MANAV RACHNA

MANAV RACHNA UNIVERSITY
DEPARTMENT OF CHEMISTRY
"T3 Examination 2018"

Semester: IV
Subject: Group Theory and its Applications
Branch: Chemistry
Course Type: Elective
Time: 3 Hrs
Max. Marks: 100

Date of Exam: 21st March, 2018
Subject Code: CHH626-T
Session: 2017 - 2018
Course Nature: Hard
Program: M.Sc. Chemistry

Signature: HOD/Associate HOD:

***Note**: Attempt six questions in all selecting two questions from each section.*

Part A

Q.1 a) What do you mean by equivalent symmetry elements and equivalent atoms? Explain using suitable examples. 4

b) Describe the concept of block factorization taking an example of any matrix. For what purpose it is being utilized? 3

c) Identify all the symmetry elements present in the molecule of trans and cis $CH_2Cl_2CH2Cl_2$. 3

Q.2 a) Given below is the character table of the point group D_3h. Using this character table answer the following in brief

D_3h	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A1'	1	1	1	1	1	1		x^2+y^2, z^2
A2'	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x,y)	(x^2-y^2, xy)
A1"	1	1	1	-1	-1	-1		
A2"	1	1	-1	-1	-1	1	Z	
E"	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)
RR	18	12	0	-4	2	-14		

i. Convert the above reducible representation into irreducible representation. 3

ii. What does the symbols of (R_x,R_y) and (x^2-y^2, xy) signify in third column of the character table? 2

b) How do the atomic orbitals used as basis to generate the molecular orbital when combined linearly to form a molecule? Evaluate any two orbitals taking example of D_3h point group. 5

Q.3 Define the following with one example to each — 2 each

a) Optical activity and dipole moments w.r.t any molecule
b) Similarity transformation and point group
c) Irreducible and reducible representations
d) Position vector and base vector
e) Vanishing integral

Part B

Q.4 a) How do the degeneracy of the atomic orbitals be lifted up during the formation of molecular orbital? Explain giving suitable example of octahedral geometry for d^3 configuration. 8

b) Evaluate the hybridization of $PtCl_4$ molecule using group theory. Write the steps in sequential manner. 6

c) Write the formation of secular equations and secular determinant for a system consisting of 2 atoms. 6

Q.5 a) What is angular momentum and spin momentum of any electronic configuration? Taking example of any two electronic configurations, describe how the angular momentum and spin momentum are coupled together to derive the total momentum. How the term symbols are represented for any configuration? 8

b) Explain the hybridization of BF_3 molecule using the character table of D_3h point group. 7

c) Explain how the secular determinants are solved using the Huckel's rule. 5

Q.6 a) Explain the ground state terms and the splitting of terms for the configuration- d^7, d^6, d^3, d^5, d^1 and d^9. 6

b) How the concept of group theory is utilized to determine the hybridization of any molecule. 8

c) Describe the level of energy values of the molecular orbitals formed by combining atomic orbitals for linear butadiene molecule. 6

Part C

Q.7 a) What do you mean by degrees of freedom and their types for molecular motions? How do we calculate them? 4

b) Generate the normalized molecular orbital set of BF_3 molecule using SALC. 8

c) In what ways the pi bonds are created in a molecule? How their hybridization determined using group theory? 8

Q. 8 a) Explain how the concept of group theory can be utilized to evaluate whether any fundamental modes of vibration of a molecule is IR active or not. (Use H_2O as example). 8

b) For the molecule of AB_3 type, determine the hybridization of atomic orbital present at perpendicular and parallel positions w. r. t to the plane of the molecule. 8

c) What is the rule of mutual exclusion? Explain using one example. 4

Q.9 a) What fundamental modes of vibration of CCl_4 molecules are Raman and IR active. 12

b) Calculate the energy values of molecular orbital formed for linear AB_2 type molecules using HMO concept? 8

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Character Table

D_{4h}	E	$2C_4$ (z)	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	linear functions, rotations	quadratic functions	cubic functions
A_{1g}	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1	-	x^2+y^2, z^2	-
A_{2g}	+1	+1	+1	-1	-1	+1	+1	+1	-1	-1	R_z	-	-
B_{1g}	+1	-1	+1	+1	-1	+1	-1	+1	+1	-1	-	x^2-y^2	-
B_{2g}	+1	-1	+1	-1	+1	+1	-1	+1	-1	+1	-	xy	-
E_g	+2	0	-2	0	0	+2	0	-2	0	0	(R_x, R_y)	(xz, yz)	-
A_{1u}	+1	+1	+1	+1	+1	-1	-1	-1	-1	-1	-	-	-
A_{2u}	+1	+1	+1	-1	-1	-1	-1	-1	+1	+1	z	-	$z^3, z(x^2+y^2)$
B_{1u}	+1	-1	+1	+1	-1	-1	+1	-1	-1	+1	-	-	xyz
B_{2u}	+1	-1	+1	-1	+1	-1	+1	-1	+1	-1	-	-	$z(x^2-y^2)$
E_u	+2	0	-2	0	0	-2	0	+2	0	0	(x, y)	-	(xz^2, yz^2) (xy^2, x^2y), (x^3, y^3)

Td	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)