Total pages: 02

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)

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