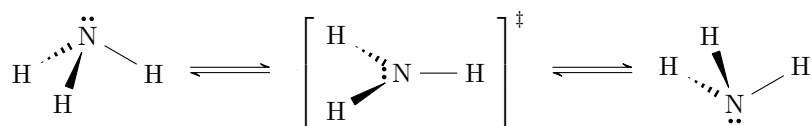


- 2/4: I) Ammonia undergoes a facile inversion (“umbrella flip”) as shown below. The activation barrier for inversion is low ( $\Delta G^\ddagger \sim 5 \text{ kcal/mol}$ ), and the transition state for this motion is planar  $\text{NH}_3$ . Note that the relevant valence shell IP’s are  $\text{N}_{2s} = -26.0 \text{ eV}$ ,  $\text{N}_{2p} = -13.4 \text{ eV}$ , and  $\text{H}_{1s} = -13.6 \text{ eV}$ .



- a) Construct an MO diagram for *planar*  $\text{NH}_3$ .

*Answer.* Point group:  $D_{3h}$

Basis functions: all three H orbitals,  $\text{N}_{2s}$ ,  $\text{N}_{2p_x}$ ,  $\text{N}_{2p_y}$ , and  $\text{N}_{2p_z}$ .

Apply operations, generate reducible representations, and reduce to irreducible representations (for orbitals of the center atom, read irreducible representations from the  $D_{3h}$  character table):

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

Combine central and peripheral orbitals by their symmetry:

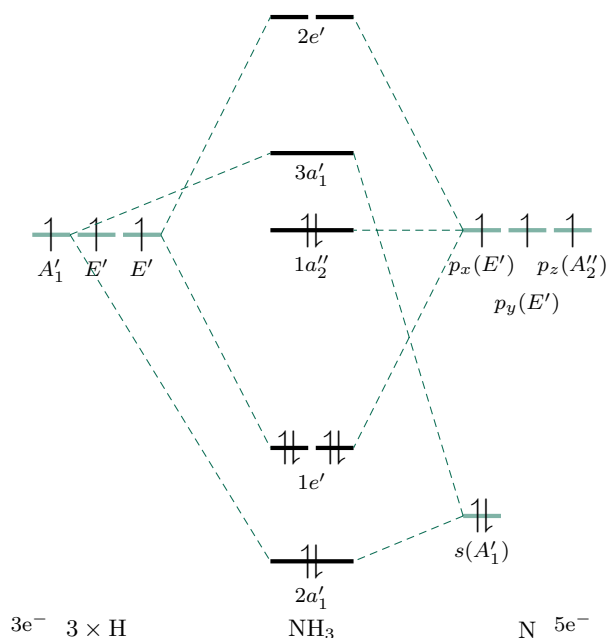


Figure 3.1: Planar  $\text{NH}_3^\ddagger$  orbital diagram.

- 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 3.1.

- c) Compare your MO diagram with that for pyramidal  $\text{NH}_3$  (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  $\text{NH}_3$  diagram must be excited to the  $1a_2''$  orbital in the planar  $\text{NH}_3$  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.*

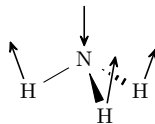


Figure 3.2: The  $A_1$  bending mode.

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  $\text{NH}_3$  and compare.

For pyramidal  $\text{NH}_3$ , the  $C_{3v}$  character table tells us 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  $\Gamma_{\text{rot}} = A_2 + E$  (again from the  $C_{3v}$  character table), 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  $\text{NH}_3$ , the  $D_{3h}$  character table tells us 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  $\Gamma_{\text{rot}} = A'_2 + E''$  (again by the  $D_{3h}$  character table), 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  $\text{NH}_3$  that causes the inversion. This derivation can be rationalized intuitively by noting that the movement that causes the inversion must look like the totally symmetric bending mode in Figure 3.2.  $\square$

II)

- a) Use group theory to construct an MO diagram for octahedral  $\text{SF}_6$ . Consider only  $\sigma$ -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 " $\sigma$ -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 (for orbitals of the center atom, read irreducible representations from the  $O_h$  character table):

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

Combine central and peripheral orbitals by their symmetry: □

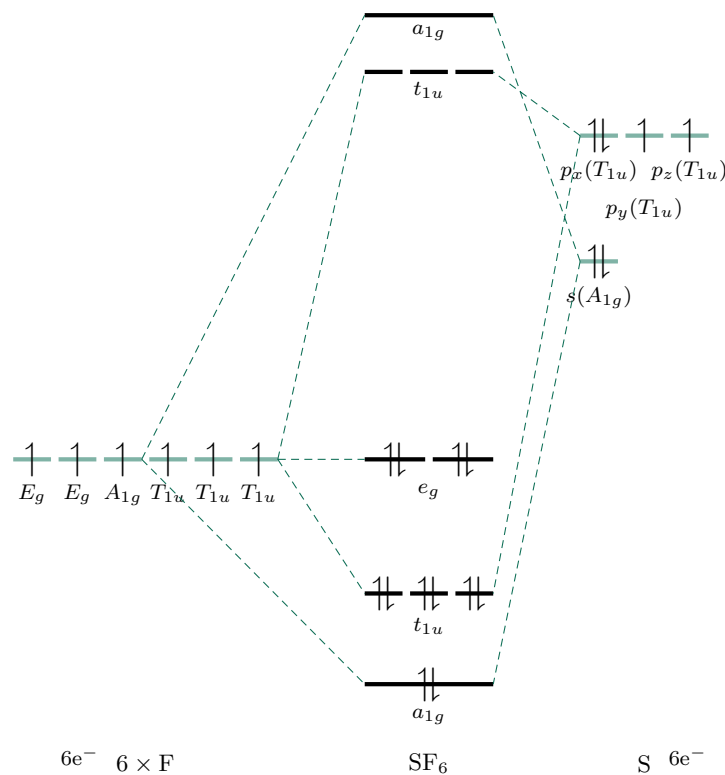


Figure 3.3:  $\text{SF}_6$  orbital diagram.

- 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 3.3. □

- c) Based on the MO diagram, comment on the number of bonding electrons in  $\text{SF}_6$  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

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

□