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PG (CBCS)
M.SC. Semester-III Examination, 2021
CHEMISTRY
PAPER: CEM 302
(PHYSICAL SPL.)

Full Marks: 40 **Time: 2 Hours**

Answer any <u>FOUR</u> questions of the following: 4×10=40

1. (a) Write down the Hamiltonian of helium atom and show how this converted into atomic unit.
   (b) State and prove the variation theorem.
   (c) Consider a hydrogen atom in an electric field in the Z-direction. Obtain the expression for the second order perturbation energy of the atom. 2+3+5

2. Write, without derivation, the appropriate expression for the probability of finding the system in a state m, Obtain the expression for the Fermi Golden Rule. 10

3. (a) From the perturbation theory, show the first order nondegenerate energy correction is given by $E_n^{(1)} = < \psi_n^0 | \mathrm{H}' | \psi_n^0 >$ where H' is the perturbed Hamiltonian and ψ_n^0 is the orthonormal wavefunction of unperturbed system.
   (b) Suppose the particle in the box is subjected to potential energy given by the expression
   $$V = \begin{cases} kx \text{ for } 0 \le x \le l \\ \infty \quad \text{otherwise} \end{cases}$$
   where k is a constant. Find perturbation energy and total energy of the system. 6+4

4. Write, without derivation, the appropriate expression for the probability of finding the system in a state m, obtain the expression for the Fermi Golden Rule. 10

5. State Hückel approximations for linear conjugated system and hence deduce the expression of energies and wave functions of π-MO for 1,3-butadiene. 10

6. What is meant by charge density and bond order for π-conjugated system? Calculate bond order of an allyl cation system. Calculate delocalization energy of 1,3-butadiene.
   3+3+4

7. Obtain the symmetry of vibrational modes of H_2O and NH_3. Character tables of C_{2v} and C_{3v} point groups are given below:

C_{2v}	E	C_2	σ_{xz}	σ_{xz}	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

(P.T.O.)

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)

5+5

8. Obtain the symmetry of IR active modes of SO_2 and $CHCl_3$. Character tables of C_{2v} and C_{3v} point groups are given in Question No. 7. 5+5

9. Obtain the symmetry of Raman active modes of H_2O and $POCl_3$. Character tables of C_{2v} and C_{3v} point groups are given in Question No. 7. 5+5

10. (a) Deduce the expression of transformation matrix which transforms one basis to another in an n-dimensional linear vector space.

    (b) Find the eigenvalues for the following matrix?

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

5+5

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