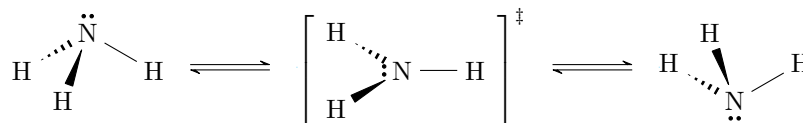


- 2/4: I) Ammonia undergoes a facile inversion (“umbrella flip”) as shown below. The activation barrier for inversion is low ($\Delta G^\ddagger \sim 5 \text{ kcal/mol}$), and the transition state for this motion is planar NH_3 . Note that the relevant valence shell IP’s are $\text{N}_{2s} = -26.0 \text{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



- a) Construct an MO diagram for *planar* 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:

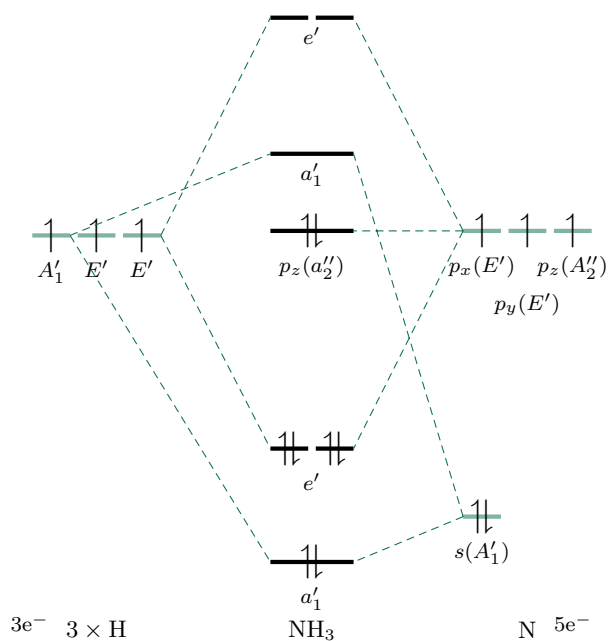


Figure 1: Planar NH_3^\ddagger orbital diagram.

- 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 1.

- 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. \square

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 $\overrightarrow{\text{N}-\text{H}}$ 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:

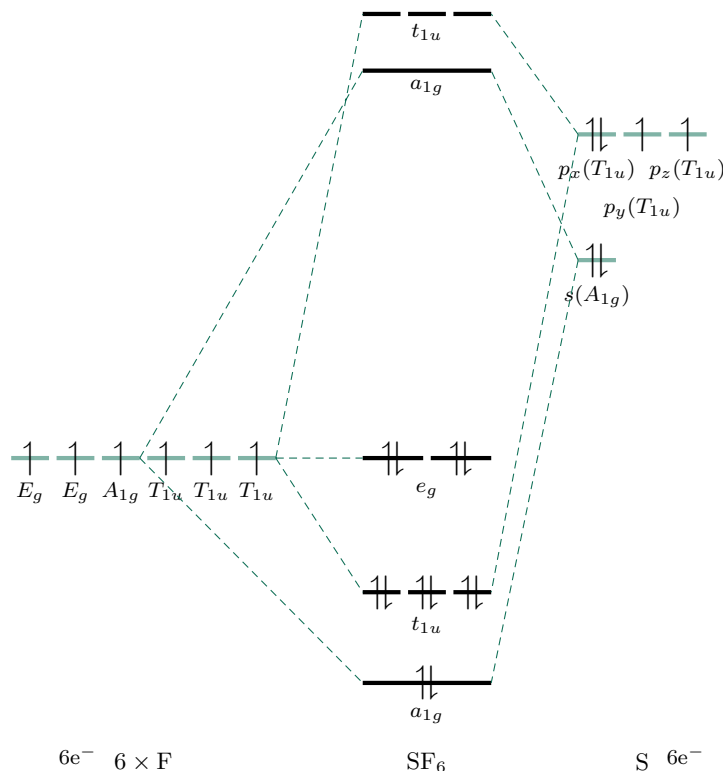
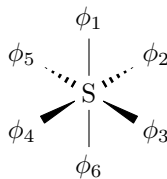


Figure 2: SF_6 orbital diagram.

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 3: SF₆ 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.

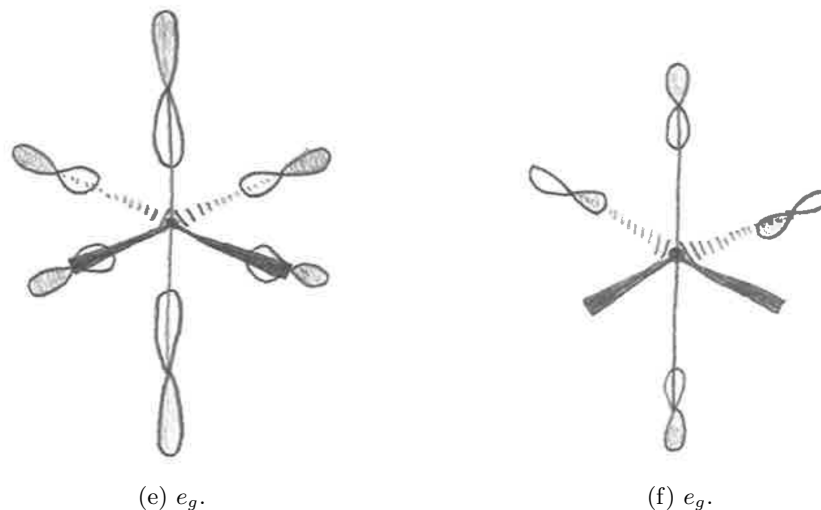
$$P^E = \frac{1}{4}(\phi_1 - \phi_2 - \phi_5 + \phi_6)$$

$$P^{T_1} = \frac{1}{6}(\phi_2 - \phi_4)$$

$$P^{T_1} = \frac{1}{6}(\phi_3 - \phi_5)$$

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} .

Figure 4: 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 2.

□

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

□