M. Sc. Chemistry Examination, 2017

(1st Semester)

Theoretical Chemistry

Paper - I

Time : Two hours Full Marks : 50

(25 marks for each unit)

Use a separate answerscript for each unit.

UNIT - U- 1011

Answer any two questions

1. (a) Explain whether the following state functions are acceptable or not in the given ranges. 3

$i)\sin^{-x}\ (-1,\ +1)$ $ii)\ e^{-|x|}\ (-\infty,\ +\infty)$

(b) Find out the commutator of $\left[\hat{P}_x, \hat{X}^n\right]$ where the terms have their usual meaning. 2

(c) Show that the commutator of $\left[\hat{L}_y, \hat{L}_z\right]$ can be expressed in terms of $\hat{L}_x$, where the symbols have their usual meaning. $2\frac{1}{2}$

(d) If two operators $\hat{A}$ and $\hat{B}$ have a common eigenfunction, ψ with the eigenvalues 'a' and 'b' respectively, Prove that the two operators commute with each other. 2

(e) Show that the Hamiltonian operator is always hermitian. 3

2. (a) Prove that the product of the measure of spreads of two incompatible observables P and Q whose operators do not commute, obeys Heisenberg's uncertainty principle. $4\frac{1}{2}$

(b) Derive the selection rule for allowed transition for a rigidly rotating diatomic molecule (using the identity $(2J+1)XP_J^{|M|}(X) = (J-|M|+1)P_{J+1}^{|M|}(X) + (J+|M|)P_{J-1}^{|M|}(X)$, where the symbols have their usual meaning). 3

(c) Define step up and step down operators in angular momentum of a particle and explain why they are called so. 2+3

3. (a) Graphically represent the radial part of the wave functions for 1s, 2s and 3s states of H-atom 3

(b) Construct Pauli spin matrices for spin angular momentum operator $\hat{S}_x$, $\hat{S}_y$ & $\hat{S}_z$ 3

(c) State the independent particle model in many electron atomic systems. Show that the total energy of such a system is the sum of the individual particle energy, assuming the total wave function is the product of individual wave function. $3\frac{1}{2}$

(d) Construct wave functions for the lowest excited state of He(1s2s) atom satisfying Pauli exclusion principle. 3

UNIT - U- 1012

4. Construct the character table for C_{4v} point group. Assign appropriate Mulliken symbols to the irreducible representations. Complete Area III and Area IV with proper justification. 7

5. (a) Find out the SALCs for hydrogen 1s orbitals in ammonia (NH_3) 4

or

(b) Write a reducible representation for the motional degrees of freedom of pyridine (point group C_{2v}) by Cartesian coordinate method. Decompose the representation into the irreducible representations contained in it. 4

6. (a) Identify the point groups of the following molecules 5

(i) Cis $[PtCl_2(NH_3)_2]$ (ii) Trans $[Co(H_2O)_4Cl_2]^+$ (iii) SF_4 (iv) PCl_3F_2 (v) XeF_4

7. Answer any three of the followings 2 x 3

(a) Prove that, if in a group, an element A is conjugate with two other elements B and C separately, then B and C are conjugate with each other.

(b) Show that any group of order 3 should be an Abelian group.

(c) The asymmetric stretching mode of the H_2O belongs to the irreducible representation A_2. Justify or contradict.

(d) Gather all the symmetry elements present in a tetrahedron.

(e) Find out the matrix representation for $C_3(Z)$ element.

8. (a) Find out the direct product **ExExA$_2$** in C_{3v} point group and decompose it into the irreducible representations contained in it. 3

or

(b) Find out the direct product **Eg** x **Eg** in O_h point group and decompose it into the irreducible representations contained in it. 3

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

(i) Character table for C_{2v}

C_{2v}	E	C_2	σ_v	σ_v'		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

(ii) 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)

(iii) Character table for O_h

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma h$	$6\sigma d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1
E_g	2	-1	0	0	2	2	0	-1	2	0
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1
E_u	2	-1	0	0	2	-2	0	1	-2	0
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1