40129/PCHJ

Time : Three hours

Maximum : 100 marks

PART A — (10 × 2 = 20 marks)

Answer ALL questions.

All questions carry equal marks.

Each answer should not exceed 50 words.

1. What is Born-Oppenheimer approximation?
2. What is term symbol and explain with an example.
3. Define forces and fluxes in irreversible thermodynamics.
4. How does Guoy-Chapman model differ from Helmholtz model for electrical double layer structure of an electrolyte?
5. Define membrane potential.
6. Define mean ionic activity and activity coefficient.

7. Indicate the difference in the rotational spectra of a rigid and non-rigid rotor.
8. What is the principle involved in Raman spectroscopy?
9. Why do ^{19}F and ^{13}C chemical shifts cover a much larger range than protons?
10. Calculate the magnetic field strength required to give a precessional frequency of 100 MHz for proton, given $g_N = 5.585$ and $\beta_N = 5.0509 \times 10^{-24}$ erg. gauss $^{-1}$.

PART B — (4 × 20 = 80 marks)

Answer ALL questions.

All questions carry equal marks.

11. (a) (i) Apply variation method to helium atom and show the screening constant (σ) in the helium atom as 0.31. (5)
- (ii) Discuss the VB treatment of hydrogen molecule. (10)
- (iii) Discuss the use of Hartree-Fock scheme to obtain many electron wave function. (5)

Or

2 **P/ID 40129/PCHJ**

- (b) (i) Deduce the expression for energy and wave function for H_2^+ system using LCAO-MO method. (10)
- (ii) Calculate the charges on four carbon atoms of butadiene in the lowest electronic excited state using HMO method. (10)
12. (a) (i) What is electrocapillary phenomenon? Explain using Lippman equation. (10)
- (ii) Distinguish the features involved in the theories of Helmholtz, Guoy-Chapman and Stern models to describe the structure of an electrical double layer. (10)

Or

- (b) (i) Define electrokinetic phenomena. Explain with examples. (10)
- (ii) Explain how do you verify Debye-Huckel Bronsted equation. (10)
13. (a) (i) Derive Einstein's coefficient for stimulated emission of electromagnetic radiation. (10)
- (ii) Discuss the vibrational spectra of a harmonic oscillator and how does it differ from that of an anharmonic one? (10)

Or

3 **P/ID 40129/PCHJ**

- (b) (i) What are group frequencies? (5)
- (ii) Discuss group symmetry and selection rules in the case of electronic spectra of molecules. (10)
- (iii) Mention the concept and application of Raman spectroscopy. (5)
14. (a) (i) Discuss the various factors affecting chemical shift in ^1H nmr spectra. (10)
- (ii) What is FT NMR? What are its advantages? (10)

Or

- (b) (i) Discuss the spin-spin coupling in AMX system. (8)
- (ii) What is Zeeman splitting in NMR? (6)
- (iii) Briefly indicate the uses of ^{31}P NMR spectroscopy. (6)