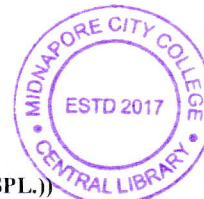


PG (CBCS)
M.SC. Semester- IV Examination, 2026
CHEMISTRY
PAPER: CEM 402

(ADVANCED PHYSICAL CHEMISTRY-III (PHYSICAL SPL.))

Full Marks: 40

Time: 2 Hours



The figures in the right-hand margin indicate full marks.
Candidates are required to give their answers in their own words as far as practicable.

GROUP-A

1. Answer any **FOUR** of the following questions:

2×4=8

- a) State Pauli's antisymmetry principle for a system of identical particles.
- b) State the Hellmann–Feynman theorem.
- c) State Koopmans' theorem.
- d) What is meant by an A–X spin system in NMR spectroscopy?
- e) What is a split-valence basis set?
- f) What is local density approximation (LDA) in DFT?

GROUP-B

2. Answer any **FOUR** of the following questions:

4×4=16

- a) Derive the essential properties of a Slater determinant for multi-electron system and show how it satisfies antisymmetry nature of the wave function.
- b) Distinguish between LS coupling and j-j coupling scheme. Deduce the terms for p^2 configuration using LS coupling scheme.
- c) Write down the magnetic interaction Hamiltonian and the wave function for A_2 spin system. Mention the symmetric / antisymmetric nature of each spin function.
- d) Discuss the basic ideas of Extended Hückel theory and its limitations.
- e) What are polarization and diffuse functions in Gaussian basis sets? Why are they needed?
- f) How many basis functions and primitive Gaussian function will be used if H_2O molecule is treated with 6-311G(d,p)?

GROUP-C

3. Answer any **TWO** of the following questions:

2×8=16

- a) Describe the Hartree–Fock theory for many-electron atoms and derive the Roothaan equations for closed-shell systems. (8)

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- b) Write down the magnetic interaction Hamiltonian and spin wave function for A–X system. Deduce the zero order and 1st order correction of energy for each state. State
- c) the selection rules for NMR transitions and show the possible transitions and show the schematic transitions of the above transitions. (2+4+2)
- d) Give a detailed account of semiempirical molecular orbital methods: INDO, and NDDO-based methods such as MNDO, AM1, and PM3. (4+4)
- e) Explain the foundations of Density Functional Theory, including the Hohenberg–Kohn theorems and Kohn–Sham formalism. (4+4)

