9. Assign Mulliken symbols for the following irreducible representations 2

E	$2C_3$	$3C_2'$	σ_h	$2S_3$	$3\sigma_v$
1	1	1	-1	-1	-1
1	1	-1	-1	-1	1

Use following character tables, if required to answer the above questions.

(i) Character table for C_{3v}

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

(ii) Character table for C_3, $\varepsilon = \exp(2\pi i/3)$

	E	C_3^1	C_3^2
A	1	1	1
E {	1	ε	ε^*
	1	ε^*	ε

—— X ——

Ex./M.Sc/CH/I/U-1011/9/2018

M.Sc. CHEMISTRY EXAMINATION, 2018

(1st Semester)

THEORITICAL CHEMISTRY

Paper - I

Time : Two hours Full Marks : 50

(25 marks for each unit)

Use a separate answerscript for each unit.

UNIT - 1011

Answer any ***two*** questions.

1. (a) If two state functions, ψ_1 and ψ_2 are the non-degenerate eigen functions of a hermitian operator. $\hat{A}$ then prove that $\langle \psi_1 | \hat{B} | \psi_2 \rangle = 0$, where $\hat{B}$ is a hermitian operator which commutes with $\hat{A}$. $2^1/_2$

(b) Find out the commutator of the following : $2^1/_2+2^1/_2$

(i) $\left[\hat{L}^2, \hat{L}_y\right]$

(ii) $\left[\hat{P}_x^n, \hat{X}\right]$, the terms have their usual meanings.

(c) Deduce an expression for the time variation of the average value of a dynamical observable in Heisenberg picture. $2^1/_2$

(d) Show that the average kinetic energy of a harmonic oscillator is exactly half of the total energy in any stationary state. $2^1/_2$

(Turn over)

2. (a) Show that the energy of a rotating quantum particle in a ring is quantized. Comment on the level of degeneracy of its eigenstates. $4^1/_2+2$

   (b) Derive the recursion formula for the Hermile polynomials. Using the formula establish the selection rule for the dipole induced transition in one-dimensional harmonic oscillator. 3+3

3. (a) Considering benzene ring to be a circular ring and assuming that the C-C bond length is 1.4Å, find out the wave length of the first electronic band in benzene. 3

   (b) Construct the ground state wave functions for the Li-atom ($1s^2 2s^1$) in the form of Slater determinant satisfying Pauli exclusion principle. 3

   (c) Find out the following quantities : 3

$$\hat{S}_+|\alpha\rangle,\ \hat{S}_-|\alpha\rangle, \hat{S}_x|\alpha\rangle,\ \hat{S}_x|\beta\rangle, \hat{S}_y|\alpha\rangle, \hat{S}_y|\beta\rangle$$

   (d) Construct Pauli spin matrices and show that they anti commute. $3^1/_2$

UNIT - 1012

4. Construct the complete character table for C_{2v} point group. 6

5. What do you mean by a class of elements in a group ? Give example. How many classes are there in D_2 point group ? 3

6. Answer any ***one*** : 4

   (a) Find out the σ-SALCs for fluorine σ-orbitals in BF_3.

   (b) Write a reducible representation for the motional degrees of freedom of $POCl_3$ (point group C_{3v}). Decompose the representation into the irreducible representations contained in it.

7. Identify the point groups of the following molecules (any ***five***) : 5

   (i) trans-$[PtCl_2(NH_3)_2]$ (ii) cis-$[Co(NH_3)_4F_2]^+$

   (iii) ICl_3 (iv) PCl_3F_2 (v) IF_7 (vi) 1,2-dichlorobenzene.

8. Answer any ***two*** of the following : $2^1/_2$x2

   (a) Under what condition, the elements E, A and B form a group (E = Identity).

   (b) Gather all the symmetry elements present in an octahedron.

   (c) Find out the matrix representation for $C_n(z)$ symmetry element, n = 360/θ, θ = angle of rotation around z axis.

(Turn over)