CHEM 20100 (Inorganic Chemistry I) Problem Sets

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Contents

0 Course Prep Problems

9/13: **2.8** The details of several steps in the particle-in-a-box model in this chapter have been omitted. Work out the details of the following steps:

a. Show that if $\Psi = A\sin rx + B\cos sx$ (A, B, r, and s are constants) is a solution to the wave equation for the one-dimensional box, then

$$r = s = \sqrt{2mE}\left(\frac{2\pi}{h}\right)$$

Solution.

$$\begin{aligned}
\frac{-h^2}{8\pi^2 m}\cdot\frac{\partial^2\Psi(x)}{\partial x^2} &= E\Psi(x)\\
\frac{-h^2}{8\pi^2 m}\cdot\frac{\partial^2}{\partial x^2}(A\sin rx + B\cos sx) &= E(A\sin rx + B\cos sx)\\
\frac{-h^2}{8\pi^2 m}\cdot\frac{\partial}{\partial x}(Ar\cos rx - Bs\sin sx) &= E(A\sin rx + B\cos sx)\\
\frac{-h^2}{8\pi^2 m}\cdot\left(-Ar^2\sin rx - Bs^2\cos sx\right) &= E(A\sin rx + B\cos sx)\\
\frac{Ar^2h^2}{8\pi^2 m}\sin rx + \frac{Bs^2h^2}{8\pi^2 m}\cos sx &= AE\sin rx + BE\cos sx\\
0 &= \left(\frac{Ar^2h^2}{8\pi^2 m} - AE\right)\sin rx + \left(\frac{Bs^2h^2}{8\pi^2 m} - BE\right)\cos sx
\end{aligned}$$

Choose $x = 0$.

$$\begin{aligned}
&= \frac{Bs^2h^2}{8\pi^2 m} - BE\\
E &= \frac{s^2h^2}{8\pi^2 m}\\
\frac{8\pi^2 mE}{h^2} &= s^2\\
s &= \sqrt{\frac{8\pi^2 mE}{h^2}}\\
&\boxed{s = \sqrt{2mE}\frac{2\pi}{h}}
\end{aligned}$$

With this result ...

$$\begin{aligned}
0 &= \left(\frac{Ar^2h^2}{8\pi^2 m} - AE\right)\sin rx + \left(\frac{Bs^2h^2}{8\pi^2 m} - BE\right)\cos sx\\
&= \left(\frac{Ar^2h^2}{8\pi^2 m} - AE\right)\sin rx + \left(B\left(\frac{s^2h^2}{8\pi^2 m}\right) - BE\right)\cos sx\\
&= \left(\frac{Ar^2h^2}{8\pi^2 m} - AE\right)\sin rx + (BE - BE)\cos sx\\
&= \left(\frac{Ar^2h^2}{8\pi^2 m} - AE\right)\sin rx
\end{aligned}$$

Choose $x = \frac{\pi}{2r}$.

$$= \frac{Ar^2h^2}{8\pi^2 m} - AE$$

$$\boxed{r = \sqrt{2mE}\frac{2\pi}{h}}$$

□

d. Show that substituting the value of r given in part c into $\Psi = A \sin rx$ and applying the normalizing requirement gives $A = \sqrt{2/a}$.

Solution.

$$\begin{aligned} 1 &= \int_{\text{all space}} \Psi\Psi^* \, \mathrm{d}\tau \\ &= \int_0^a \left(A \sin \frac{n\pi x}{a}\right)\left(A \sin \frac{n\pi x}{a}\right) \mathrm{d}x \\ &= \int_0^a A^2 \sin^2 \frac{n\pi x}{a} \, \mathrm{d}x \end{aligned}$$

Use $\sin^2 u = \frac{1-\cos 2u}{2}$.

$$\begin{aligned} &= A^2 \int_0^a \frac{1 - \cos \frac{2n\pi x}{a}}{2} \, \mathrm{d}x \\ &= \frac{A^2}{2}\left(\int_0^a \mathrm{d}x - \int_0^a \cos \frac{2n\pi x}{a} \, \mathrm{d}x\right) \\ &= \frac{A^2}{2}\left([x]_0^a - \left[\frac{a}{2n\pi} \sin \frac{2n\pi x}{a}\right]_0^a\right) \\ &= \frac{A^2}{2}\left((a-0) - \left(\frac{a}{2n\pi}\sin 2n\pi - \frac{a}{2n\pi}\sin 0\right)\right) \\ &= \frac{A^2}{2}\left(a - \left(\frac{a}{2n\pi}\sin 2n\pi\right)\right) \end{aligned}$$

Since n is an integer, $\sin 2n\pi = 0$.

$$\begin{aligned} &= \frac{aA^2}{2} \\ \frac{2}{a} &= A^2 \\ \end{aligned}$$

$$\boxed{A = \sqrt{\frac{2}{a}}}$$

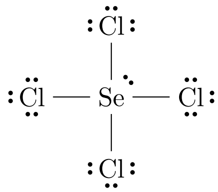
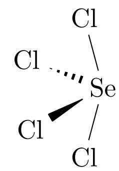
□

1 VSEPR and Point Groups

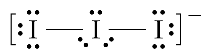
1/21: I) Do the following (VSEPR) problems from your text (Miessler et al. (2014)): Chapter 3: #8, 9f-i, 20, 29.

3.8 Give Lewis dot structures and sketch the shapes of the following:

a. $SeCl_4$

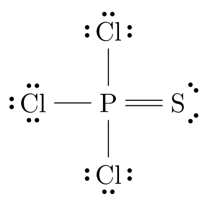
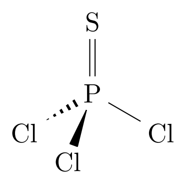



b. I_3^-

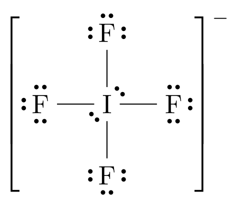
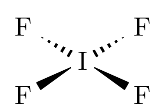


I — I — I

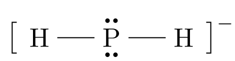
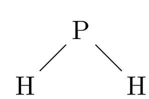
c. $PSCl_3$

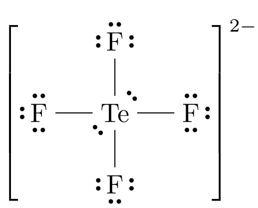
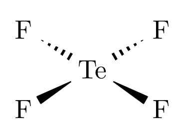
d. IF_4^-

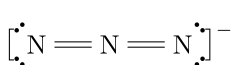
e. PH_2^-

f. TeF_4^{2-}

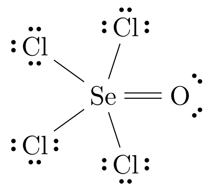
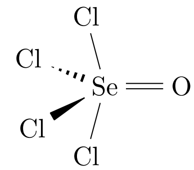



g. N_3^-

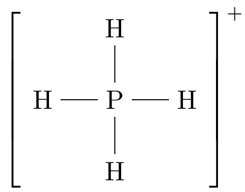
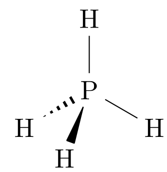


N == N == N

h. $SeOCl_4$

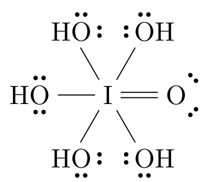
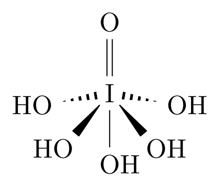
 

i. PH_4^+

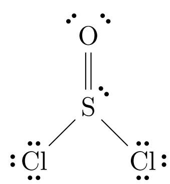
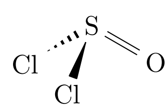
 

3.9 Give Lewis dot structures and sketch the shapes of the following.

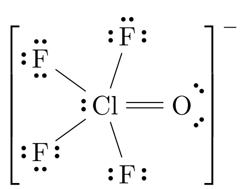
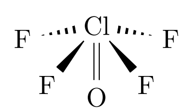
f. $IO(OH)_5$

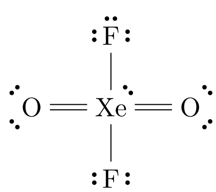
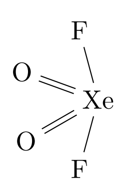
g. $SOCl_2$

h. $ClOF_4^-$[1]

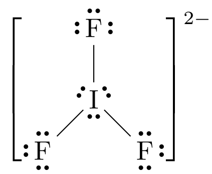
 

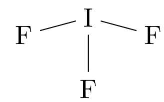
i. XeO_2F_2

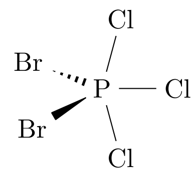
[1] Note that it is unclear whether the equatorial fluorines will be bent away from the lone pair and toward the oxygen, or the other way around. Hence, I arbitrarily chose to show them pointed away from the lone pair.

3.20 Predict and sketch the structure of the (as yet) hypothetical ion ${IF_3}^{2-}$.





3.29 Sketch the most likely structure of PCl_3Br_2 and explain your reasoning.



Answer. Bromine is more electropositive than chlorine. Thus, by Bent's rule, the bromines will bond to the hybrid orbitals with greater *s*-character (the equatorial sp^2 ones) first. □

II) Assign the symmetry point group to the 13 ions and molecules in problems #8, 9f-i in Chapter 3 of your text.

3.8

a. $SeCl_4$

Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. No σ_h. Has two perpendicular σ_v planes.
Therefore, $SeCl_4$ is of the C_{2v} point group. □

b. I_3^-

Answer. I_3^- is of the $D_{\infty h}$ point group. □

c. $PSCl_3$

Answer. Not low or high symmetry. Has a C_3 axis. No perpendicular C_2 axes. No σ_h. Has three σ_v planes all offset by 60°.
Therefore, $PSCl_3$ is of the C_{3v} point group. □

d. IF_4^-

Answer. Not low or high symmetry. Has a C_4 axis. Has 4 perpendicular C_2 axes. Has σ_h.
Therefore, IF_4^- is of the D_{4h} point group. □

e. PH_2^-

Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. No σ_h. Has two perpendicular σ_v planes.
Therefore, PH_2^- is of the C_{2v} point group. □

f. TeF_4^{2-}

Answer. Not low or high symmetry. Has a C_4 axis. Has 4 perpendicular C_2 axes. Has σ_h.
Therefore, TeF_4^{2-} is of the D_{4h} point group. □

g. N_3^-

Answer. N_3^- is of the $D_{\infty h}$ point group. □

h. $SeOCl_4$

Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. No σ_h. Has two perpendicular σ_v planes.
Therefore, $SeOCl_4$ is of the C_{2v} point group. □

i. PH_4^+

Answer. PH_4^+ is of the T_d point group. □

3.9

f. $IO(OH)_5$

Answer. Not low or high symmetry. Has a C_4 axis. No perpendicular C_2 axes. No σ_h. Has two perpendicular σ_v planes and two perpendicular σ_d planes.
Therefore, $IO(OH)_5$ is of the C_{4v} point group. □

g. $SOCl_2$

Answer. $SOCl_2$ is of the C_s point group. □

h. $ClOF_4^-$

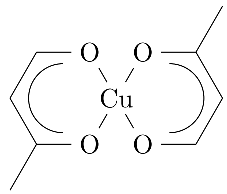
Answer. Not low or high symmetry. Has a C_4 axis. No perpendicular C_2 axes. No σ_h. Has two perpendicular σ_v planes and two perpendicular σ_d planes.
Therefore, $ClOF_4^-$ is of the C_{4v} point group. □

i. XeO_2F_2

Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. No σ_h. Has two perpendicular σ_v planes.
Therefore, XeO_2F_2 is of the C_{2v} point group. □

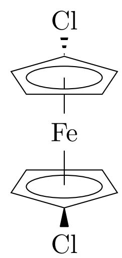
III) Assign the symmetry point group of the following molecules and objects. Ignore the H atoms in (a), (e), and (g). Note that (e) has pseudooctahedral geometry and (g) is square-planar.

a) The molecule pictured below.



Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. Has a σ_h.
Therefore, the above molecule is of the C_{2h} point group. □

b) The molecule pictured below.



Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. Has a σ_h
Therefore, the above molecule is of the C_{2h} point group. □

c) $POCl_3$

Answer. Not low or high symmetry. Has a C_3 axis. No perpendicular C_2 axes. No σ_h. Has three σ_v planes all offset by 60°.
Therefore, $POCl_3$ is of the C_{3v} point group. □

d) Tennis ball (including the seam)

Answer. Not low or high symmetry. Has a C_2 axis. Has 2 perpendicular C_2 axes. No σ_h. Has two perpendicular σ_d planes.
Therefore, a tennis ball is of the D_{2d} point group. □

e) *trans*-$[CrCl_2(H_2O)_4]^+$

Answer. Not low or high symmetry. Has a C_4 axis. Has 4 perpendicular C_2 axes. Has σ_h.
Therefore, *trans*-$[CrCl_2(H_2O)_4]^+$ is of the D_{4h} point group. □

f) 1,3,5-trichlorobenzene.

Answer. Not low or high symmetry. Has a C_3 axis. Has 3 perpendicular C_2 axes. Has σ_h.
Therefore, 1,3,5-trichlorobenzene is of the D_{3h} point group. □

g) *trans*-$Pt(NH_3)_2Cl_2$

Answer. Not low or high symmetry. Has a C_2 axis. Has 2 perpendicular C_2 axes. Has σ_h.
Therefore, *trans*-$Pt(NH_3)_2Cl_2$ is of the D_{2h} point group. □

h) SF_5Cl

Answer. Not low or high symmetry. Has a C_4 axis. No perpendicular C_2 axes. No σ_h. Has two perpendicular σ_v planes and two perpendicular σ_d planes.
Therefore, SF_5Cl is of the C_{4v} point group. □

i) BFClBr

Answer. BFClBr is of the C_s point group. □

j) PF_2^+

Answer. Not low or high symmetry. Has a C_2 axis. No perpendicular C_2 axes. No σ_h. Has two perpendicular σ_v planes.
Therefore, PF_2^+ is of the C_{2v} point group. □

IV) In the octahedral ion ${FeF_6}^{3-}$, what symmetry elements are destroyed if two *trans* F ions are moved away from the Fe^{3+} center in an equidistant fashion?

Answer. If the described change is made, the point group changes from O_h to D_{4h}. In this change, every C_3 and S_6 axis, two of the three C_4 axes, four C_2 axes, and every σ_d that does not contain the axis along which the F ions are stretched are destroyed. □

2 Representations, Character Tables, and Vibrations

1/28: I) Do the following problem from your text: Chapter 4: #22.

4.22 Using the D_{2d} character table,

a. Determine the order of the group.

Answer. $h = 8$; count the number of symmetry elements. □

b. Verify that the E irreducible representation is orthogonal to each of the other irreducible representations.

Answer.

$$\sum_{R_c} g_c \chi_E(R_c)\chi_{A_1}(R_c) = (1)(2)(1) + (2)(0)(1) + (1)(-2)(1) + (2)(0)(1) + (2)(0)(1) = 0$$
$$\sum_{R_c} g_c \chi_E(R_c)\chi_{A_2}(R_c) = (1)(2)(1) + (2)(0)(1) + (1)(-2)(1) + (2)(0)(-1) + (2)(0)(-1) = 0$$
$$\sum_{R_c} g_c \chi_E(R_c)\chi_{B_1}(R_c) = (1)(2)(1) + (2)(0)(-1) + (1)(-2)(1) + (2)(0)(1) + (2)(0)(-1) = 0$$
$$\sum_{R_c} g_c \chi_E(R_c)\chi_{B_2}(R_c) = (1)(2)(1) + (2)(0)(-1) + (1)(-2)(1) + (2)(0)(-1) + (2)(0)(1) = 0$$

□

c. For each of the irreducible representations, verify that the sum of the squares of the characters equals the order of the group.

Answer.

$$\sum_{R_c} g_c[\chi_{A_1}(R_c)]^2 = 1\cdot 1^2 + 2\cdot 1^2 + 1\cdot 1^2 + 2\cdot 1^2 + 2\cdot 1^2 = 8$$
$$\sum_{R_c} g_c[\chi_{A_2}(R_c)]^2 = 1\cdot 1^2 + 2\cdot 1^2 + 1\cdot 1^2 + 2\cdot (-1)^2 + 2\cdot (-1)^2 = 8$$
$$\sum_{R_c} g_c[\chi_{B_1}(R_c)]^2 = 1\cdot 1^2 + 2\cdot (-1)^2 + 1\cdot 1^2 + 2\cdot 1^2 + 2\cdot (-1)^2 = 8$$
$$\sum_{R_c} g_c[\chi_{B_2}(R_c)]^2 = 1\cdot 1^2 + 2\cdot (-1)^2 + 1\cdot 1^2 + 2\cdot (-1)^2 + 2\cdot 1^2 = 8$$
$$\sum_{R_c} g_c[\chi_{E}(R_c)]^2 = 1\cdot 2^2 + 2\cdot 0^2 + 1\cdot (-2)^2 + 2\cdot 0^2 + 2\cdot 0^2 = 8$$

□

d. Reduce the following representations to their component irreducible representations.

D_{2d}	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$
Γ_1	6	0	2	2	2
Γ_2	6	4	6	2	0

Answer. For Γ_1:

$$a_{A_1} = \frac{1}{8}\sum_{R_c} g_c \chi_{\Gamma_1}(R_c)\chi_{A_1}(R_c) = \frac{1}{8}[(1)(6)(1) + (2)(0)(1) + (1)(2)(1) + (2)(2)(1) + (2)(2)(1)] = 2$$
$$a_{A_2} = \frac{1}{8}\sum_{R_c} g_c \chi_{\Gamma_1}(R_c)\chi_{A_2}(R_c) = \frac{1}{8}[(1)(6)(1) + (2)(0)(1) + (1)(2)(1) + (2)(2)(-1) + (2)(2)(-1)] = 0$$
$$a_{B_1} = \frac{1}{8}\sum_{R_c} g_c \chi_{\Gamma_1}(R_c)\chi_{B_1}(R_c) = \frac{1}{8}[(1)(6)(1) + (2)(0)(-1) + (1)(2)(1) + (2)(2)(1) + (2)(2)(-1)] = 1$$

$$a_{B_2} = \frac{1}{8}\sum_{R_c} g_c \chi_{\Gamma_1}(R_c)\chi_{B_2}(R_c) = \frac{1}{8}[(1)(6)(1) + (2)(0)(-1) + (1)(2)(1) + (2)(2)(-1) + (2)(2)(1)] = 1$$
$$a_E = \frac{1}{8}\sum_{R_c} g_c \chi_{\Gamma_1}(R_c)\chi_E(R_c) = \frac{1}{8}[(1)(6)(2) + (2)(0)(0) + (1)(2)(-2) + (2)(2)(0) + (2)(2)(0)] = 1$$

Therefore, we know that

$$\Gamma_1 = 2A_1 + B_1 + B_2 + E$$

For Γ_2:

$$a_{A_1} = \frac{1}{8}\sum_{R_c} g_c \chi_{\Gamma_2}(R_c)\chi_{A_1}(R_c) = \frac{1}{8}[(1)(6)(1) + (2)(4)(1) + (1)(6)(1) + (2)(2)(1) + (2)(0)(1)] = 3$$
$$a_{A_2} = \frac{1}{8}\sum_{R_c} g_c \chi_{\Gamma_2}(R_c)\chi_{A_2}(R_c) = \frac{1}{8}[(1)(6)(1) + (2)(4)(1) + (1)(6)(1) + (2)(2)(-1) + (2)(0)(-1)] = 2$$
$$a_{B_1} = \frac{1}{8}\sum_{R_c} g_c \chi_{\Gamma_2}(R_c)\chi_{B_1}(R_c) = \frac{1}{8}[(1)(6)(1) + (2)(4)(-1) + (1)(6)(1) + (2)(2)(1) + (2)(0)(-1)] = 1$$
$$a_{B_2} = \frac{1}{8}\sum_{R_c} g_c \chi_{\Gamma_2}(R_c)\chi_{B_2}(R_c) = \frac{1}{8}[(1)(6)(1) + (2)(4)(-1) + (1)(6)(1) + (2)(2)(-1) + (2)(0)(1)] = 0$$
$$a_E = \frac{1}{8}\sum_{R_c} g_c \chi_{\Gamma_2}(R_c)\chi_E(R_c) = \frac{1}{8}[(1)(6)(2) + (2)(4)(0) + (1)(6)(-2) + (2)(2)(0) + (2)(0)(0)] = 0$$

Therefore, we know that

$$\Gamma_2 = 3A_1 + 2A_2 + B_1$$

□

II) Decompose the following reducible representations into their irreducible components. Ordering of the classes is the same as in the character tables in Appendix C of your text.

a) D_{3h}: $5, 2, 1, 3, 0, 3$

Answer.

$$a_{A_1'} = \frac{1}{12}\sum_{R_c} g_c\chi_\Gamma(R_c)\chi_{A_1'}(R_c) = \frac{1}{12}[(1)(5)(1) + (2)(2)(1) + (3)(1)(1) + (1)(3)(1) + (2)(0)(1) + (3)(3)(1)] = 2$$

$$a_{A_2'} = \frac{1}{12}\sum_{R_c} g_c\chi_\Gamma(R_c)\chi_{A_2'}(R_c) = \frac{1}{12}[(1)(5)(1) + (2)(2)(1) + (3)(1)(-1) + (1)(3)(1) + (2)(0)(1) + (3)(3)(-1)] = 0$$

$$a_{E'} = \frac{1}{12}\sum_{R_c} g_c\chi_\Gamma(R_c)\chi_{E'}(R_c) = \frac{1}{12}[(1)(5)(2) + (2)(2)(-1) + (3)(1)(0) + (1)(3)(2) + (2)(0)(-1) + (3)(3)(0)] = 1$$

$$a_{A_1''} = \frac{1}{12}\sum_{R_c} g_c\chi_\Gamma(R_c)\chi_{A_1''}(R_c) = \frac{1}{12}[(1)(5)(1) + (2)(2)(1) + (3)(1)(1) + (1)(3)(-1) + (2)(0)(-1) + (3)(3)(-1)] = 0$$

$$a_{A_2''} = \frac{1}{12}\sum_{R_c} g_c\chi_\Gamma(R_c)\chi_{A_2''}(R_c) = \frac{1}{12}[(1)(5)(1) + (2)(2)(1) + (3)(1)(-1) + (1)(3)(-1) + (2)(0)(-1) + (3)(3)(1)] = 1$$

$$a_{E''} = \frac{1}{12}\sum_{R_c} g_c\chi_\Gamma(R_c)\chi_{E''}(R_c) = \frac{1}{12}[(1)(5)(2) + (2)(2)(-1) + (3)(1)(0) + (1)(3)(-2) + (2)(0)(1) + (3)(3)(0)] = 0$$

Therefore, we know that

$$\Gamma = 2A_1' + E' + A_2''$$

□

b) D_{3h}: $3, 0, -1, -3, 0, 1$

Answer.

$$a_{A_1'} = \frac{1}{12}\sum_{R_c} g_c\chi_\Gamma(R_c)\chi_{A_1'}(R_c) = \frac{1}{12}[(1)(3)(1) + (2)(0)(1) + (3)(-1)(1) + (1)(-3)(1) + (2)(0)(1) + (3)(1)(1)] = 0$$

$$a_{A_2'} = \frac{1}{12}\sum_{R_c} g_c\chi_\Gamma(R_c)\chi_{A_2'}(R_c) = \frac{1}{12}[(1)(3)(1) + (2)(0)(1) + (3)(-1)(-1) + (1)(-3)(1) + (2)(0)(1) + (3)(1)(-1)] = 0$$

$$a_{E'} = \frac{1}{12}\sum_{R_c} g_c\chi_\Gamma(R_c)\chi_{E'}(R_c) = \frac{1}{12}[(1)(3)(2) + (2)(0)(-1) + (3)(-1)(0) + (1)(-3)(2) + (2)(0)(-1) + (3)(1)(0)] = 0$$

$$a_{A_1''} = \frac{1}{12}\sum_{R_c} g_c\chi_\Gamma(R_c)\chi_{A_1''}(R_c) = \frac{1}{12}[(1)(3)(1) + (2)(0)(1) + (3)(-1)(1) + (1)(-3)(-1) + (2)(0)(-1) + (3)(1)(-1)] = 0$$

$$a_{A_2''} = \frac{1}{12}\sum_{R_c} g_c\chi_\Gamma(R_c)\chi_{A_2''}(R_c) = \frac{1}{12}[(1)(3)(1) + (2)(0)(1) + (3)(-1)(-1) + (1)(-3)(-1) + (2)(0)(-1) + (3)(1)(1)] = 1$$

$$a_{E''} = \frac{1}{12}\sum_{R_c} g_c\chi_\Gamma(R_c)\chi_{E''}(R_c) = \frac{1}{12}[(1)(3)(2) + (2)(0)(-1) + (3)(-1)(0) + (1)(-3)(-2) + (2)(0)(1) + (3)(1)(0)] = 1$$

Therefore, we know that

$$\Gamma = A_2'' + E''$$

□

c) C_{2v}: $4, 0, 0, 0$

Answer. We know the following by inspection.

$$\Gamma = A_1 + A_2 + B_1 + B_2$$

□

d) C_{2h}: $5, 1, 1, 1$

Answer. We know the following by inspection.

$$\Gamma = 2A_g + B_g + A_u + B_u$$

$\square$

e) T_d: $13, 1, 5, -3, -3$

Answer.

$$a_{A_1} = \frac{1}{24}\sum_{R_c} g_c \chi_\Gamma(R_c)\chi_{A_1}(R_c) = \frac{1}{24}[(1)(13)(1) + (8)(1)(1) + (3)(5)(1) + (6)(-3)(1) + (6)(-3)(1)] = 0$$

$$a_{A_2} = \frac{1}{24}\sum_{R_c} g_c \chi_\Gamma(R_c)\chi_{A_2}(R_c) = \frac{1}{24}[(1)(13)(1) + (8)(1)(1) + (3)(5)(1) + (6)(-3)(-1) + (6)(-3)(-1)] = 3$$

$$a_E = \frac{1}{24}\sum_{R_c} g_c \chi_\Gamma(R_c)\chi_E(R_c) = \frac{1}{24}[(1)(13)(2) + (8)(1)(-1) + (3)(5)(2) + (6)(-3)(0) + (6)(-3)(0)] = 2$$

$$a_{T_1} = \frac{1}{24}\sum_{R_c} g_c \chi_\Gamma(R_c)\chi_{T_1}(R_c) = \frac{1}{24}[(1)(13)(3) + (8)(1)(0) + (3)(5)(-1) + (6)(-3)(1) + (6)(-3)(-1)] = 1$$

$$a_{T_2} = \frac{1}{24}\sum_{R_c} g_c \chi_\Gamma(R_c)\chi_{T_2}(R_c) = \frac{1}{24}[(1)(13)(3) + (8)(1)(0) + (3)(5)(-1) + (6)(-3)(-1) + (6)(-3)(1)] = 1$$

Therefore, we know that

$$\Gamma = 3A_2 + 2E + T_1 + T_2$$

$\square$

f) T_h: $8, -1, -1, 4, 8, -1, -1, 4$

Answer. With respect to the two doubly degenerate groups, we must add the two parts together and also double the order that we are dividing out. Note that $\varepsilon = \mathrm{e}^{2\pi i/3} = \cos\left(\frac{2\pi}{3}\right) + i\sin\left(\frac{2\pi}{3}\right) = -0.5 + i\frac{\sqrt{3}}{2}$ and, thus, $\varepsilon^* = -0.5 + i\frac{\sqrt{3}}{2}$. It follows that $\varepsilon + \varepsilon^* = -1$.

$$\begin{aligned}
a_{A_g} &= \frac{1}{24}\sum_{R_c} g_c \chi_\Gamma(R_c)\chi_{A_g}(R_c) \\
&= \frac{1}{24}[(1)(8)(1) + (4)(-1)(1) + (4)(-1)(1) + (3)(4)(1) + (1)(8)(1) + (4)(-1)(1) + (4)(-1)(1) + (3)(4)(1)] \\
&= 1
\end{aligned}$$

$$\begin{aligned}
a_{A_u} &= \frac{1}{24}\sum_{R_c} g_c \chi_\Gamma(R_c)\chi_{A_u}(R_c) \\
&= \frac{1}{24}[(1)(8)(1) + (4)(-1)(1) + (4)(-1)(1) + (3)(4)(1) + (1)(8)(-1) + (4)(-1)(-1) + (4)(-1)(-1) + (3)(4)(-1)] \\
&= 0
\end{aligned}$$

$$\begin{aligned}
2a_{E_g} &= \frac{1}{24}\sum_{R_c} g_c \chi_\Gamma(R_c)\chi_{E_g}(R_c) \\
a_{E_g} &= \frac{1}{48}[(1)(8)(2) + (4)(-1)(-1) + (4)(-1)(-1) + (3)(4)(2) + (1)(8)(2) + (4)(-1)(-1) + (4)(-1)(-1) + (3)(4)(2)] \\
&= 2
\end{aligned}$$

$$
\begin{aligned}
2a_{E_u} &= \frac{1}{24}\sum_{R_c} g_c \chi_\Gamma(R_c)\chi_{E_u}(R_c) \\
a_{E_u} &= \frac{1}{48}[(1)(8)(2) + (4)(-1)(-1) + (4)(-1)(-1) + (3)(4)(2) + (1)(8)(-2) + (4)(-1)(1) + (4)(-1)(1) + (3)(4)(-2)] \\
&= 0
\end{aligned}
$$

$$
\begin{aligned}
a_{T_g} &= \frac{1}{24}\sum_{R_c} g_c \chi_\Gamma(R_c)\chi_{T_g}(R_c) \\
&= \frac{1}{24}[(1)(8)(3) + (4)(-1)(0) + (4)(-1)(0) + (3)(4)(-1) + (1)(8)(3) + (4)(-1)(0) + (4)(-1)(0) + (3)(4)(-1)] \\
&= 1
\end{aligned}
$$

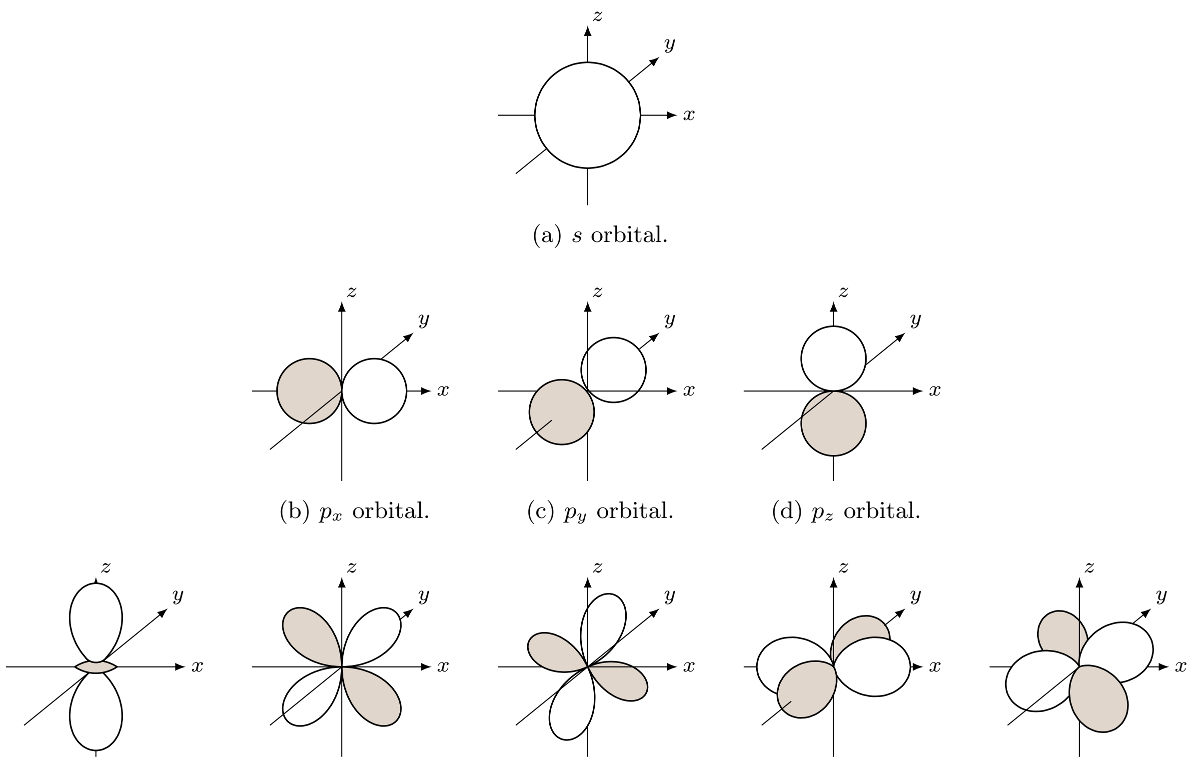
$$
\begin{aligned}
a_{T_u} &= \frac{1}{24}\sum_{R_c} g_c \chi_\Gamma(R_c)\chi_{T_u}(R_c) \\
&= \frac{1}{24}[(1)(8)(3) + (4)(-1)(0) + (4)(-1)(0) + (3)(4)(-1) + (1)(8)(-3) + (4)(-1)(0) + (4)(-1)(0) + (3)(4)(1)] \\
&= 0
\end{aligned}
$$

Therefore, we know that

$$\Gamma = A_g + 2\{E_g\} + T_g$$

$\square$

III) Draw the set of s, p, and d orbitals, indicating the Cartesian axes and the proper phases of the orbitals. By noting how each orbital is affected by the symmetry operations in the C_{2h} point group (E, C_2, i, σ_h), write an irreducible representation for each orbital. Compare your results with the listing of the orbitals in the character table in Appendix C of the text.



(a) s orbital.

(b) p_x orbital. (c) p_y orbital. (d) p_z orbital.

(e) d_{z^2} orbital. (f) d_{xz} orbital. (g) d_{yz} orbital. (h) $d_{x^2-y^2}$ orbital. (i) d_{xy} orbital.

Figure 1: s, p, and d orbitals.

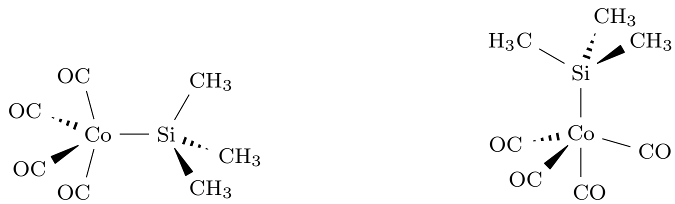
Answer. In Figure 1, white shading means positive phase and orange means negative phase.

Here are irreducible representations for each orbital:

$$\begin{aligned}
\Gamma_s &= (1,1,1,1) = A_g \\
\Gamma_{p_x} &= (1,-1,-1,1) = B_u \\
\Gamma_{p_y} &= (1,-1,-1,1) = B_u \\
\Gamma_{p_z} &= (1,1,-1,-1) = A_u \\
\Gamma_{d_{z^2}} &= (1,1,1,1) = A_g \\
\Gamma_{d_{xz}} &= (1,-1,1,-1) = B_g \\
\Gamma_{d_{yz}} &= (1,-1,1,-1) = B_g \\
\Gamma_{d_{x^2-y^2}} &= (1,1,1,1) = A_g \\
\Gamma_{d_{xy}} &= (1,1,1,1) = A_g
\end{aligned}$$

□

IV) The molecule $Co(CO)_4(SiMe_3)$ has a structure based on a trigonal bipyramid. The infrared spectrum of $Co(CO)_4(SiMe_3)$ exhibits three ν(CO) stretching vibrations at 2100, 2041, and 2009 cm^{-1}. Draw the two possible structures based on the TBP geometry, assign their proper point groups, and use the infrared data to determine which is the correct structure.



(a) Equatorial trimethylsilyl group.

(b) Axial trimethylsilyl group.

Figure 2: Structures of $Co(CO)_4(SiMe_3)$.

Answer. Note that for the sake of point group assignments, the CO ligands will be treated as identical spheres. Additionally, the $SiMe_3$ ligand will be treated as a sphere distinguishable from the CO "spheres."

The structure in Figure 2a: Not high or low symmetry. Has a C_2 axis. No perpendicular C_2 axes. No σ_h. Has two perpendicular σ_v planes. Therefore, it is of the C_{2v} point group.

We can determine that $\Gamma_\nu = (4, 0, 2, 2) = 2A_1 + B_1 + B_2$ by counting how many $\overrightarrow{\text{Co}-\text{CO}}$ vectors stay the same under each symmetry operation and decomposing by inspection. With four stretching modes that are all IR active, we can expect there to be four peaks in the infrared spectrum of $Co(CO)_4(SiMe_3)$. Therefore, this is not the correct structure.

The structure in Figure 2b: Not high or low symmetry. Has a C_3 axis. No perpendicular C_2 axes. No σ_h. Has three σ_v planes all offset by 60°. Therefore, it is of the C_{3v} point group.

We can determine that $\Gamma_\nu = (4, 1, 2) = 2A_1 + E$ by counting how many $\overrightarrow{\text{Co}-\text{CO}}$ vectors stay the same under each symmetry operation and decomposing by inspection. With four ν(CO) stretching modes that are all IR active (but two of the four being degenerate), we can expect there to be three peaks in the infrared spectrum of $Co(CO)_4(SiMe_3)$. This confirms that this is the correct structure. □

V) Determine the number and symmetry types of normal vibrations in the following molecules:

a) H_3PBH_3: with a staggered ethane-like geometry.

Answer. H_3PBH_3 has $3(8) - 6 = 18$ normal vibrations.

Not high or low symmetry. Has a C_3 axis. No perpendicular C_2 axes. No σ_h. Has three σ_v planes all offset by 60°. Therefore, H_3PBH_3 is of the C_{3v} point group.

We can determine that $\Gamma_{x,y,z} = (3, 0, 1)$. We can also figure out that the number of atoms unmoved after applying each symmetry operation is $(8, 2, 4)$. Thus, $\Gamma_{3N} = (24, 0, 4)$. We can reduce this by inspection to $\Gamma_{3N} = 6A_1 + 2A_2 + 8E$.

Since $\Gamma_{\text{trans}} = A_1 + E$ and $\Gamma_{\text{rot}} = A_2 + E$, we have by subtraction that $\Gamma_{\text{vibs}} = 5A_1 + A_2 + 6E$. Thus, of the 18 normal vibrations, 5 have symmetry A_1, 1 has symmetry A_2, and 12 have symmetry E (note that these 12 modes pair up into 6 pairs of vibration modes of the same type). □

b) $Zr_2F_{13}{}^{5-}$: Each Zr is seven coordinate with monocapped trigonal prismatic geometry. The cap is a bridging F (linear Zr−F−Zr linkage) on the unique square face of the prism. The anionic complex has an eclipsed geometry about the bridging F.

Answer. $Zr_2F_{13}{}^{5-}$ has $3(15) - 6 = 39$ normal vibrations.

Not high or low symmetry. Has a C_2 axis. Has 2 perpendicular C_2 axes. Has a σ_h plane. Therefore, $Zr_2F_{13}{}^{5-}$ is of the D_{2h} point group.

We can determine that $\Gamma_{x,y,z} = (3, -1, -1, -1, -3, 1, 1, 1)$. We can also figure out that the number of atoms unmoved after applying each symmetry operation is $(15, 3, 1, 1, 1, 1, 7, 3)$. Thus, $\Gamma_{3N} = (45, -3, -1, -1, -3, 1, 7, 3)$. We can reduce this as follows.

$$
\begin{aligned}
a_{A_g} &= \frac{1}{8}\sum_{R_c} g_c \chi_{\Gamma_{3N}}(R_c)\chi_{A_g}(R_c) \\
&= \frac{1}{8}[(1)(45)(1) + (1)(-3)(1) + (1)(-1)(1) + (1)(-1)(1) + (1)(-3)(1) + (1)(1)(1) + (1)(7)(1) + (1)(3)(1)] \\
&= 6
\end{aligned}
$$

$$
\begin{aligned}
a_{B_{1g}} &= \frac{1}{8}\sum_{R_c} g_c \chi_{\Gamma_{3N}}(R_c)\chi_{B_{1g}}(R_c) \\
&= \frac{1}{8}[(1)(45)(1) + (1)(-3)(1) + (1)(-1)(-1) + (1)(-1)(-1) + (1)(-3)(1) + (1)(1)(1) + (1)(7)(-1) + (1)(3)(-1)] \\
&= 4
\end{aligned}
$$

$$
\begin{aligned}
a_{B_{2g}} &= \frac{1}{8}\sum_{R_c} g_c \chi_{\Gamma_{3N}}(R_c)\chi_{B_{2g}}(R_c) \\
&= \frac{1}{8}[(1)(45)(1) + (1)(-3)(-1) + (1)(-1)(1) + (1)(-1)(-1) + (1)(-3)(1) + (1)(1)(-1) + (1)(7)(1) + (1)(3)(-1)] \\
&= 6
\end{aligned}
$$

$$
\begin{aligned}
a_{B_{3g}} &= \frac{1}{8}\sum_{R_c} g_c \chi_{\Gamma_{3N}}(R_c)\chi_{B_{3g}}(R_c) \\
&= \frac{1}{8}[(1)(45)(1) + (1)(-3)(-1) + (1)(-1)(-1) + (1)(-1)(1) + (1)(-3)(1) + (1)(1)(-1) + (1)(7)(-1) + (1)(3)(1)] \\
&= 5
\end{aligned}
$$

$$
\begin{aligned}
a_{A_u} &= \frac{1}{8}\sum_{R_c} g_c \chi_{\Gamma_{3N}}(R_c)\chi_{A_u}(R_c) \\
&= \frac{1}{8}[(1)(45)(1) + (1)(-3)(1) + (1)(-1)(1) + (1)(-1)(1) + (1)(-3)(-1) + (1)(1)(-1) + (1)(7)(-1) + (1)(3)(-1)] \\
&= 4
\end{aligned}
$$

$$
\begin{aligned}
a_{B_{1u}} &= \frac{1}{8}\sum_{R_c} g_c \chi_{\Gamma_{3N}}(R_c)\chi_{B_{1u}}(R_c) \\
&= \frac{1}{8}[(1)(45)(1) + (1)(-3)(1) + (1)(-1)(-1) + (1)(-1)(-1) + (1)(-3)(-1) + (1)(1)(-1) + (1)(7)(1) + (1)(3)(1)] \\
&= 7
\end{aligned}
$$

$$
\begin{aligned}
a_{B_{2u}} &= \frac{1}{8}\sum_{R_c} g_c \chi_{\Gamma_{3N}}(R_c)\chi_{B_{2u}}(R_c) \\
&= \frac{1}{8}[(1)(45)(1) + (1)(-3)(-1) + (1)(-1)(1) + (1)(-1)(-1) + (1)(-3)(-1) + (1)(1)(1) + (1)(7)(-1) + (1)(3)(1)] \\
&= 6
\end{aligned}
$$

$$
\begin{aligned}
a_{B_{3u}} &= \frac{1}{8}\sum_{R_c} g_c \chi_{\Gamma_{3N}}(R_c)\chi_{B_{3u}}(R_c) \\
&= \frac{1}{8}[(1)(45)(1) + (1)(-3)(-1) + (1)(-1)(-1) + (1)(-1)(1) + (1)(-3)(-1) + (1)(1)(1) + (1)(7)(1) + (1)(3)(-1)] \\
&= 7
\end{aligned}
$$

Therefore, we know that $\Gamma_{3N} = 6A_g + 4B_{1g} + 6B_{2g} + 5B_{3g} + 4A_u + 7B_{1u} + 6B_{2u} + 7B_{3u}$. Since $\Gamma_{\text{trans}} = B_{1u} + B_{2u} + B_{3u}$ and $\Gamma_{\text{rot}} = B_{1g} + B_{2g} + B_{3g}$, we have by subtraction that $\Gamma_{\text{vibs}} = 6A_g + 3B_{1g} + 5B_{2g} + 4B_{3g} + 4A_u + 6B_{1u} + 5B_{2u} + 6B_{3u}$. Thus, of the 39 normal vibrations, 6 have symmetry A_g, 3 have symmetry B_{1g}, 5 have symmetry B_{2g}, 4 have symmetry B_{3g}, 4 have symmetry A_u, 6 have symmetry B_{1u}, 5 have symmetry B_{2u}, and 6 have symmetry B_{3u}. $\square$

VI) Benzene (C_6H_6) is a planar molecule.

a) Assign the symmetry group.

Answer. Not high or low symmetry. Has a C_6 axis. Has 6 perpendicular C_2 axes. Has a σ_h plane. Therefore, C_6H_6 is of the D_{6h} point group. □

b) Determine the number and symmetries of the C−H stretching modes in benzene.

Answer. We can determine that $\Gamma_\nu = (6,0,0,0,2,0,0,0,0,6,0,2)$ by counting how many $\overrightarrow{\text{C}{-}\text{H}}$ vectors stay the same under each symmetry operation. We can reduce this as follows.

$$\begin{aligned}
a_{A_{1g}} &= \frac{1}{24}\sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c)\chi_{A_{1g}}(R_c) \\
&= \frac{1}{24}[(1)(6)(1)+(2)(0)(1)+(2)(0)(1)+(1)(0)(1)+(3)(2)(1)+(3)(0)(1) \\
&\quad +(1)(0)(1)+(2)(0)(1)+(2)(0)(1)+(1)(6)(1)+(3)(0)(1)+(3)(2)(1)] \\
&= 1
\end{aligned}$$

$$\begin{aligned}
a_{A_{2g}} &= \frac{1}{24}\sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c)\chi_{A_{2g}}(R_c) \\
&= \frac{1}{24}[(1)(6)(1)+(2)(0)(1)+(2)(0)(1)+(1)(0)(1)+(3)(2)(-1)+(3)(0)(-1) \\
&\quad +(1)(0)(1)+(2)(0)(1)+(2)(0)(1)+(1)(6)(1)+(3)(0)(-1)+(3)(2)(-1)] \\
&= 0
\end{aligned}$$

$$\begin{aligned}
a_{B_{1g}} &= \frac{1}{24}\sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c)\chi_{B_{1g}}(R_c) \\
&= \frac{1}{24}[(1)(6)(1)+(2)(0)(-1)+(2)(0)(1)+(1)(0)(-1)+(3)(2)(1)+(3)(0)(-1) \\
&\quad +(1)(0)(1)+(2)(0)(-1)+(2)(0)(1)+(1)(6)(-1)+(3)(0)(1)+(3)(2)(-1)] \\
&= 0
\end{aligned}$$

$$\begin{aligned}
a_{B_{2g}} &= \frac{1}{24}\sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c)\chi_{B_{2g}}(R_c) \\
&= \frac{1}{24}[(1)(6)(1)+(2)(0)(-1)+(2)(0)(1)+(1)(0)(-1)+(3)(2)(-1)+(3)(0)(1) \\
&\quad +(1)(0)(1)+(2)(0)(-1)+(2)(0)(1)+(1)(6)(-1)+(3)(0)(-1)+(3)(2)(1)] \\
&= 0
\end{aligned}$$

$$\begin{aligned}
a_{E_{1g}} &= \frac{1}{24}\sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c)\chi_{E_{1g}}(R_c) \\
&= \frac{1}{24}[(1)(6)(2)+(2)(0)(1)+(2)(0)(-1)+(1)(0)(-2)+(3)(2)(0)+(3)(0)(0) \\
&\quad +(1)(0)(2)+(2)(0)(1)+(2)(0)(-1)+(1)(6)(-2)+(3)(0)(0)+(3)(2)(0)] \\
&= 0
\end{aligned}$$

$$
\begin{aligned}
a_{E_{2g}} &= \frac{1}{24}\sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c)\chi_{E_{2g}}(R_c) \\
&= \frac{1}{24}[(1)(6)(2) + (2)(0)(-1) + (2)(0)(-1) + (1)(0)(2) + (3)(2)(0) + (3)(0)(0) \\
&\quad + (1)(0)(2) + (2)(0)(-1) + (2)(0)(-1) + (1)(6)(2) + (3)(0)(0) + (3)(2)(0)] \\
&= 1
\end{aligned}
$$

$$
\begin{aligned}
a_{A_{1u}} &= \frac{1}{24}\sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c)\chi_{A_{1u}}(R_c) \\
&= \frac{1}{24}[(1)(6)(1) + (2)(0)(1) + (2)(0)(1) + (1)(0)(1) + (3)(2)(1) + (3)(0)(1) \\
&\quad + (1)(0)(-1) + (2)(0)(-1) + (2)(0)(-1) + (1)(6)(-1) + (3)(0)(-1) + (3)(2)(-1)] \\
&= 0
\end{aligned}
$$

$$
\begin{aligned}
a_{A_{2u}} &= \frac{1}{24}\sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c)\chi_{A_{2u}}(R_c) \\
&= \frac{1}{24}[(1)(6)(1) + (2)(0)(1) + (2)(0)(1) + (1)(0)(1) + (3)(2)(-1) + (3)(0)(-1) \\
&\quad + (1)(0)(-1) + (2)(0)(-1) + (2)(0)(-1) + (1)(6)(-1) + (3)(0)(1) + (3)(2)(1)] \\
&= 0
\end{aligned}
$$

$$
\begin{aligned}
a_{B_{1u}} &= \frac{1}{24}\sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c)\chi_{B_{1u}}(R_c) \\
&= \frac{1}{24}[(1)(6)(1) + (2)(0)(-1) + (2)(0)(1) + (1)(0)(-1) + (3)(2)(1) + (3)(0)(-1) \\
&\quad + (1)(0)(-1) + (2)(0)(1) + (2)(0)(-1) + (1)(6)(1) + (3)(0)(-1) + (3)(2)(1)] \\
&= 1
\end{aligned}
$$

$$
\begin{aligned}
a_{B_{2u}} &= \frac{1}{24}\sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c)\chi_{B_{2u}}(R_c) \\
&= \frac{1}{24}[(1)(6)(1) + (2)(0)(-1) + (2)(0)(1) + (1)(0)(-1) + (3)(2)(-1) + (3)(0)(1) \\
&\quad + (1)(0)(-1) + (2)(0)(1) + (2)(0)(-1) + (1)(6)(1) + (3)(0)(1) + (3)(2)(-1)] \\
&= 0
\end{aligned}
$$

$$
\begin{aligned}
a_{E_{1u}} &= \frac{1}{24}\sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c)\chi_{E_{1u}}(R_c) \\
&= \frac{1}{24}[(1)(6)(2) + (2)(0)(1) + (2)(0)(-1) + (1)(0)(-2) + (3)(2)(0) + (3)(0)(0) \\
&\quad + (1)(0)(-2) + (2)(0)(-1) + (2)(0)(1) + (1)(6)(2) + (3)(0)(0) + (3)(2)(0)] \\
&= 1
\end{aligned}
$$

$$
\begin{aligned}
a_{E_{2u}} &= \frac{1}{24}\sum_{R_c} g_c \chi_{\Gamma_\nu}(R_c)\chi_{E_{2u}}(R_c) \\
&= \frac{1}{24}[(1)(6)(2) + (2)(0)(-1) + (2)(0)(-1) + (1)(0)(2) + (3)(2)(0) + (3)(0)(0) \\
&\quad + (1)(0)(-2) + (2)(0)(1) + (2)(0)(1) + (1)(6)(-2) + (3)(0)(0) + (3)(2)(0)] \\
&= 0
\end{aligned}
$$

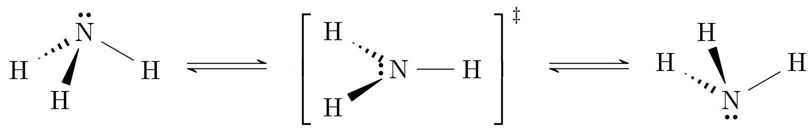
Therefore, we know that $\Gamma_\nu = A_{1g} + E_{2g} + B_{1u} + E_{1u}$. Thus, there are 6 C−H stretching modes in benzene: 1 with symmetry A_{1g}, 2 with symmetry E_{2g} (note that these 2 modes form a pair vibration modes of the same type), 1 with symmetry B_{1u}, and 2 with symmetry E_{1u} (again, these pair up). □

c) Determine the Raman and infrared activities for each vibration.

Answer. Since the A_{1g}, E_{1g}, and E_{2g} irreducible representations are Raman active, we know that the A_{1g} and E_{2g} C−H stretching modes are Raman active. The others are Raman silent. Additionally, since the A_{2u} and E_{1u} irreducible representations are IR active and two of the C−H stretching vibration modes are of the E_{1u} type, the E_{1u} vibrations are both IR active. The others are IR silent. □

3 Constructing Molecular Orbitals

2/4: I) Ammonia undergoes a facile inversion ("umbrella flip") as shown below. The activation barrier for inversion is low ($\Delta G^{\ddagger} \sim 5\,\mathrm{kcal/mol}$), and the transition state for this motion is planar NH_3. Note that the relevant valence shell IP's are $N_{2s} = -26.0\,\mathrm{eV}$, $N_{2p} = -13.4\,\mathrm{eV}$, and $H_{1s} = -13.6\,\mathrm{eV}$.



a) Construct an MO diagram for *planar* NH_3.

Answer. Point group: D_{3h}

Basis functions: all three H orbitals, N_{2s}, N_{2p_x}, N_{2p_y}, and N_{2p_z}.

Apply operations, generate reducible representations, and reduce to irreducible representations:

$$\begin{aligned}\Gamma_{\mathrm{H}} &= (3,0,1,3,0,1) = A_1' + E' \\ \Gamma_{\mathrm{N}_{2s}} &= A_1' \\ \Gamma_{\mathrm{N}_{2p_x}} &= E' \\ \Gamma_{\mathrm{N}_{2p_y}} &= E' \\ \Gamma_{\mathrm{N}_{2p_z}} &= A_2''\end{aligned}$$

Combine central and peripheral orbitals by their symmetry:

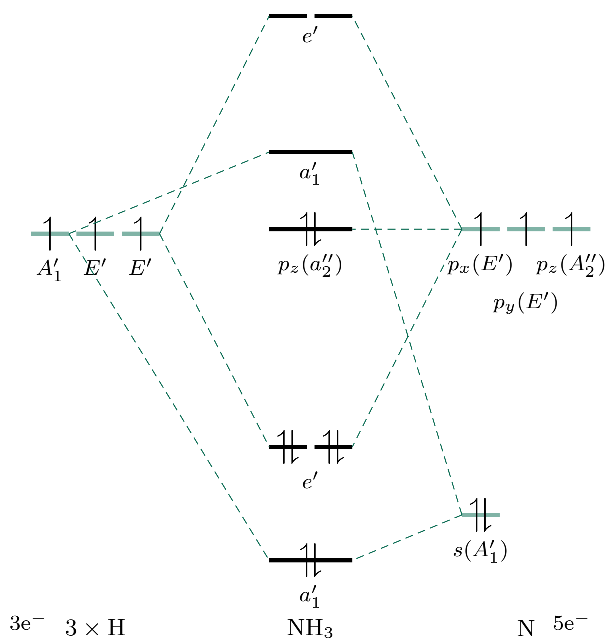


Figure 3: Planar $NH_3{}^{\ddagger}$ orbital diagram.

□

b) Label the MOs with the appropriate Mulliken symbols (a_{1g}, e_g, etc.) and add electrons to show the proper orbital occupancies.

Answer. See Figure 3. □

c) Compare your MO diagram with that for pyramidal NH_3 (Figure 5.30 in your text), and comment qualitatively on why this process is a low-energy one.

Answer. It appears that the only change between the two MO diagrams is that the two $3a_1$ electrons in the pyramidal NH_3 diagram must be excited to the $p_z(a_2'')$ orbital in the planar NH_3 diagram. Since $p_z(a_2'')$ is higher in energy than $3a_1$, there will be an increase in energy, but since it is only marginally higher, the increase will be very small. □

d) What vibrational mode is responsible for the inversion?

Proof. If any vibrational mode is responsible for the inversion, it certainly won't be a stretching mode since these have no effect on molecular geometry about the central atom. On the other hand, a bending mode could well achieve such a transition. Thus, we will find the bending modes in both pyramidal and planar NH_3 and compare.

For pyramidal NH_3, we can determine that $\Gamma_{x,y,z} = (3, 0, 1)$. We can also figure out that the number of atoms unmoved after applying each symmetry operation is $(4, 1, 2)$. Thus, $\Gamma_{3N} = (12, 0, 2)$. We can decompose this by inspection to $\Gamma_{3N} = 3A_1 + A_2 + 4E$. Since $\Gamma_{\text{trans}} = A_1 + E$ and $\Gamma_{\text{rot}} = A_2 + E$, we have by subtraction that $\Gamma_{\text{vibs}} = 2A_1 + 2E$.
We can determine that $\Gamma_\nu = (3, 0, 1)$ by counting how many $\overrightarrow{\text{N−H}}$ vectors stay the same under each symmetry operation. We can decompose this by inspection to $\Gamma_\nu = A_1 + E$. Thus, we have by subtraction that $\Gamma_\delta = A_1 + E$.

For planar NH_3, we can determine that $\Gamma_{x,y,z} = (3, 0, -1, 1, -2, 1)$. We can also figure out that the number of atoms unmoved after applying each symmetry operation is $(4, 1, 2, 4, 1, 2)$. Thus, $\Gamma_{3N} = (12, 0, -2, 4, -2, 2)$. We can decompose this by repeated applications of the reduction formula to $\Gamma_{3N} = A_1' + A_2' + 3E' + 2A_2'' + E''$. Since $\Gamma_{\text{trans}} = E' + A_2''$ and $\Gamma_{\text{rot}} = A_2' + E''$, we have by subtraction that $\Gamma_{\text{vibs}} = A_1' + 2E' + A_2''$.
We can determine that $\Gamma_\nu = (3, 0, 1, 3, 0, 1)$ by counting how many $\overrightarrow{\text{N−H}}$ vectors stay the same under each symmetry operation. We can decompose this by inspection to $\Gamma_\nu = A_1' + E'$. Thus, we have by subtraction that $\Gamma_\delta = E' + A_2''$.

Since the E pyramidal bending modes transform into the analogous E' planar bending modes, but the A_1 pyramidal bending mode has no planar analogue, it is the A_1 bending mode in pyramidal NH_3 that causes the inversion. □

II)

a) Use group theory to construct an MO diagram for octahedral SF_6. Consider only σ-bonding between S and the F's and use only the sulfur $3s$ and $3p$ valence orbitals (i.e., ignore the $3d$-orbital involvement). For fluorine, just use a "σ-type" orbital to determine the $6 \times$ F group orbitals.

Answer. Point group: O_h

Basis functions: all six F orbitals, S_{3s}, S_{3p_x}, S_{3p_y}, and S_{3p_z}.

Apply operations, generate reducible representations, and reduce to irreducible representations:

$$\begin{aligned}\Gamma_{\mathrm{F}} &= (6,0,0,2,2,0,0,0,4,2) = A_{1g} + E_g + T_{1u}\\ \Gamma_{\mathrm{S}_{3s}} &= A_{1g}\\ \Gamma_{\mathrm{S}_{3p_x}} &= T_{1u}\\ \Gamma_{\mathrm{S}_{3p_y}} &= T_{1u}\\ \Gamma_{\mathrm{S}_{3p_z}} &= T_{1u}\end{aligned}$$

Combine central and peripheral orbitals by their symmetry:

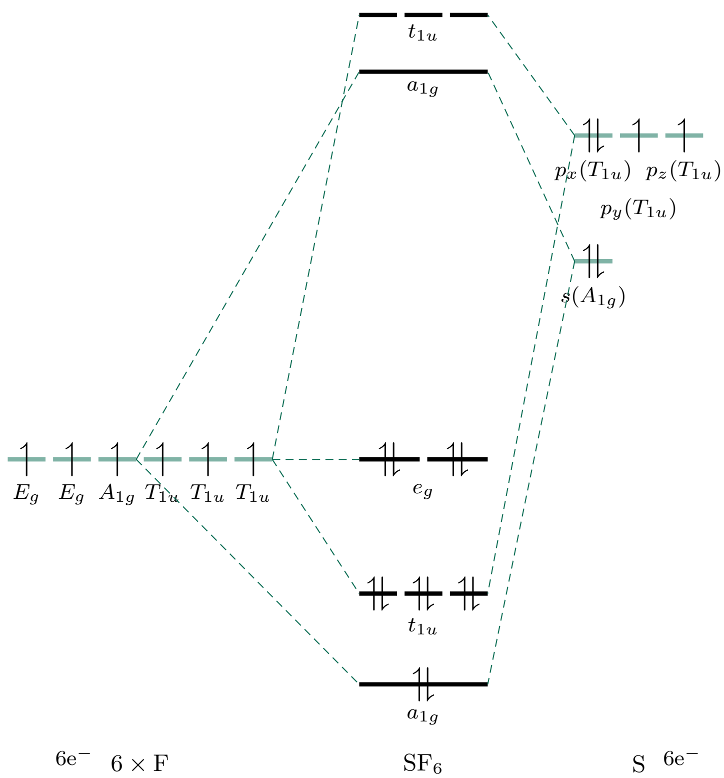


Figure 4: SF_6 orbital diagram.

Generate SALCs of peripheral atoms: We will use the following orbital naming scheme with the z-axis collinear with the vertical axis in the picture. In the following math, we will apply every operation in a class at once, eliminating several transitional steps for the sake of concision. We

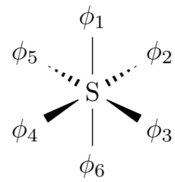


Figure 5: SF_6 atomic orbital labeling.

also choose to work within the purely rotational subgroup O instead of O_h for simplicity's sake.

$$\begin{aligned}
P^{A_1} &= \frac{1}{24}(1(\phi_1) + 1(2\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5) + 1(\phi_1 + 2\phi_6) \\
&\quad + 1(2\phi_2 + 2\phi_3 + 2\phi_4 + 2\phi_5) + 1(\phi_2 + \phi_3 + \phi_4 + \phi_5 + 2\phi_6)) \\
&= \frac{1}{24}(4\phi_1 + 4\phi_2 + 4\phi_3 + 4\phi_4 + 4\phi_5 + 4\phi_6) \\
&= \frac{1}{6}(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)
\end{aligned}$$

$$\begin{aligned}
P^{E} &= \frac{1}{24}(2(\phi_1) + 0(2\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5) + 2(\phi_1 + 2\phi_6) \\
&\quad - 1(2\phi_2 + 2\phi_3 + 2\phi_4 + 2\phi_5) + 0(\phi_2 + \phi_3 + \phi_4 + \phi_5 + 2\phi_6)) \\
&= \frac{1}{24}(4\phi_1 - 2\phi_2 - 2\phi_3 - 2\phi_4 - 2\phi_5 + 4\phi_6) \\
&= \frac{1}{12}(2\phi_1 - \phi_2 - \phi_3 - \phi_4 - \phi_5 + 2\phi_6)
\end{aligned}$$

$$\begin{aligned}
P^{T_1} &= \frac{1}{24}(3(\phi_1) + 1(2\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5) - 1(\phi_1 + 2\phi_6) \\
&\quad + 0(2\phi_2 + 2\phi_3 + 2\phi_4 + 2\phi_5) - 1(\phi_2 + \phi_3 + \phi_4 + \phi_5 + 2\phi_6)) \\
&= \frac{1}{24}(4\phi_1 - 4\phi_6) \\
&= \frac{1}{6}(\phi_1 - \phi_6)
\end{aligned}$$

By choosing other numberings and taking linear combinations, we can create one additional E type orbital and two other T_1 type orbitals.

$$\begin{aligned}
P^{E} &= \frac{1}{4}(\phi_1 - \phi_2 - \phi_5 + \phi_6) \\
P^{T_1} &= \frac{1}{6}(\phi_2 - \phi_4) \\
P^{T_1} &= \frac{1}{6}(\phi_3 - \phi_5)
\end{aligned}$$

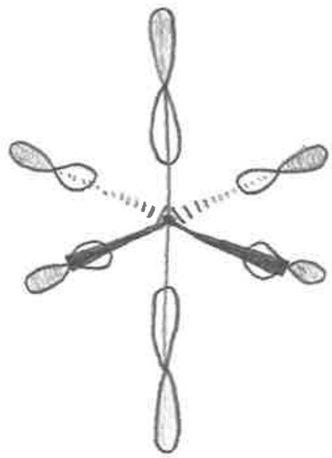
Draw peripheral atom SALC with central atom orbital to generate bonding/anti-bonding MOs:

(a) a_{1g}.

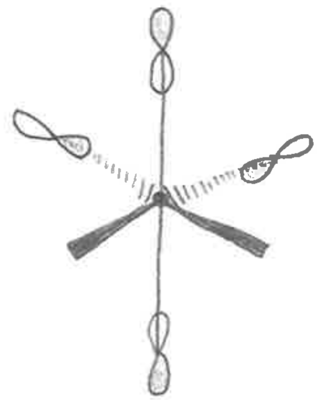
(b) t_{1u}.

(c) t_{1u}.

(d) t_{1u}.



(e) e_g.



(f) e_g.

Figure 6: SALCs for SF_6.

□

b) Label the MO's with the appropriate Mulliken symbols and show the orbital occupancies (i.e., fill in the MO levels with the proper number of electrons).

Answer. See Figure 4. □

c) Based on the MO diagram, comment on the number of bonding electrons in SF_6 and the bond-order of each S−F bond.

Answer. There are 8 bonding electrons (the two in the $1a_{1g}$ orbital, and the six in the degenerate $1t_{1u}$ orbitals; the four in the degenerate $1e_g$ orbitals are nonbonding and all anti-bonding orbitals are unfilled). Since the bond order is one half the number of bonding electrons divided by the number of bonds, we have B.O. $= \frac{2}{3}$. □