Chem 370 - Spring, 2019
Assignment 3

Reading Assignment

If you have not completed reading Chapter 4, do so now. That will be the cut-off point for the first test (currently scheduled for March 4^{th}). Material in Chapter 5 will be covered on the second test.

Homework Assignment

Owing to the Presidents' Day holiday, Discussion 3 will be shifted to Friday, February 22^{nd}, during what would normally be our regular lecture time. Complete the following exercises before coming to tht discussion.

Do the following problems, which are adapted from my book, *Molecular Symmetry and Group Theory*.

1. The operations of the group C_{2h} are E, C_2, i, σ_h.
   (a) Without consulting the C_{2h} character table, determine the sets of characters comprising the irreducible representations by which the unit vectors **x**, **y**, and **z** transform in C_{2h}.
   (b) Do the same for the rotational vectors $\boldsymbol{R_x}$, $\boldsymbol{R_y}$, and $\boldsymbol{R_z}$.

2. Consider a general vector **v**, whose base is at (0,0,0) and whose tip is at (x,y,z), in the point group C_{2h}.
   (a) Derive the set of 3×3 transformation matrices that constitute the reducible representation, Γ_m, by which **v** transforms.
   (b) Reduce Γ_m into its component irreducible representations by block diagonalization.
   (c) Write the reducible representation of characters, Γ_v, that corresponds to the matrix representation, Γ_m.
   (d) Show that Γ_v reduces to the same irreducible representations as Γ_m.
   (e) Show that the four transformation matrices comprising Γ_m obey the same combinational relationships as the operations of C_{2h}. [*Hint:* You will need to work out the multiplication table for C_{2h}.]

3. Consider the three *p* orbitals p_x, p_y, and p_z, which are degenerate for an isolated atom M. If M is surrounded by several X atoms, the electrostatic field they create may lift the degeneracy among the *p* orbitals. By consulting the appropriate character table (Appendix C in Miessler & Tarr), describe the degree of degeneracy among the *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_3, T-shaped (as in ClF_3); (f) MX_4, tetrahedral; (g) MX_4, square planar; (h) MX_4, disphenoid (as in SF_4); (i) MX_5, square pyramidal; (j) MX_5, trigonal bipyramidal; (k) MX_6, octahedral.

4. Use the C_{3v} multiplication table below. By taking all of the necessary similarity transforms verify that the three σ_v planes belong to the same class.

C_{3v}	E	C_3	C_3^2	σ_1	σ_2	σ_3
E	E	C_3	C_3^2	σ_1	σ_2	σ_3
C_3	C_3	C_3^2	E	σ_3	σ_1	σ_2
C_3^2	C_3^2	E	C_3	σ_2	σ_3	σ_1
σ_1	σ_1	σ_2	σ_3	E	C_3	C_3^2
σ_2	σ_2	σ_3	σ_1	C_3^2	E	C_3
σ_3	σ_3	σ_1	σ_2	C_3	C_3^2	E

5. In C_{3v} both C_3 and C_3^2 belong to the same class, listed as $2C_3$ in the character table. As members of the same class their characters for any representation are the same.
   (a) Demonstrate that both C_3 and C_3^2 have a character of 1 for the A_1 representation, by which the unit vector **z** transforms.
   (b) Demonstrate that both C_3 and C_3^2 have a character of –1 for the E representation, by which the unit vectors **x** and **y** transform degenerately. [*Hint:* Write the 2×2 transformation matrices describing the actions of the operations on a point (x,y) and determine their characters.]

6. Describe the implied symmetry of the following irreducible representations on the basis of their Mulliken symbols: (a) A_{1g} in C_{2h}, (b) B_2 in C_{4v}, (c) E in D_3, (d) A_1'' in D_{3h}, (e) E' in D_{3h}, (f) B_{1g} in D_{4h}, (g) E_u in D_{4h}, (h) T_g in T_h.

7. Construct real-number representations by combining the complex-conjugate paired irreducible representations in the following point groups: (a) C_4, (b) C_6, (c) C_5, (d) C_7.

8. Reduce the following representations into their component species (irreducible representations):

D_{2d}	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$
Γ_a	4	0	0	0	2

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_b	12	0	2

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_c	5	2	1	3	0	3

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Γ_d	15	0	–1	–1	3

D_{5h}	E	C_5	$2C_5^2$	$5C_5$	σ_h	$2S_5$	$2S_5^3$	$5\sigma_v$
Γ_e	7	2	2	1	5	0	0	3

9. Reduce the following representations, from groups whose irreducible representations contain imaginary characters, into their component species.

C_4	E	C_4	C_2	C_4^3
Γ_a	15	1	–1	1

C_{3h}	E	C_3	C_3^2	σ_h	S_3	S_3^5
Γ_b	21	0	0	7	–2	–2

C_5	E	C_5	C_5^2	C_5^3	C_5^4
Γ_c	7	2	2	2	2

10. Using the transformation properties listed in the character tables, determine the correlations between species of the following groups and their indicated subgroups, presenting your results as correlation diagrams:
    (a) $C_{4v} \to C_4$, (b) $D_{3h} \to D_3$, (c) $D_{5d} \to C_{5v}$

11. Assume that the following representations were generated in C_{2v} and D_{2h} to avoid working in the molecules' true infinite-order groups, $C_{\infty v}$ and $D_{\infty h}$. Determine the species into which each representation reduces, and by correlation determine what the corresponding species would be in the true infinite-order group.

C_{2v}	E	C_2	σ_v	σ_v'
Γ_a	15	–5	5	5

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
Γ_b	9	–3	–1	–1	–3	1	3	3