Reg. No ..... Name **23P2045**

M. Sc. DEGREE END SEMESTER EXAMINATION : MARCH 2023

SEMESTER 2 : CHEMISTRY / PHARMACEUTICAL CHEMISTRY

COURSE : **21P2CHET08 / 21P2CPHT08: THEORETICAL AND COMPUTATIONAL CHEMISTRY**

(For Regular - 2022 Admission and Supplementary - 2021 Admission)

Duration : Three Hours Max. Weights: 30

PART A

Answer any 8 questions **Weight: 1**

1. The character for operation R in the reducible representation = number of unshifted atoms × χ(R). Why only the unshifted atoms are considered? (E)
2. Two functions associated with a molecule (C_{2v} point group), ϕ_1 and ϕ_2 belong to A_1 and A_2 symmetry, respectively. Find out if the integral of the two functions is zero or non-zero. (E)
3. State the variation theorem. Mention its significance. (U)
4. What is Roothan's modification to HF theory? (U)
5. Construct the molecular orbital energy level diagram of HF molecule. (R)
6. Calculate the bond order of NO^+, NO and NO^-. Which is more stable? (A)
7. Apply HMO theory to determine the wavefunctions and corresponding energies of π MOs of benzene. Sketch the MOs. (U)
8. Write the Z matrix for ammonia molecule. (A)
9. What are pseudo potentials? Give example. (U)
10. Define basis set ? (R)

(1 x 8 = 8)

PART B

Answer any 6 questions **Weights: 2**

11. Determine the symmetries of the vibrational modes of $CHCl_3$ molecules using Cartesian co-ordinates. (A)
12. Apply the reduction formula and decompose the following RR. Find out the coefficients of each IRR in the D3h character table.

D3h	**E**	**$2C_3$**	**$3C'_2$**	**σ_h**	**$2S_3$**	**$3\sigma_d$**
Γ_{RR}	**5**	**2**	**1**	**3**	**0**	**3**

(A)

13. Explain the variation treatment for the ground state of the helium atom. (A)
14. The perturbed Hamiltonian, $\widehat{H}$, is given by the relation $\widehat{H} = \widehat{H_0} + \widehat{H'}$. Show that $\widehat{H}$ and $\widehat{H_0}$ are Hermitian, $\widehat{H'}$ must also be Hermitian. (A)
15. Prove that the three sp^2 hybrid orbitals are directed at angles of 120° with respect to one another. (U)
16. Solve the secular determinant for butadiene to obtain the Molecular Orbital energies. (U)

17. Geometry optimization calculation is closely to related to PES. How? Differentiate energy minimization and transition state optimization. (E)

18. What are split valence basis sets ? Explain basis functions present in the following basis sets for Carbon atom a) 3-21G* b) 6-311+G(d,p) . (An)

(2 x 6 = 12)

PART C

Answer any 2 questions **Weights: 5**

19. Explain all possible electronic transitions involving pi bonded electrons in ethylene and trans 1,3 butadiene and its symmetry. Find out the allowed and forbidden transitions among these using the applications of group theory. (An)

20. State and explain Helmann – Feynmann theorem. Find the expectation value of 1/r for the hydrogen atoms. (A)

21. Compare and contrast Valence Bond and Molecular Orbital theories of bonding. (An)

22. What are the basic differences between *ab initio* methods and molecular mechanics methods? What are the widely used applications of molecular mechanics methods? (An)

(5 x 2 = 10)

OBE: Questions to Course Outcome Mapping

CO	Course Outcome Description	CL	Questions	Total Wt.

Cognitive Level (CL): Cr - CREATE; E - EVALUATE; An - ANALYZE; A - APPLY; U - UNDERSTAND; R - REMEMBER;