2/5/19.

CH4208-2019 End-Sem exam. Time= 2 & half hrs.

Answer any 5 questions. Full Marks = 50

(Special credit will be given to precise, clear-cut and to-the-point answers.

1. Consider a trigonal bipyramidal ML_5 transition metal complex. (a) Construct a simplified sigma-only MO scheme, assuming that only $(n-1)d$ orbitals on the central metal participate in bonding interactions with ligand σ-SALCs (i.e., ignore interactions with metal ns and np AOs). Assume that the energies of SALCs lie lower than those of the metal AOs. (b) How does the electron filling in this MO scheme compare with the presumed filling in the d orbitals in the CFT model? (7+3)

2. Determine the number of frequencies, their symmetries, and the IR and Raman activities of the normal modes for (a) BeF_3^- (b) PF_5. (5+5)

3. Using projection operators, derive normalized functions for four H SALCs in the $CH_2{=}C{=}CH_2$ molecule. (10)

4. Determine the sets of specific AOs that can be combined to form hybrid orbitals with the following geometries: (a) trigonal planar (b) trigonal bipyramid.

5. Assuming a trigonal planar geometry for BH_3, develop a general MO scheme for BH_3. Derive the SALCs. Assume that only $2s$ and $2p$ orbitals of B interact with the H $1s$ orbitals, i.e., B $1s$ orbital is non-bonding. (10)

6. Using group theory and Hückel method, develop a qualitative π-MO scheme for cyclic $(CH)_3$ system in planar geometry. Find the representation choosing a proper basis. Then derive the form of MOs. Show filling of electrons in the scheme for neutral molecule, +1 cation and -1 anion. Discuss their relative stability in terms of usual α, β integrals. (10)

7. Consider three degenerate p orbitals p_x, p_y, p_z, for an isolated atom M. If M is surrounded by several X atoms, the electrostatic field may lift the degeneracy among them. Describe the degree of degeneracy among p orbitals allowed by symmetry for each of the following structures: (a) MX_2, linear (b) MX_2, bent (c) MX_3, trigonal planar (d) MX_3, pyramidal (e) MX_4, tetrahedral (f) MX_4, square planar (g) MX_5, square pyramidal (h) MX_5, trigonal bipyramidal (i) MX_6, octahedral. (10)

D_2	E	$C_2(z)$	$C_2(y)$	$C_2(x)$		
A	1	1	1	1		$z^2; x^2; y^2$
B_1	1	1	-1	-1	z, R_z	xy
B_2	1	-1	1	-1	$y; R_y$	xz
B_3	1	-1	-1	1	$x; R_x$	yz

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)