

PG CBCS  
M.Sc. Semester-III Examination, 2022

CHEMISTRY  
PAPER: CEM 302

ADVANCED PHYSICAL CHEMISTRY-I (PHYSICAL SPL.)

Full Marks: 40

Time: 2 Hours

**GROUP – A**

1. Answer any **FOUR** questions from the following questions:  $2 \times 4 = 8$

- Write the matrix representation for the Schrodinger equation.
- Write secular determinant for the cyclo-butadiene molecule.
- Write the Hamiltonian for a helium atom and identify the perturbation term, if any.
- Define the Variation Principle and mention its significance.
- Define delocalization energy.
- Write the matrix representation of angular momentum.
- Explain 'mutual exclusion principle' with an example.
- Write the expression of the Hamiltonian operator of Lithium atom.

**GROUP - B**

2. Answer any **FOUR** questions from the following questions:  $4 \times 4 = 16$

- Discuss the Zeeman Effect with the help of perturbation theory.
- Write the assumptions of Hückel molecular orbital theory.
- What is meant by charge density and bond order for  $\pi$ -conjugated system? Calculate bond order of an allyl cation system.
- Write the Hamiltonian operator for the  $H_2^+$  molecule defining each term involved in it.
- Obtain the symmetry of vibrational modes of  $H_2O$ . Character tables of  $C_{2v}$  point groups are given below:

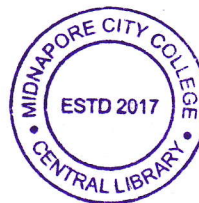
$C_{2v}$	E	$C_2$	$\sigma_{xz}$	$\sigma_{yz}$	I	II
$A_1$	1	1	1	1	$T_z, Z$	$x^2, y^2, z^2$
$A_2$	1	1	-1	-1	$R_z$	xy
$B_1$	1	-1	1	-1	$T_x, R_y$	zx
$B_2$	1	-1	-1	1	$T_y, R_x$	yz

- Obtain the symmetry of IR active modes of  $SO_2$ . The character table of  $C_{2v}$  point groups is given in Question No. 2c.

(P.T.O.)

- g) Obtain the symmetry of Raman active modes of  $\text{POCl}_3$ . Character tables of  $C_{3v}$  point groups are given below:

$C_{3v}$	E	$2C_3(z)$	$3\sigma_v$	Linear functions, rotations
$A_1$	+1	+1	+1	z
$A_2$	+1	+1	-1	$R_z$
E	+2	-1	0	(x, y) ( $R_x, R_y$ )



- h) Find the eigenvalues for the following matrix.

$$\begin{bmatrix} -6 & 3 \\ 4 & 5 \end{bmatrix}$$

### GROUP - C

**3. Answer any TWO questions from the following questions: 8×2 = 16**

- a) Write down the Hückel secular determinant for 1,3-butadiene molecules. Using the Hückel approximation methods, calculate the ground state energy and delocalization energy of butadiene molecules. 2+6
- b) Write down the Hückel secular determinant for the cyclopropenyl system. Using the Hückel approximation methods, calculate the ground state energy and delocalization energy for cyclopropenyl carbonium, cyclopropenyl radical, and cyclopropenyl carbanion system. 2+6
- c) From the perturbation theory,
- Show the first-order nondegenerate energy correction is given by  $E_n^{(1)} = \langle \psi_n^0 | H' | \psi_n^0 \rangle$
  - Show the first-order nondegenerate wave function correction given by 
$$\psi_n^{(1)} = \sum_{m \neq n} \left( \frac{\int \psi_m^0 | H' | \psi_n^0 d\tau}{E_n^0 - E_m^0} \right)$$
 where  $H'$  is the perturbed Hamiltonian and  $\psi_n^0$  is the orthonormal wave function of an unperturbed system. 3+5
- d) Considering the time dependent perturbation theory show that the probability of finding the system in a state  $m$  is proportional to the Fourier transform of the perturbation. 8

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