

(6 pages)

Reg. No. :

Code No. : 7169

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M.Sc. (CBCS) DEGREE EXAMINATION, APRIL 2013.

Fourth Semester

Chemistry

PHYSICAL CHEMISTRY — III

(For those who joined in July 2008-2011)

Time : Three hours

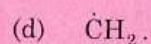
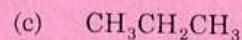
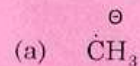
Maximum : 75 marks

PART A — (10 × 1 = 10 marks)

Answer ALL questions.

1. How does microwave spectroscopy useful in determining in the atomic mass on molecules?
2. How are molecules classified into groups according to the relative values of their three principle moments of inertia? Give one example for each.
3. When does the coupling constant J_{AB} in NMR become negative? Explain with an example.
4. Solid state NMR signals are broader than ligand. Why?

5. Which of the following species will be ESR active?



6. Comment on the internal reference used in the ESR spectroscopy.
7. What are well defined (or) acceptable wave functions?
8. Comment on the super position principle.
9. Write the Slater determinant for the ground state of beryllium atom.
10. Explain the significance of Slater determinant regarding the total wave function for a poly electronic system.

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PART B — (5 × 5 = 25 marks)

Answer ALL questions, choosing either (a) or (b).

11. (a) Give an account of the reemission of energy by an excited molecule in terms of fluorescence and phosphorescence.

Or

- (b) What is Born-Oppenheimer approximation and how does it break down in real molecules?

12. (a) Explain how the chemical shift is affected by shielding and deshielding.

Or

- (b) A compound shows a proton NMR peak at 240 Hz downfield from the TMS peak in a spectrometer operating at 60 MHz. What are the values of the chemical shift δ and τ in ppm relative to TMS.

13. (a) How does ESR spectroscopy help in calculating the π -electron density present in conjugate systems.

Or

- (b) Write a note on g values in ESR spectroscopy.

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14. (a) Solve the Schrodinger equation for a particle in a three dimensional box.

Or

- (b) Consider $\hat{P} = \frac{d}{dx}$ and $\hat{Q} = x$. Find out whether these two operators commute using the function $f = x^2 + 2x + 1$.

15. (a) Apply perturbation method for the calculation of GS energy of He atom.

Or

- (b) Discuss the first order perturbation theory.

PART C — (5 × 8 = 40 marks)

Answer ALL questions, choosing either (a) or (b).

16. (a) (i) The spectroscopic bond dissociation energy of $^{35}\text{Cl}, ^{16}\text{O}$ radical is 1.9 eV. Calculate the equilibrium bond dissociation energy of ClO, if the fundamental vibrational frequency is 780 cm^{-1} .

- (ii) Photoelectron spectroscopy of core electrons has become a very powerful technique for structure determination. Explain.

Or

- (b) Discuss the theory of dissociation in electronic spectra.

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17. (a) Discuss the proper energy level diagram for the signal pattern of AM_x system in PMR spectra. Assume $J_{AM} \neq J_{AX} \neq J_{MX}$. What changes will occur if proton A is selectively decoupled?

Or

- (b) Discuss the theory of ^{31}P NMR spectroscopy.

18. (a) (i) Explain how the electron density of carbon atom in a molecule is computed by ESR studies.
- (ii) Calculate the average π -electron spin density in benzene anion radical.

Or

- (b) (i) Explain McConnell equation.
- (ii) For the applied field strength 0.3 T. Calculate the frequency of an unpaired electron (g_e for electron = 2 and Bohr magneton $\beta_e = 9.274 \times 10^{-24} \text{ J/T}$).

19. (a) Setup and solve the SWE for a hydrogen atom.

Or

- (b) (i) Prove that the linear momentum operator is Hermitian.
- (ii) What is the degeneracy of the level for which $E = 27 \left(\frac{h^2}{8ma^2} \right)$ for a particle in a 3D box.

20. (a) Explain variation method of getting the wave function of 'H' atom.

Or

- (b) How are the bond energy and bond length of H_2^+ ion determined by MO theory using variation method?

