

CHEM 20100 (Inorganic Chemistry I) Problem Sets

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February 15, 2021

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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.

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

Choose $x = 0$.

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

With this result ...

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

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

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

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

□

- 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.

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

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

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

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

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

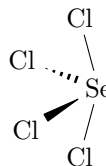
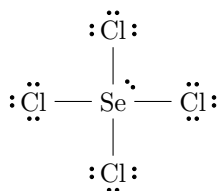
□

1 VSEPR and Point Groups

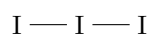
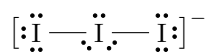
1/21: I) Do the following (VSEPR) problems from your text (Miessler et al. (2014)): Chapter 3: #8, 9f-i, 20, 29.

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

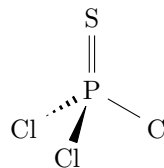
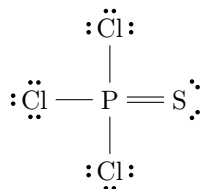
a. SeCl_4



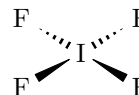
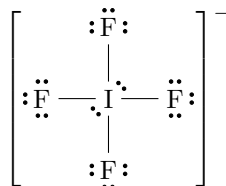
b. I_3^-



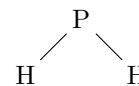
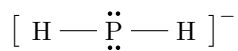
c. PSCl_3



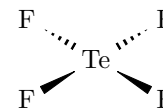
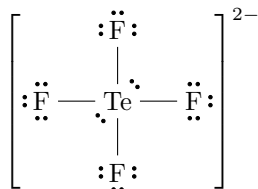
d. IF_4^-



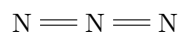
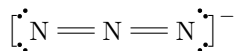
e. PH_2^-



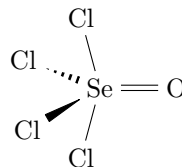
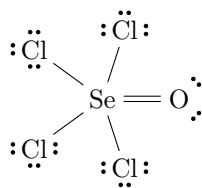
f. TeF_4^{2-}



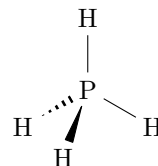
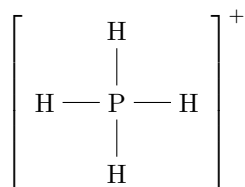
g. N_3^-



h. SeOCl_4

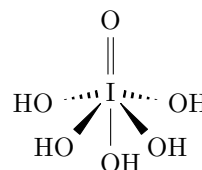
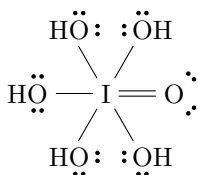


i. PH_4^+

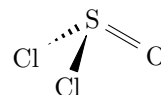
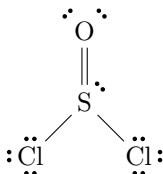


3.9 Give Lewis dot structures and sketch the shapes of the following.

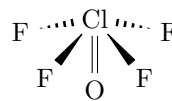
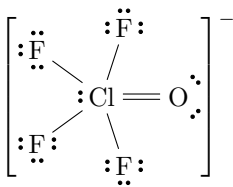
f. $\text{IO}(\text{OH})_5$



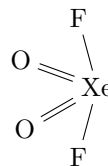
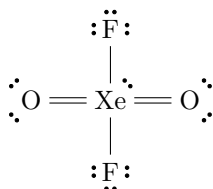
g. SOCl_2



h. $\text{ClOF}_4^{-[1]}$

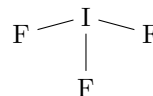
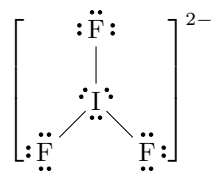


i. XeO_2F_2

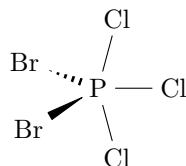


¹Note that it is unclear whether the equatorial fluorines will be bent away from the lone pair and toward the oxygen, or the other way around. Hence, I arbitrarily chose to show them pointed away from the lone pair.

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. \square

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. $\text{IO}(\text{OH})_5$

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, $\text{IO}(\text{OH})_5$ 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. ☐

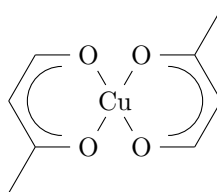
i. XeO_2F_2

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. ☐

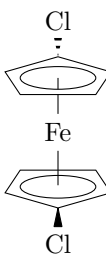
III) Assign the symmetry point group of the following molecules and objects. Ignore the H atoms in (a), (e), and (g). Note that (e) has pseudooctahedral geometry and (g) is square-planar.

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) $\text{trans}[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$

Answer. Not low or high symmetry. Has a C_4 axis. Has 4 perpendicular C_2 axes. Has σ_h .

Therefore, $\text{trans}[\text{CrCl}_2(\text{H}_2\text{O})_4]^+$ 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) $\text{trans-Pt}(\text{NH}_3)_2\text{Cl}_2$

Answer. Not low or high symmetry. Has a C_2 axis. Has 2 perpendicular C_2 axes. Has σ_h .

Therefore, $\text{trans-Pt}(\text{NH}_3)_2\text{Cl}_2$ 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. \square

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. \square

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

Answer.

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

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

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

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

\square

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

Answer.

$$\sum_{R_c} g_c [\chi_{A_1}(R_c)]^2 = 1 \cdot 1^2 + 2 \cdot 1^2 + 1 \cdot 1^2 + 2 \cdot 1^2 + 2 \cdot 1^2 = 8$$

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

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

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

$$\sum_{R_c} g_c [\chi_E(R_c)]^2 = 1 \cdot 2^2 + 2 \cdot 0^2 + 1 \cdot (-2)^2 + 2 \cdot 0^2 + 2 \cdot 0^2 = 8$$

\square

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.

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

□

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

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

□

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 $\varepsilon = e^{2\pi i/3} = \cos\left(\frac{2\pi}{3}\right) + i \sin\left(\frac{2\pi}{3}\right) = -0.5 + i\frac{\sqrt{3}}{2}$ and, thus, $\varepsilon^* = -0.5 + i\frac{\sqrt{3}}{2}$. It follows that $\varepsilon + \varepsilon^* = -1$.

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

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

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

$$2a_{E_u} = \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{E_u}(R_c)$$

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

$$a_{T_g} = \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{T_g}(R_c)$$

$$\begin{aligned} &= \frac{1}{24} [(1)(8)(3) + (4)(-1)(0) + (4)(-1)(0) + (3)(4)(-1) + (1)(8)(3) + (4)(-1)(0) + (4)(-1)(0) + (3)(4)(-1)] \\ &= 1 \end{aligned}$$

$$a_{T_u} = \frac{1}{24} \sum_{R_c} g_c \chi_{\Gamma}(R_c) \chi_{T_u}(R_c)$$

$$\begin{aligned} &= \frac{1}{24} [(1)(8)(3) + (4)(-1)(0) + (4)(-1)(0) + (3)(4)(-1) + (1)(8)(-3) + (4)(-1)(0) + (4)(-1)(0) + (3)(4)(1)] \\ &= 0 \end{aligned}$$

Therefore, we know that

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

□

- 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.

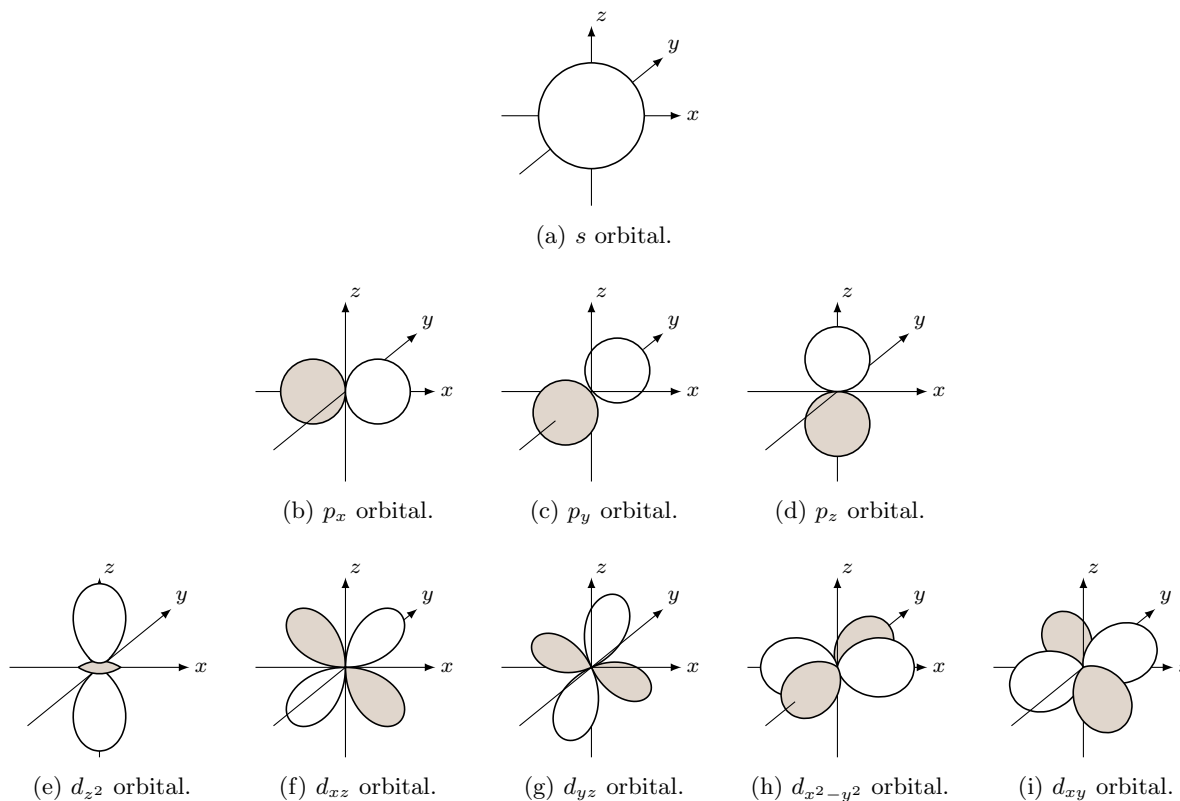


Figure 1: s , p , and d orbitals.

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 $\text{Co}(\text{CO})_4(\text{SiMe}_3)$ has a structure based on a trigonal bipyramid. The infrared spectrum of $\text{Co}(\text{CO})_4(\text{SiMe}_3)$ exhibits three $\nu(\text{CO})$ 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.

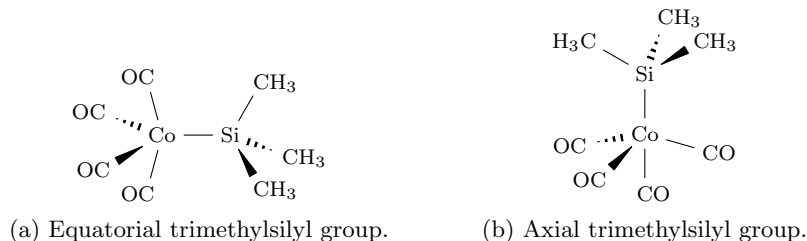


Figure 2: Structures of $\text{Co}(\text{CO})_4(\text{SiMe}_3)$.

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 $\overrightarrow{\text{Co}-\text{C}\ddot{\text{O}}}$ 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 $\text{Co}(\text{CO})_4(\text{SiMe}_3)$. 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 $\overrightarrow{\text{Co}-\text{C}\ddot{\text{O}}}$ vectors stay the same under each symmetry operation and decomposing by inspection. With four $\nu(\text{CO})$ 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 $\text{Co}(\text{CO})_4(\text{SiMe}_3)$. This confirms that this is the correct structure. \square

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). \square

- b) $\text{Zr}_2\text{F}_{13}^{5-}$: 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. $\text{Zr}_2\text{F}_{13}^{5-}$ 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, $\text{Zr}_2\text{F}_{13}^{5-}$ 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. \square

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 $\overrightarrow{\text{C-H}}$ vectors stay the same under each symmetry operation. We can reduce this as follows.

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

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

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

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

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

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

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

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

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

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

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

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

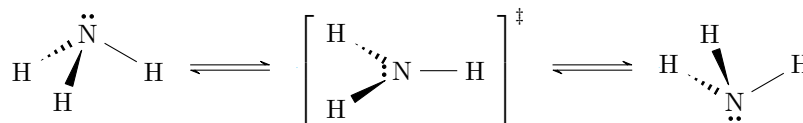
Therefore, we know that $\Gamma_\nu = A_{1g} + E_{2g} + B_{1u} + E_{1u}$. Thus, there are 6 C–H stretching modes in benzene: 1 with symmetry A_{1g} , 2 with symmetry E_{2g} (note that these 2 modes form a pair vibration modes of the same type), 1 with symmetry B_{1u} , and 2 with symmetry E_{1u} (again,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

- 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. \square

3 Constructing Molecular Orbitals

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

$$\begin{aligned}\Gamma_{\text{H}} &= (3, 0, 1, 3, 0, 1) = A'_1 + E' \\ \Gamma_{\text{N}_{2s}} &= A'_1 \\ \Gamma_{\text{N}_{2p_x}} &= E' \\ \Gamma_{\text{N}_{2p_y}} &= E' \\ \Gamma_{\text{N}_{2p_z}} &= A''_2\end{aligned}$$

Combine central and peripheral orbitals by their symmetry:

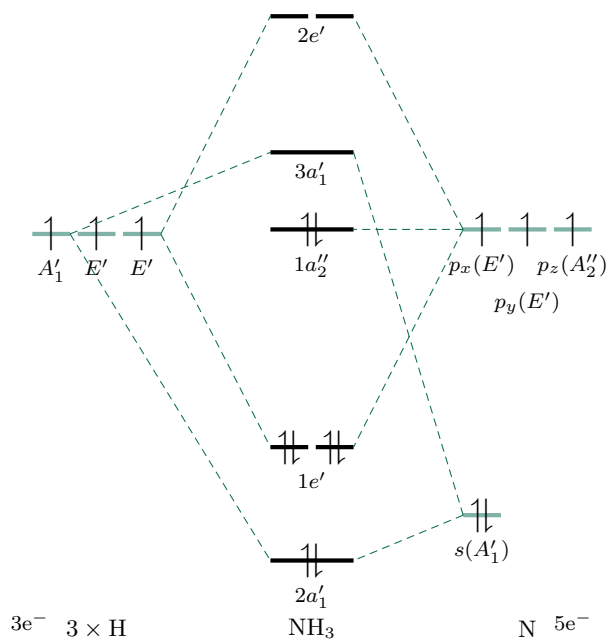


Figure 3: Planar NH_3^\ddagger orbital diagram.

□

- 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 $1a_2''$ orbital in the planar NH_3 diagram. Since $1a_2''$ 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. \square

- d) What vibrational mode is responsible for the inversion?

Answer. 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 $\overrightarrow{\text{N}-\text{H}}$ 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 $\overrightarrow{\text{N}-\text{H}}$ 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. \square

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 $6 \times \text{F}$ 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:

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

Combine central and peripheral orbitals by their symmetry: □

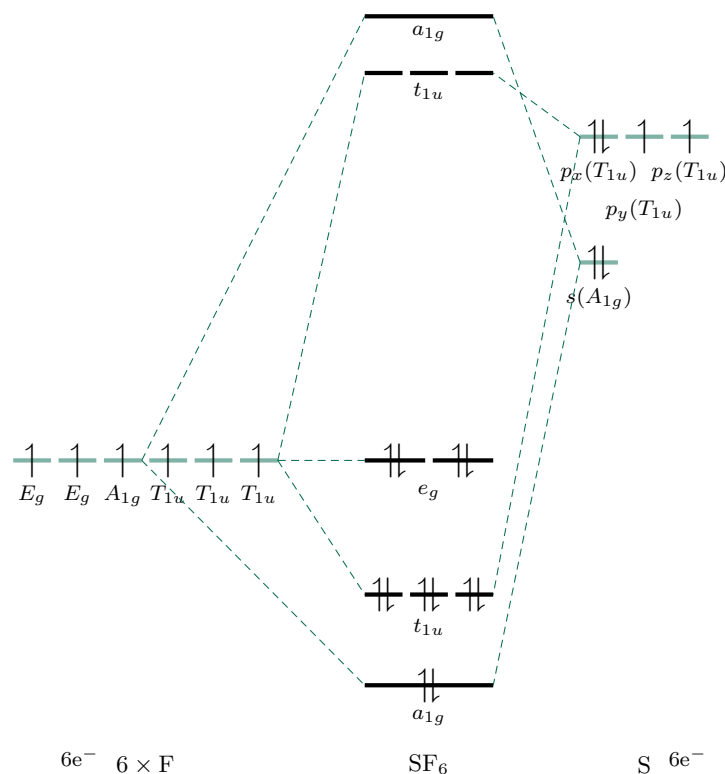


Figure 4: SF_6 orbital diagram.

- 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 $\text{B.O.} = \frac{2}{3}$. \square

4 Band Theory and Acid-Base Interactions

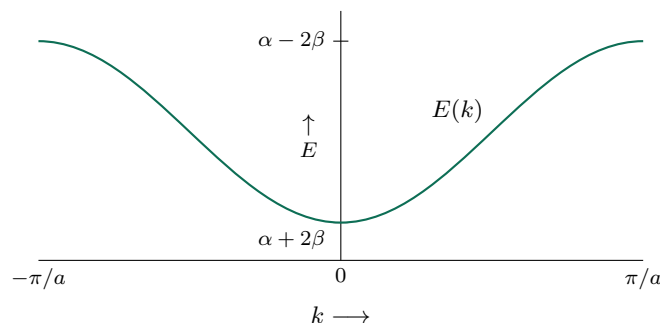
- 2/15: I) In our description for a one-dimensional s -orbital chain with period a , the allowed energy states broaden into a band whose dispersion (dependence of the energy E on the wavevector k) is given by

$$E(k) = \alpha + 2\beta \cos ka$$

where β is the nearest-neighbor interaction energy and is less than zero for neighboring s -type orbitals.

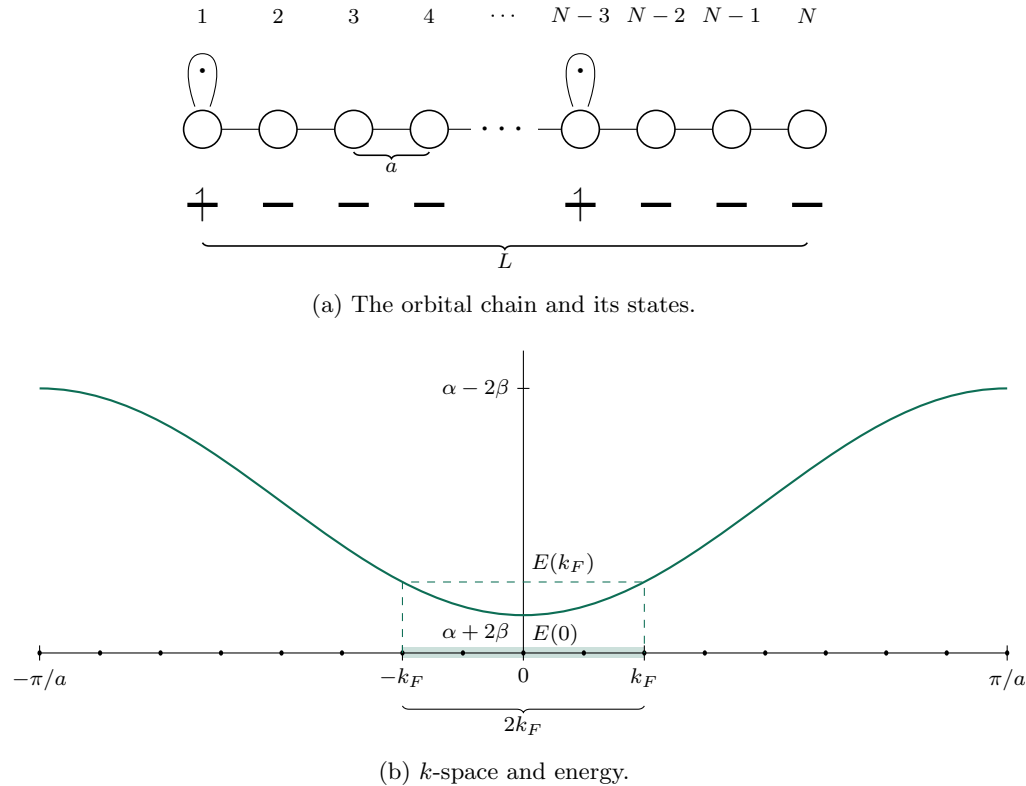
- a. Sketch $E(k)$ over the range $-\frac{\pi}{a} < k < \frac{\pi}{a}$, assuming that $\beta < 0$.

Answer.



□

- b. Suppose there is one electron for every 4 atoms; that is, if there are N atoms in the chain, there are $N/4$ electrons. With $a = 2.00 \times 10^{-10}$ m (i.e., 2.00 \AA) and $\beta = -2.00 \text{ eV}$, calculate the value of k corresponding to the highest occupied electronic state (also known as Fermi wavevector k_F , the wavevector at the Fermi surface) and the height of the Fermi energy E_F above the bottom of the band. Note that a chain of N atoms will have a total length $L = Na$ and that states are uniformly distributed in the k -space.

Figure 5: Theory describing a one-dimensional s -orbital chain.

Answer. As in Figure 5a, consider a one-dimensional chain of N atoms with one s -orbital each. The orbitals are separated by period a , and the length of the chain is $L = Na$. As in Figure 5b, each orbital contributes a state indexed by k . These states are evenly distributed in one-dimensional k -space between $-\frac{\pi}{a}$ and $\frac{\pi}{a}$. Now imagine that the one-dimensional s -orbital chain is devoid of electrons, and we have to fill them in. The first electron will go in the lowest energy state at $k = 0$ (see Figure 5b). The second will go into either $k = a$ or $k = -a$, and the third will go into the other one. As we add more and more electrons, the states that they go into will expand outwards evenly from the origin, always filling the lowest energy states available first. Eventually, all electrons will be filled in; however, this does not mean that all states will be filled, as there is one electron for every four atoms and, thus, for every eight states (again, see Figure 5a). Indeed, some region evenly surrounding the origin will be completely filled in, and by definition the Fermi surface will be the boundary between occupied and unoccupied states. Since the Fermi wavevector k_F is the radius of the Fermi surface (i.e., the distance from the origin to the boundary of the Fermi sphere), we can label the boundary points k_F and $-k_F$. Having established the theoretical design, let's start the actual calculations.

Since k -space within the first Brillouin zone runs from $-\frac{\pi}{a}$ to $\frac{\pi}{a}$, the length of the s -orbital chain in k -space is $L = \frac{\pi}{a} - (-\frac{\pi}{a}) = \frac{2\pi}{a}$. It follows that each orbital is separated by $a = \frac{2\pi}{L}$, and that there are $\frac{L}{2\pi}$ orbitals per unit length. Now the length of the occupied region is $k_F - (-k_F) = 2k_F$, so combining this with the previous result gives us that there are $2k_F \times \frac{L}{2\pi} = \frac{k_F L}{\pi}$ occupied orbitals. Since each orbital adds 2 quantum states, we have $\frac{2k_F L}{\pi}$ occupied states. But the number of occupied states is simply equal to the number of electrons $\frac{N}{4}$. Since we also know that $L = Na$,

we have that

$$\begin{aligned}\frac{2k_F Na}{\pi} &= \frac{N}{4} \\ \frac{k_F a}{\pi} &= \frac{1}{8} \\ k_F &= \frac{\pi}{8a}\end{aligned}$$

$$k_F = 6.25 \times 10^8 \text{ m}^{-1}$$

As to the other part of the question, refer to Figure 5b once again. It tells us that the height of the Fermi energy above the bottom of the band is given by

$$\begin{aligned}h &= E(k_F) - E(0) \\ &= \alpha + 2\beta \cos\left(\frac{\pi}{8a} \cdot a\right) - (\alpha + 2\beta \cos(0 \cdot a)) \\ &= 2\beta \left(\cos\left(\frac{\pi}{8}\right) - 1\right)\end{aligned}$$

$$h = 0.304 \text{ eV}$$

□

II) Do the following problems from Chapter 6: 13, 25, 30, 37.

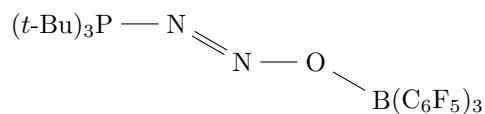
6.13 If an equimolar mixture of $P(t\text{-C}_4\text{H}_9)_3$ and $B(\text{C}_6\text{F}_5)_3$ is mixed with 1 bar of the gas N_2O in bromobenzene solution, a white product is formed in good yield. A variety of NMR evidence has been gathered on the product: there is a single ^{31}P NMR resonance; ^{11}B and ^{19}F NMR are considered consistent with a 4-coordinate boron atom; and ^{15}N NMR indicates two nonequivalent nitrogen atoms. In addition, no gas is released in the reaction.

a. Suggest the role of N_2O in this reaction.

Answer. N_2O reorganizes into a bridge linking the phosphorous and boron central atoms of $P(t\text{-C}_4\text{H}_9)_3$ and $B(\text{C}_6\text{F}_5)_3$, respectively. $P(t\text{-C}_4\text{H}_9)_3$ contains a frustrated Lewis pair that could not normally react with the boron in $B(\text{C}_6\text{F}_5)_3$, but by virtue of this bridge, there is enough separation between all of the substituents (i.e., steric hindrance is sufficiently reduced) to permit the formation of a combined product. \square

b. Propose a structure of the product.

Answer.



\square

- 6.25** The most common source of mercury is cinnabar (HgS), whereas Zn and Cd in the same group occur as sulfide, carbonate, silicate, and oxide. Why?

Answer. Mercury is soft, so it forms a stable product with the similarly soft sulfide ion. However, zinc and cadmium are intermediate-hard, so they can form stable products with harder anions, such as carbonate, silicate, and oxide. \square

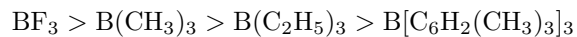
6.30 CsI is much less soluble in water than CsF, and LiF is much less soluble than LiI. Why?

Answer. Cesium iodide is formed from two soft ions, which grants it extra stability in comparison to soft-hard compounds such as cesium fluoride. As such, CsI will dissolve much less in water than CsF since it prefers to be in the molecular state rather than the ionic state.

The same is true for the hard-hard compound lithium fluoride in comparison to the hard-soft compound lithium iodide. \square

- 6.37** List the following acids in order of their acid strength when reacting with NH_3 : BF_3 , $\text{B}(\text{CH}_3)_3$, $\text{B}(\text{C}_2\text{H}_5)_3$, and $\text{B}[\text{C}_6\text{H}_2(\text{CH}_3)_3]_3$.

Answer. We have



BF_3 will be the strongest Lewis acid because it is the only one out of the collection that has electron-withdrawing groups as opposed to electron donating groups. Among the three compounds with electron-donating groups, we rank as stronger acids the ones with smaller groups, both because smaller groups donate less and the reduction in steric hindrance. \square