BIRLA INSTITUTE OF TECHNOLOGY, MESRA, RANCHI
(END SEMESTER EXAMINATION)

CLASS: IMSc | **SEMESTER: X**
BRANCH: CHEMISTRY | **SESSION: SP/2023**

SUBJECT: CH514 CHEMICAL APPLICATION OF GROUP THEORY

TIME: 3 Hours | **FULL MARKS: 50**

INSTRUCTIONS:
1. The question paper contains 5 questions each of 10 marks and total 50 marks.
2. Attempt all questions.
3. The missing data, if any, may be assumed suitably.
4. Before attempting the question paper, be sure that you have got the correct question paper.
5. Tables/Data hand book/Graph paper etc. to be supplied to the candidates in the examination hall.

			CO	**BL**
Q.1(a)	Derive an expression for Projection Operator and discuss the utility of Projection Operators.	[5]	5	2
Q.1(b)	(i) Use the 3N Cartesian basis and the appropriate Character table to determine the symmetries of vibrational modes of H_2O. (ii) Identify the Infra-red active vibrational modes in trans-N_2F_2 molecule by taking help from appropriate character table.	[3+2]	5	3
Q.2(a)	Show that, the symmetry of $2p_z$ orbitals of naphthalene belongs B_{2g}, B_{3g}, A_u, and B_{1u} representation.	[5]	5	2
Q.2(b)	Using HMO approach form the secular determinant of π-orbitals of ethylene and calculate the energy of π-bonding and anti-bonding orbitals.	[5]	5	2
Q.3(a)	Determine the symmetry of hybrid orbitals of boron in BF_3.	[5]	5	3
Q.3(b)	Show that the symmetry representation of □-MOs in H_2O.	[5]	5	2
Q.4(a)	Consider a transition metal atom embedded in O_h symmetry. Quantitatively explain the fate of degeneracy of p and d orbitals in such an environment by taking help from any one symmetry operation present within O_h point group.	[5]	5	3
Q.4(b)	Explain the concept of tetragonal elongation/compression by taking help from the Correlation Table for O_h point group.	[5]	5	3
Q.5(a)	(i) Explain the emergence of band gaps and band structures within solids by taking help from a 1 dimensional Kronig-Penney model. You may assume the concerned potential to be a delta function. (ii) Consider a free particle wave function. Does this wave function obey Bloch's theorem?	[3+2]	5	3
Q.5(b)	Show that in 2-dimensional lattice 5 order rotation is not possible.	[5]	5	1

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Character and Correlation Tables

O_h	O	T_d	D_{4h}	D_{2d}	C_{4v}	C_{2v}	D_{3d}	D_3	C_{2h}
A_{1g}	A_1	A_1	A_{1g}	A_1	A_1	A_1	A_{1g}	A_1	A_g
A_{2g}	A_2	A_2	B_{1g}	B_1	B_1	A_2	A_{2g}	A_2	B_g
E_g	E	E	$A_{1g}+B_{1g}$	A_1+B_1	A_1+B_1	A_1+A_2	E_g	E	A_g+B_g
T_{1g}	T_1	T_1	$A_{2g}+E_g$	A_2+E	A_2+E	$A_2+B_1+B_2$	$A_{2g}+E_g$	A_2+E	A_g+2B_g
T_{2g}	T_2	T_2	$B_{2g}+E_g$	B_2+E	B_2+E	$A_1+B_1+B_2$	$A_{1g}+E_g$	A_1+E	$2A_g+B_g$
A_{1u}	A_1	A_2	A_{1u}	B_1	A_2	A_2	A_{1u}	A_1	A_u
A_{2u}	A_2	A_1	B_{1u}	A_1	B_2	A_1	A_{2u}	A_2	B_u
E_u	E	E	$A_{1u}+B_{1u}$	A_1+B_1	A_2+B_2	A_1+A_2	E_u	E	A_u+B_u
T_{1u}	T_1	T_2	$A_{2u}+E_u$	B_2+E	A_1+E	$A_1+B_1+B_2$	$A_{2u}+E_u$	A_2+E	A_u+2B_u
T_{2u}	T_2	T_1	$B_{2u}+E_u$	A_2+E	B_1+E	$A_2+B_1+B_2$	$A_{1u}+E_u$	A_1+E	$2A_u+B_u$

Free-Ion Terms	States in Point Groups		
	O_h	T_d	D_{4h}
^1S	$^1A_{1g}$	$^1A_1$	$^1A_{1g}$
^1G	$^1A_{1g}$ $^1T_{2g}$ ^1E_g $^1T_{1g}$	$^1A_1$ $^1T_2$ ^1E $^1T_1$	$2\,^1A_{1g}$ $^1B_{2g}$ $^1A_{2g}$ $2\,^1E_g$ $^1B_{1g}$
^3P	$^3T_{1g}$	$^3T_1$	$^3A_{2g}$ ^3E_g
^1D	^1E_g $^1T_{2g}$	^1E $^1T_2$	$^1A_{1g}$ ^1E_g $^1B_{1g}$ $^1B_{2g}$
^3F	$^3A_{2g}$ $^3T_{1g}$ $^3T_{2g}$	$^3A_2$ $^3T_1$ $^3T_2$	$^3A_{2g}$ $2\,^3E_g$ $^3B_{1g}$ $^3B_{2g}$

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	1	−1
B_2	1	−1	−1	1

C_{2h}	E	C_2	i	σ_h
A_g	1	1	1	1
B_g	1	−1	1	−1
A_u	1	1	−1	−1
B_u	1	−1	−1	1

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		x^2+y^2, z^2
A_2'	1	1	−1	1	1	−1	R_z	
E'	2	−1	0	2	−1	0	(x, y)	(x^2-y^2, xy)
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1	z	
E''	2	−1	0	−2	1	0	(R_x, R_y)	(xz, yz)

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
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		
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1		(xz, yz, xy)
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	(x, y, z)	
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1		

D_{2h}	E	C_2 (z)	C_2 (y)	C_2 (x)	i	σ (xy)	σ (xz)	σ (yz)	linear functions, rotations	quadratic functions	cubic functions
A_g	+1	+1	+1	+1	+1	+1	+1	+1	-	x^2, y^2, z^2	-
B_{1g}	+1	+1	-1	-1	+1	+1	-1	-1	R_z	xy	-
B_{2g}	+1	-1	+1	-1	+1	-1	+1	-1	R_y	xz	-
B_{3g}	+1	-1	-1	+1	+1	-1	-1	+1	R_x	yz	-
A_u	+1	+1	+1	+1	-1	-1	-1	-1	-	-	xyz
B_{1u}	+1	+1	-1	-1	-1	-1	+1	+1	z	-	z^3, y^2z, x^2z
B_{2u}	+1	-1	+1	-1	-1	+1	-1	+1	y	-	yz^2, y^3, x^2y
B_{3u}	+1	-1	-1	+1	-1	+1	+1	-1	x	-	xz^2, xy^2, x^3