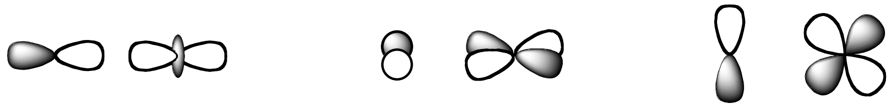
CHAPTER 5: MOLECULAR ORBITALS

5.1 There are three possible bonding interactions:



p_z d_{z^2} p_y d_{yz} p_x d_{xz}

5.2 **a.** Li_2 has a bond order of 1.0 (two electrons in a σ bonding orbital; see Figures 5.7 and 5.1). Li_2^+ has a bond order of only 0.5 (one electron in a σ bonding orbital). Therefore, Li_2 has the shorter bond.

b. F_2 has a bond order of 1.0 (see Figure 5.7). F_2^+ has one less antibonding (π*) electron and a higher bond order, 1.5. F_2^+ would be expected to have the shorter bond.

c. Expected bond orders (see Figure 5.1):

	Bonding electrons	Antibonding electrons	Bond order
He_2^+	2	1	$\frac{1}{2}(2-1) = 0.5$
HHe^+	2	0	$\frac{1}{2}(2-0) = 1$
H_2^+	1	0	$\frac{1}{2}(2-1) = 0.5$

Both He_2^+ and H_2^+ have bond orders of 0.5. HHe^+ would therefore be expected to have the shortest bond because it has a bond order of 1.

5.3 **a.** These diatomic molecules should have similar bond orders to the analogous diatomics from the row directly above them in the periodic table:

P_2 bond order = 3 (like N_2)
S_2 bond order = 2 (like O_2)
Cl_2 bond order = 1 (like F_2) Cl_2 has the weakest bond.

b. The bond orders match those of the analogous oxygen species (Section 5.2.3):

S_2^+ bond order = 2.5
S_2 bond order = 2
S_2^- bond order = 1.5 S_2^- has the weakest bond.

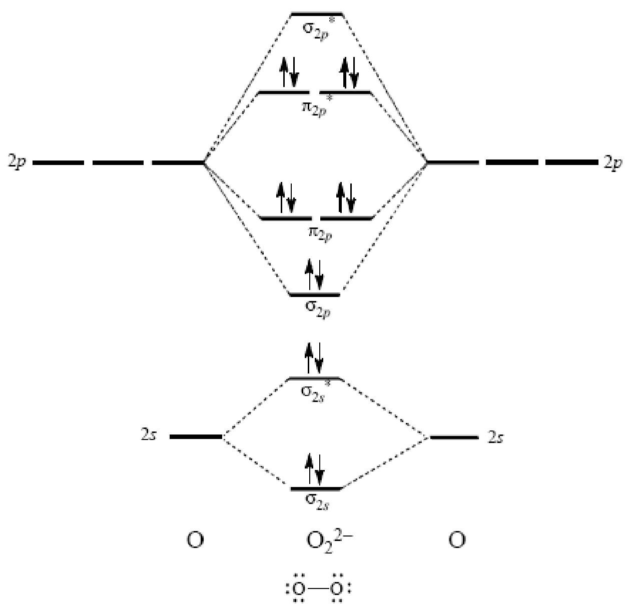
c. Bond orders:

NO^+ bond order = 3 (isoelectronic with CO, Figure 5.13)
NO bond order = 2.5 (one more (antibonding) electron than CO)
NO^- bond order = 2 (two more (antibonding) electrons than CO)

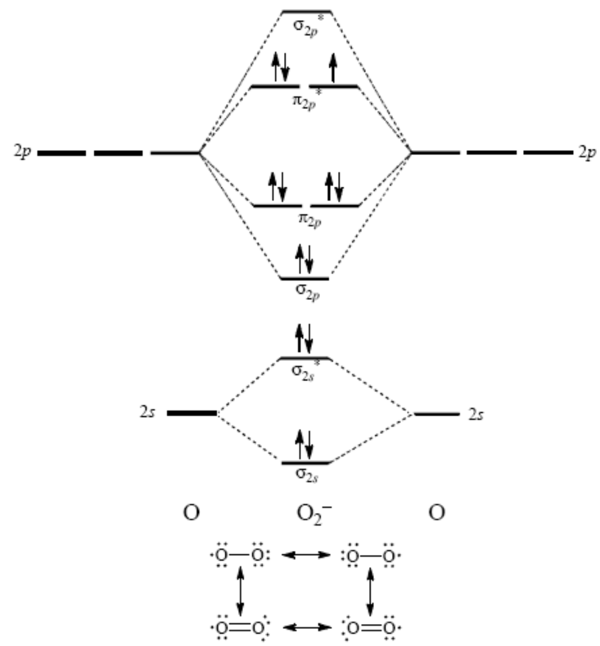
NO^- has the lowest bond order and therefore the weakest bond.

5.4

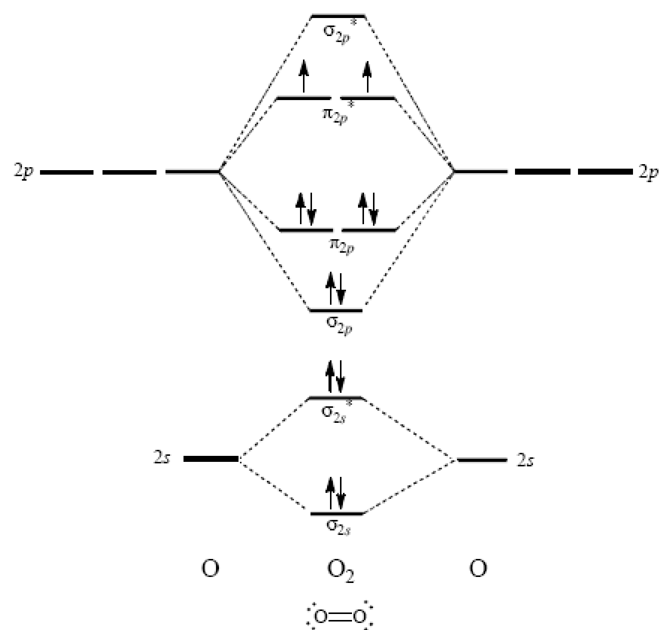
O_2^{2-} has a single bond, with four electrons in the π^* orbitals canceling those in the π orbitals.



O_2^- has three electrons in the π^* orbitals, and a bond order of 1.5. The Lewis structures have an unpaired electron and an average bond order of 1.5.



O_2 has two unpaired electrons in its π^* orbitals, and a bond order of 2. The simple Lewis structure has all electrons paired, which does not match the paramagnetism observed experimentally.



Bond lengths are therefore in the order $O_2^{2-} > O_2^- > O_2$, and bond strengths are the reverse of this order.

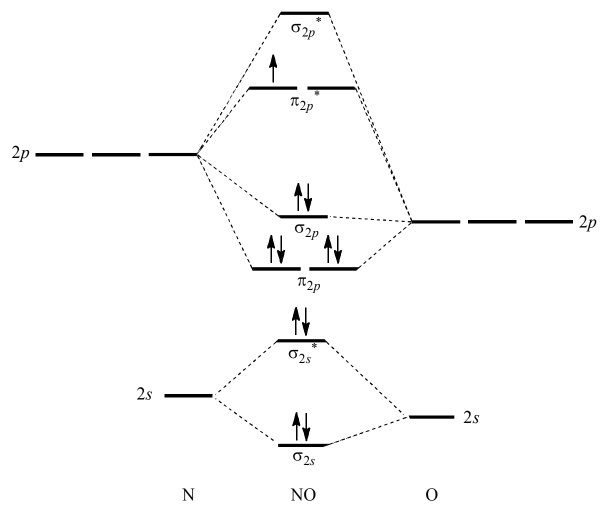
5.5

	Bond Order (Figures 5.5 and 5.7)	Bond Distance (pm)	Unpaired Electrons
C_2^{2-}	3	119	0
N_2^{2-}	2	122.4	2
O_2^{2-}	1	149 (very long)	0
O_2	2	120.7	2

The bond distance in N_2^{2-} is very close to the expected bond distance for a diatomic with 12 valence electrons, as shown in Figure 5.8.

5.6 The energy level pattern would be similar to the one shown in Figure 5.5, with the interacting orbitals the 3*s* and 3*p* rather than 2*s* and 2*p*. All molecular orbitals except the highest would be occupied by electron pairs, and the highest orbital (σ_u*) would be singly occupied, giving a bond order of 0.5. Because the bond in Ar_2^+ would be weaker than in Cl_2, the Ar–Ar distance would be expected to be longer (calculated to be > 300 pm; see the reference).

5.7 **a.** The energy level diagram for NO is on the right. The odd electron is in a π_{2p}* orbital.



b. O is more electronegative than N, so its orbitals are slightly lower in energy. The bonding orbitals are slightly more concentrated on O.

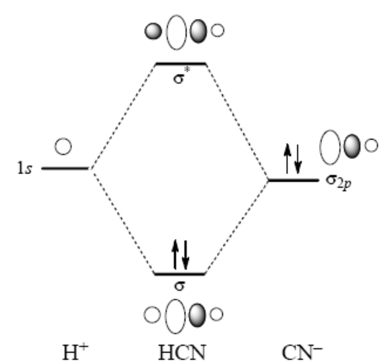
c. The bond order is 2.5, with one unpaired electron.

d.
NO^+ Bond order = 3
shortest bond (106 pm)
NO Bond order = 2.5
intermediate (115 pm)
NO^- Bond order = 2
longest bond (127 pm), two electrons in antibonding orbitals.

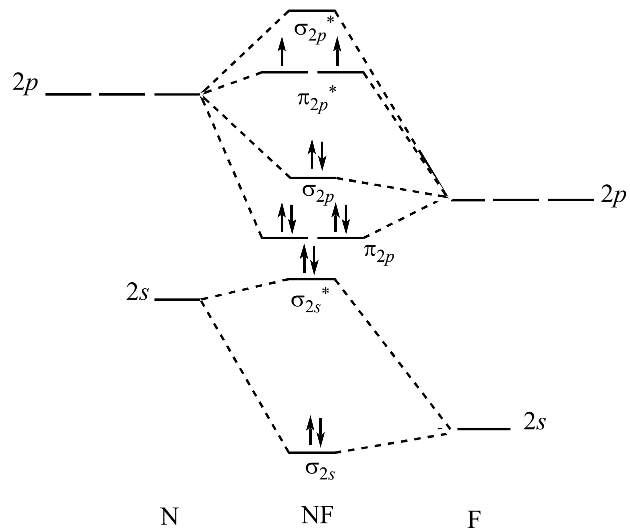
5.8 **a.** The CN^- energy level diagram is similar to that of NO (Problem 5.7) without the antibonding π* electron.

b. The bond order is three, with no unpaired electrons.

c. The HOMO is the σ_{2p} orbital, which can interact with the 1*s* of the H^+, as in the diagram at right. The bonding orbital has an energy near that of the π orbitals; the antibonding orbital becomes the highest energy orbital.



5.9 **a**. A diagram is sketched at the right. Since the difference in valence orbital potential energy between the 2*s* of N (-25.56 eV) and the 2*p* of F (-18.65 eV) is 6.91 eV, the σ_{2p} orbital is expected to be higher in energy relative to the degenerate π_{2p} set.



b. NF is isoelectronic (has the same number of valence electrons) with O_2. Therefore, NF is predicted to be paramagnetic with a bond order of 2. The populations of the bonding (8 electrons) and antibonding (4 electrons) molecular orbitals in the diagram suggest a double bond.

c. The σ_{2s}, σ_{2s}^*, σ_{2p}, and σ_{2p}^* orbitals exhibit $C_{\infty v}$ symmetry, with the NF bond axis the infinite-fold rotation axis. The π_{2p} and π_{2p}^* orbitals exhibit C_s symmetry. The latter do not possess C_2 rotation axes coincident to the infinite-fold rotation axis of the σ orbitals on the basis of the change in wave function sign upon crossing the nodes on the bond axis.

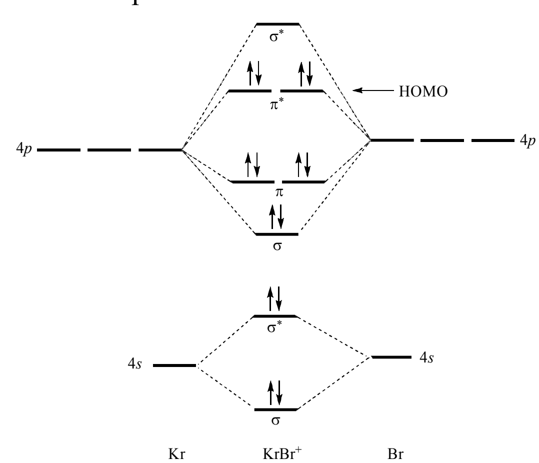
5.10 **a.** OF^- has 14 valence electrons, four in the π_{2p}* orbitals (see the diagram in the answer to Problem 5.9).

b. The net result is a single bond between two very electronegative atoms, and no unpaired electrons.

c. The concentration of electrons in the π* orbital is more on the O, so combination with the positive proton at that end is more likely. In fact, H^+ bonds to the oxygen atom, at an angle of 97°, as if the bonding were through a *p* orbital on O.

5.11 The molecular orbital description of KrF^+ would predict that this ion, which has the same number of valence electrons as F_2, would have a single bond. KrF_2 would also be expected, on the basis of the VSEPR approach, to have single Kr–F bonds, in addition to three lone pairs on Kr. Reported Kr–F distances: KrF^+: 176.5-178.3 pm; KrF_2: 186.8-188.9 pm. The presence of lone pairs in KrF_2 may account for the longer bond distances in this compound.

5.12 **a.** The $KrBr^+$ energy level diagram is at the right.



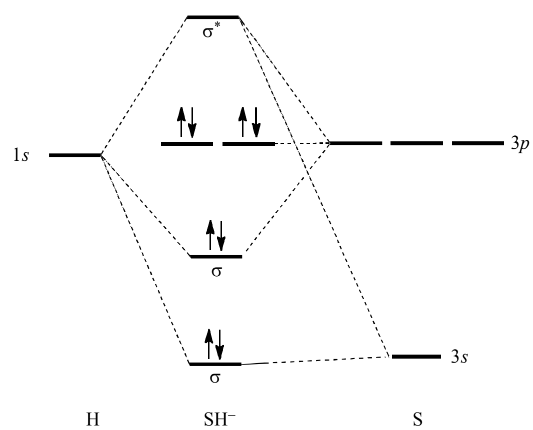
b. The HOMO is polarized toward Br, since its energy is closer to that of the Br 4*p* orbital.

c. Bond order = 1

d. Kr is more electronegative. Its greater nuclear charge exerts a stronger pull on the shared electrons.

5.13 The energy level diagram for SH^- is shown below. A bond order of 1 is predicted.

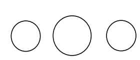
The S orbital energies are –22.7 eV (3*s*) and –11.6 eV (3*p*); the 1*s* of H has an energy of –13.6 eV. Because of the difference in their atomic orbital energies, the 1*s* orbital of hydrogen and the 3*s* orbital of sulfur interact only weakly; this is shown in the diagram by a slight stabilization of the lowest energy molecular orbital with respect to the 3*s* orbital of sulfur. This lowest energy orbital is essentially nonbonding. These orbitals are similar in appearance to those of HF in Example 5.3, with more balanced contribution of the hydrogen 1*s* and sulfur valence orbitals since the valence orbitals of sulfur are closer to the energy of the hydrogen 1*s* orbital than the valence orbitals of fluorine.



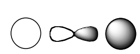
5.14 **a.** The group orbitals on the hydrogen atoms are

and

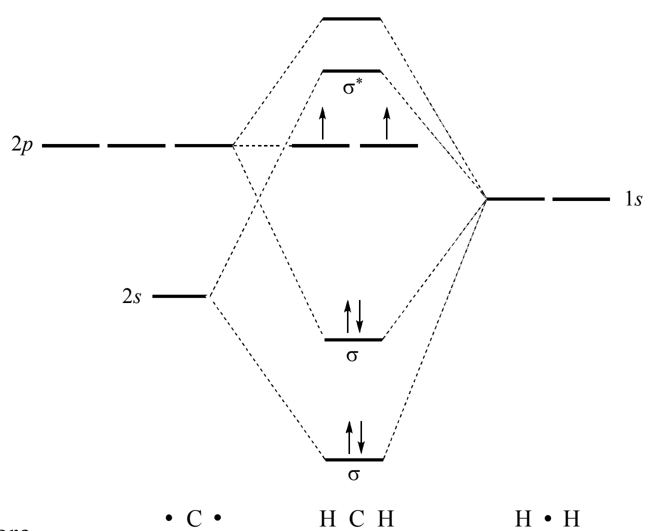
The first group orbital interacts with the 2*s* orbital on carbon:



And the second group orbital interacts with a 2*p* orbital on carbon:



Carbon's remaining 2*p* orbitals are nonbonding.

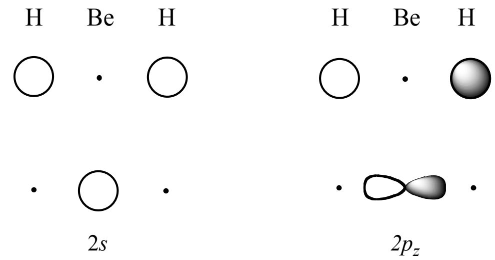


b. Linear CH_2 is a paramagnetic diradical, with one electron in each of the p_x and p_y orbitals of carbon. (A bent singlet state, with all electrons paired, is also known, with a calculated bond angle of approximately 130°.)

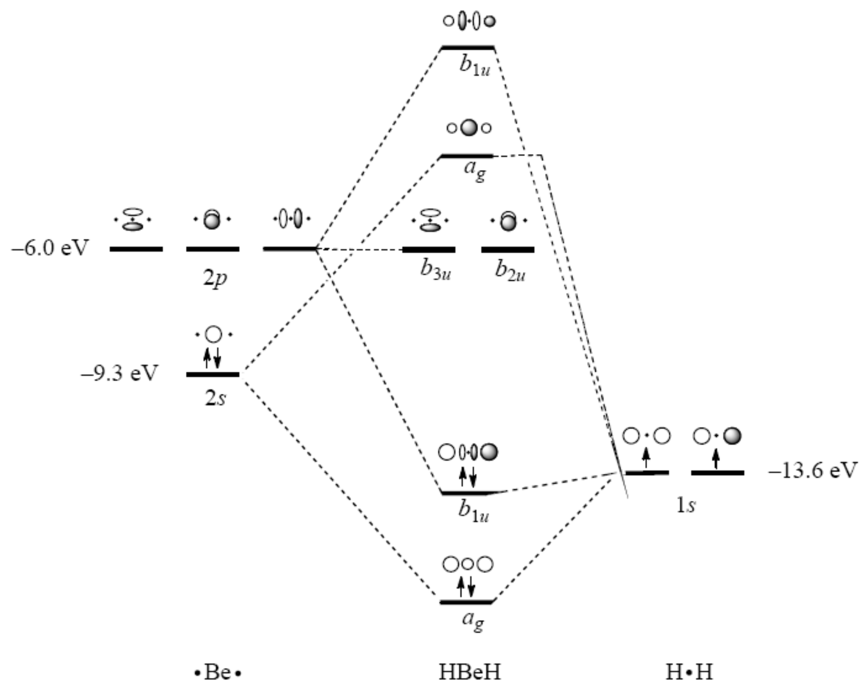
5.15 **a.** BeH_2

Group Orbitals:

Be Orbitals with Matching Symmetry:

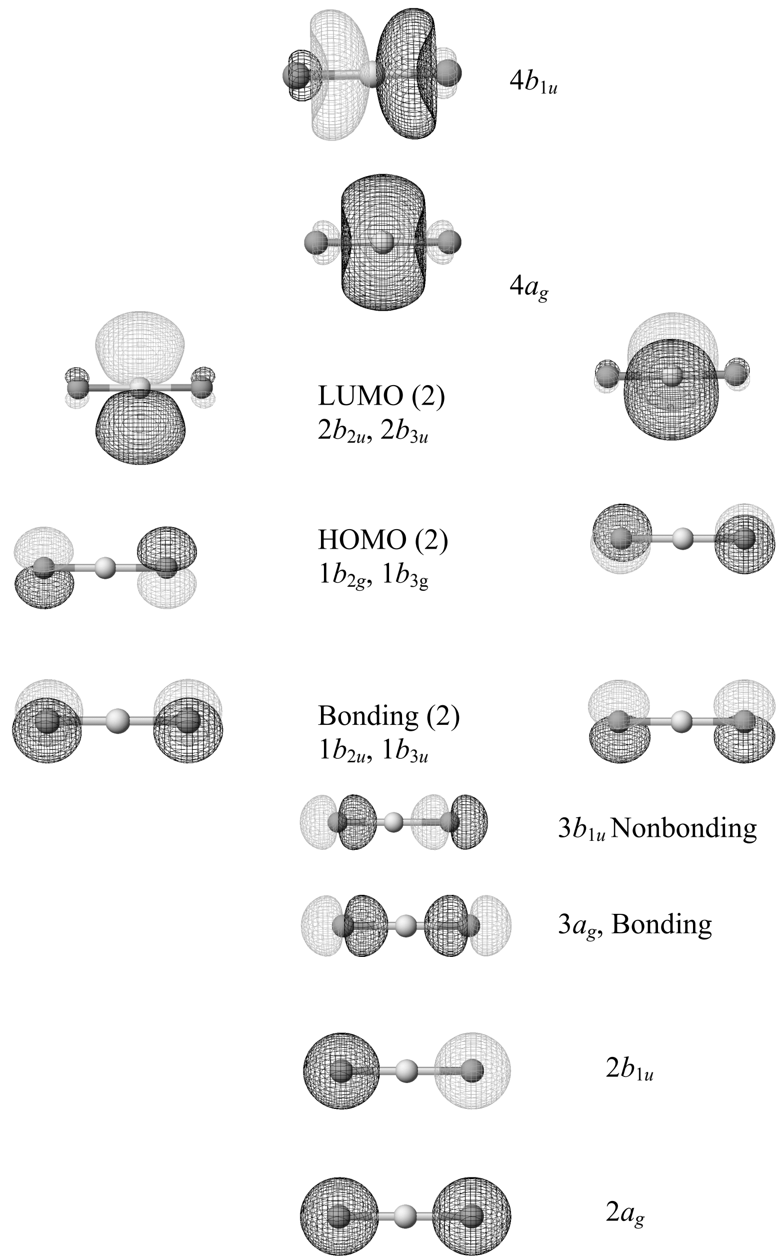


MO Diagram:



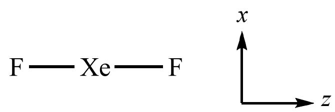
b. The energy level diagrams for CH_2 and BeH_2 feature the same orbital interactions. One difference is that the different number of valence electrons renders the linear species BeH_2 diamagnetic and CH_2 paramagnetic. The energy difference between the Be and H valence orbitals is larger than that between the valence orbitals of C and H, and both the 2*s* and 2*p* orbitals of Be are higher in energy than the 1*s* orbital of H. The result is greater bond polarity in BeH_2.

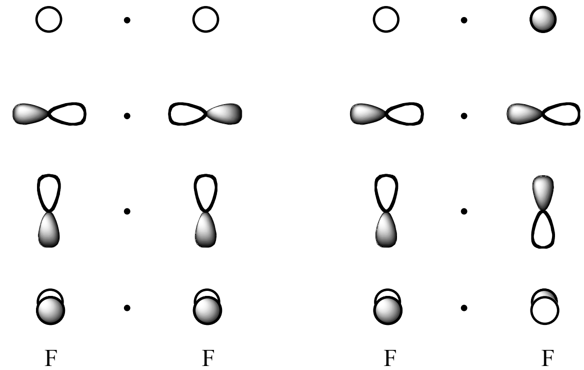
5.16 BeF_2 uses *s* and *p* orbitals on all three atoms, and is isoelectronic with CO_2. The energy level diagram for CO_2 in Figure 5.25 can be used as a guide, with the orbitals of Be higher in energy than those of C and the orbitals of F lower in energy than those of O. Calculated molecular orbital shapes are below, for comparison for those of CO_2 in Figure 5.25.



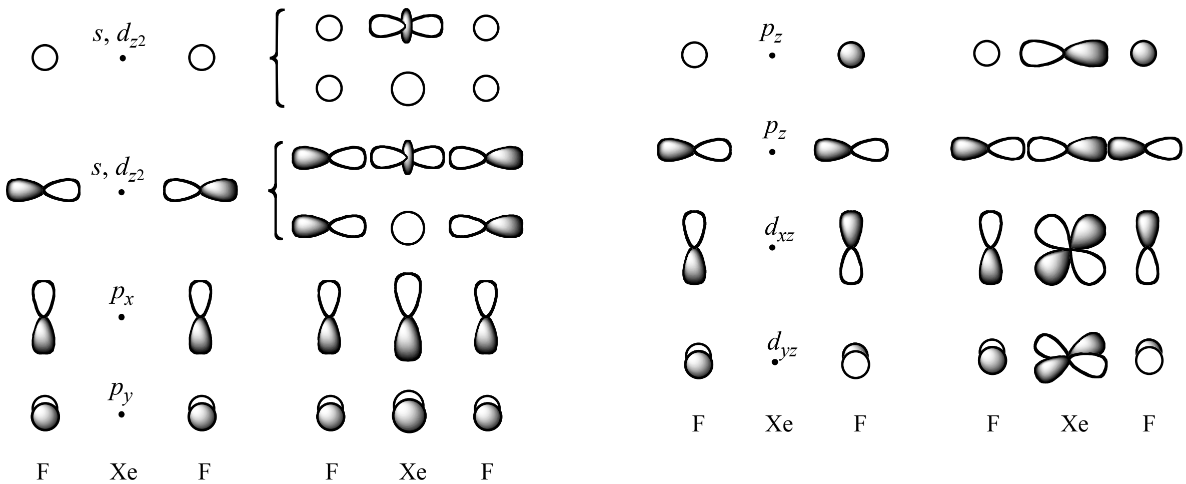
Of the occupied orbitals, there are three bonding (two π and one σ) and five nonbonding (two π and three σ). (References: W. R. Wadt, W. A. Goddard III, *J. Am. Chem. Soc.*, **1974**, *96*, 5996; R. Gleiter, R. Hoffmann, *J. Am. Chem. Soc.*, **1968**, *90*, 5457; C. W. Bauschlicher, Jr., I. Shavitt, *J. Am. Chem. Soc.*, **1978**, *100*, 739.)

5.17 **a.** The group orbitals of the fluorines are:

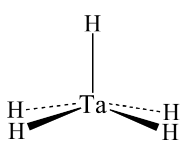




b. The matching orbitals on xenon are:

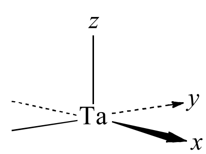


5.18 1.



The point group of TaH_5 is C_{4v}.

2. Axes can be assigned as shown:

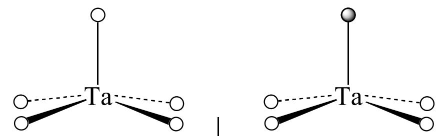


3. Construction of reducible representation:

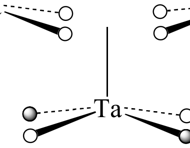
C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
Γ	5	1	1	3	1		
A_1	1	1	1	1	1	z	z^2
A_2	1	1	1	–1	–1	R_z	
B_1	1	–1	1	1	–1		$x^2–y^2$
B_2	1	–1	1	–1	1		xy
E	2	0	–2	0	0	$(x, y), (R_x, R_y)$	(xz, yz)

4. Γ reduces to 2 $A_1 + B_1 + E$

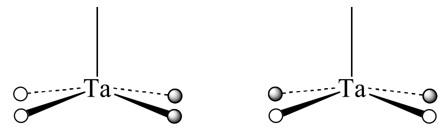
5, 6. Two group orbitals, shown at right, have A_1 symmetry. These may interact with the p_z, d_{z^2}, and s orbitals of Ta.



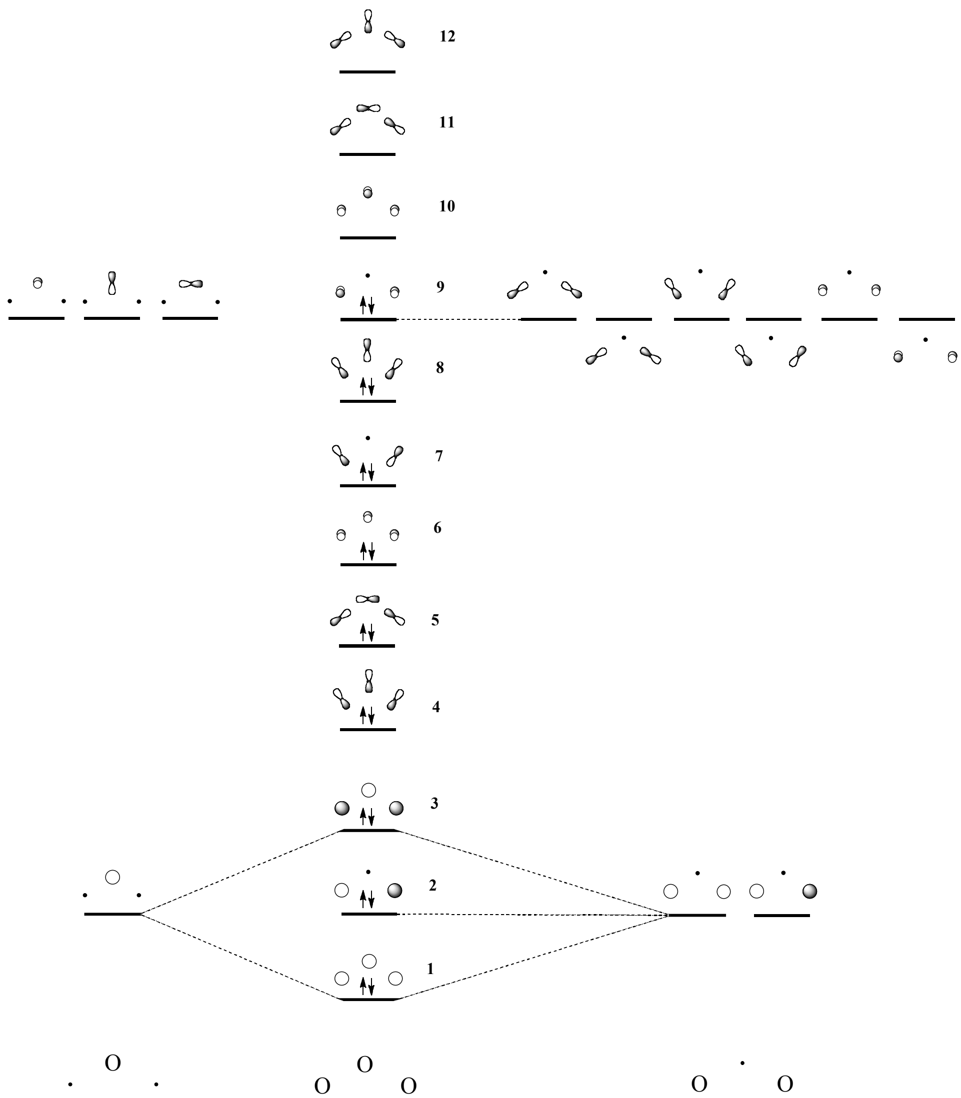
One group orbital has B_1 symmetry. It can interact with the $d_{x^2-y^2}$ orbital of Ta.



A degenerate pair of group orbitals has E symmetry. It may interact with the (p_x, p_y) and (d_{xz}, d_{yz}) pairs of Ta.



5.19 The energy level diagram for O_3 with the simple combinations of s and p orbitals is shown below. Mixing of s and p orbitals is fairly small, showing mostly in the four lowest orbitals. The order of orbitals may vary depending on the calculation method (for example, PM3 and AM1 methods reverse the orders of HOMO and HOMO –1).

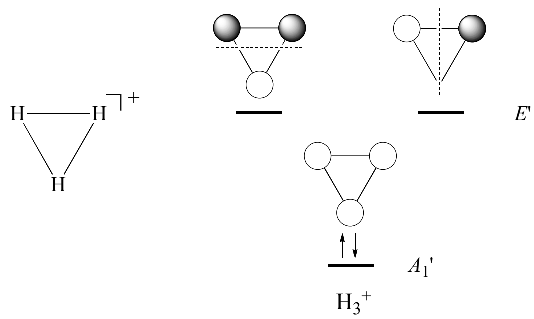


5.20 SO_3 has molecular orbitals similar to those of BF_3 (Section 5.4.6). The irreducible representations below are labeled for the oxygen orbitals.

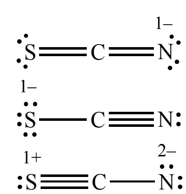
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	
$\Gamma(s)$	3	0	1	3	0	1	
$\Gamma(p_y)$	3	0	1	3	0	1	
$\Gamma(p_x) \parallel$	3	0	–1	3	0	–1	
$\Gamma(p_z)\perp$	3	0	–1	–3	0	1	
A_1'	1	1	1	1	1	1	
A_2'	1	1	–1	1	1	–1	
A_2''	1	1	–1	–1	–1	1	z
E'	2	–1	0	2	–1	0	(x, y)
E''	2	–1	0	–2	1	0	

σ	$\Gamma(s) = A_1' + E'$	Sulfur s, p_x, and p_y
σ	$\Gamma(p_y) = A_1' + E'$	Sulfur s, p_x, and p_y
$\pi_{\parallel}$	$\Gamma(p_x) = A_2' + E'$	Sulfur p_x and p_y
$\pi_{\perp}$	$\Gamma(p_z) = A_2'' + E''$	Sulfur p_z

5.21 As a cyclic (triangular) ion, H_3^+ has a pair of electrons in a bonding orbital and two vacant orbitals that are slightly antibonding:



5.22 The thiocyanate ion, SCN^-, has molecular orbitals similar to those of CO_2, but with more mixing between the s orbital of C and the s and p orbitals of S. The valence orbital potential energies of S are very close to those of C, and those of N are only slightly lower. There is significant double bonding in thiocyanate on the basis of this excellent orbital energy compatibility. This is consistent with the resonance structures shown at right, with the top structure favored.



For cyanate, OCN^-, the s and p orbitals of carbon effectively interact with valence orbitals on the N side, but less on the O side because the oxygen orbital energies are much more negative. The structures described in Section 3.1.3 (a mix of two double bonds and O–C and C≡N) fit this ion also.

For fulminate, CNO^-, the large differences between the C and O orbital energies render the contributions of the terminal atom orbitals to the group orbitals relatively uneven. A practical result of this imbalance is less delocalization of electron density within this anion. This is suggested by the formal charge effects described in Example 3.3. As a result, the bonding in this ion is weak. Fulminate is stable only when complexed with a metal ion.

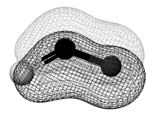
5.23 The highest occupied orbitals in SCN^- or OCN^- are π nonbonding orbitals (see Figure 5.25 for the similar CO_2 orbitals). Combination with H^+ or with metal ions depends on the energy match of these orbitals with those of the positive ion. The preference for attack can be examined by comparing the energies of the valence orbitals of the terminal atoms that contribute to these nonbonding molecular orbitals. For example, the H 1*s* orbital energy matches the energy of the N valence orbitals orbital better than either the S or O valence orbitals, and the nitrogen atom is the site of protonation in both anions. The energies of metal ion valence orbitals vary from element to element (and with oxidation state). Some metal ions will be more compatible energetically with the S orbitals while others will be more compatible with the N orbitals. These electronic effects contribute to which site of thiocyanate is appropriate for bonding to metals. The S can also use the empty 3*d* orbitals to accept electron density via π bonding from some metal ions.

5.24 The CN^- molecular orbitals are similar to those of CO (Figure 5.13), but with less difference between the C and N atomic orbital energies than between C and O orbitals. As a result, the HOMO should be more evenly balanced between the two atoms, and bonding at both ends seems more likely with CN^- relative CO. The Prussian blue structures ($Fe_4[Fe(CN)_6]_3$ or $KFe(Fe(CN)_6)$) have iron and CN^- in arrangements that have both Fe–C and Fe–N bonds.

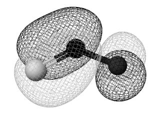
5.25 **a.** The resonance structures were considered in Problem 3.3, showing bent structures with primarily double bond character in S=N and single bonding in N–O or S–O. SNO^- is more stable on the basis of formal charges.

b. The molecular orbitals should be similar to those of O_3, with more mixing of *s* and *p* orbitals because of the difference between atomic orbital energies of S and O as terminal atoms. The π bonding, nonbonding, and antibonding orbitals are numbers 6, 9, and 10 in the ozone diagram in the Problem 5.19 answer.

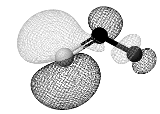
The relative contributions of the valence orbitals of each atom to the π molecular orbitals of SNO^- can be partially rationalized on the basis of electronegativity. In the π bonding orbital, the electron density is highest on the *most electronegative* O atom, a reasonable expectation for the most stabilized π interaction. In the π antibonding orbital, the electron density is highest on the *least electronegative* S atom, a feature that contributes to the destabilization of this orbital. The π molecular orbitals of NSO^- are not as clearly explained by these electronegativity arguments, possibly due to the ability of S to expand its valence shell to increase its participation in bonding as a central atom.



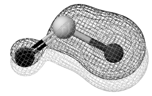
π
S—N—O⁻



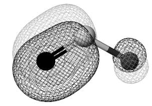
π_n
S—N—O⁻



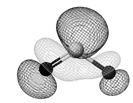
π*
S—N—O⁻



π
N—S—O⁻



π_n
N—S—O⁻



π*
N—S—O⁻

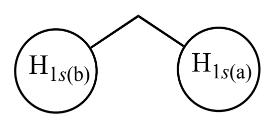
c. The calculated bond distances for these ions are:

ion	N–S	S–O	N–O
SNO^-	171 pm		120 pm
NSO^-	146 pm	149 pm	

NSO^- has the shorter N–S bond and the higher energy N–S stretching vibration.

5.26 H_2O has C_{2v} symmetry. Figure 5.26 defines the coordinate system to be used. The representation that describes the symmetry of the group orbitals (Section 5.4.3) is $A_1 + B_1$. The next step is to track the fate of one of the hydrogen 1*s* orbitals as the symmetry operations are carried out:

Original Orbital	E	C_2	$\sigma_{v(xz)}$	$\sigma'_{v(yz)}$
$H_{1s(a)}$ becomes….	$H_{1s(a)}$	$H_{1s(b)}$	$H_{1s(a)}$	$H_{1s(b)}$



Now we multiply these outcomes by the characters associated with each operation for the A_1 and B_1 representations, and then add the results to obtain the linear combinations of the H 1*s* atomic orbitals that define the group orbitals.

	E		C_2		$\sigma_{v(xz)}$		$\sigma'_{v(yz)}$	SALCs
A_1	$H_{1s(a)}$	+	$H_{1s(b)}$	+	$H_{1s(a)}$	+	$H_{1s(b)}$	$= 2(H_{1s(a)}) + 2(H_{1s(b)})$
B_1	$H_{1s(a)}$	–	$H_{1s(b)}$	+	$H_{1s(a)}$	–	$H_{1s(b)}$	$= 2(H_{1s(a)}) - 2(H_{1s(b)})$

Each group orbital equation must be normalized, so that the sum of the squares of the coefficients within each equation equals 1. The normalization factors, $N = \left(\sqrt{(c_a^2 + c_b^2)}\right)^{-1}$, where c_a and c_b are the lowest common integer coefficients for the hydrogen 1*s* orbital wave functions in each SALC, are:

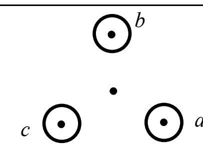
$$A_1 : N = \left(\sqrt{(1)^2 + (1)^2}\right)^{-1} = \frac{1}{\sqrt{2}} \quad B_1 : N = \left(\sqrt{(1)^2 + (-1)^2}\right)^{-1} = \frac{1}{\sqrt{2}}.$$

This results in the normalized SALC equations for the two group orbitals:

$$A_1 : \frac{1}{\sqrt{2}}\left[\Psi(H_a) + \Psi(H_b)\right] \quad B_1 : \frac{1}{\sqrt{2}}\left[\Psi(H_a) - \Psi(H_b)\right].$$

SALC Coefficients and Evidence of Normalization:

Coefficients in Normalized SALCs			Squares of SALC Coefficients		Sum of Squares =1 for Normalization
	c_a	c_b	c_a^2	c_b^2	
A_1	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$	$\frac{1}{2}$	$\frac{1}{2}$	1
B_1	$\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$	$\frac{1}{2}$	$\frac{1}{2}$	1
Sum of the squares for each 1*s* wavefunction must total 1 for an identical contribution of each atomic orbital to the group orbitals			1	1	



5.27 The irreducible representation associated with the 2*s* set is $\Gamma = A_1' + E'$. The atoms will be labeled as shown. The next step is to track the fate of one of the fluorine 2*s* orbitals as the symmetry operations are carried out:

Original Orbital	E	C_3	C_3^2	$C_{2(a)}$	$C_{2(b)}$	$C_{2(c)}$	σ_h	S_3	S_3^2	$\sigma_{v(a)}$	$\sigma_{v(b)}$	$\sigma_{v(c)}$
$2s_a$ becomes…	$2s_a$	$2s_b$	$2s_c$	$2s_a$	$2s_c$	$2s_b$	$2s_a$	$2s_b$	$2s_c$	$2s_a$	$2s_c$	$2s_b$

Now we multiply these outcomes by the characters associated with each operation for A_1' in the D_{3h} character table to obtain the linear combination. All of the characters are 1 for the totally symmetric A_1' irreducible representation. Therefore:

$$A_1' : 2s_a + 2s_b + 2s_c + 2s_a + 2s_c + 2s_b + 2s_a + 2s_b + 2s_c + 2s_a + 2s_c + 2s_b = 4(2s_a) + 4(2s_b) + 4(2s_c)$$

The lowest common integer coefficient is 1, and $N = \left(\sqrt{(1)^2 + (1)^2 + (1)^2}\right)^{-1} = \frac{1}{\sqrt{3}}$. The normalized A_1' SALC is $\frac{1}{\sqrt{3}}\left[\Psi(2s_a) + \Psi(2s_b) + \Psi(2s_c)\right]$. Next we multiply the terms in the table above by the characters of the E' irreducible representation. The characters for C_2 and σ_v are 0, so multiplication by these characters leads to no contribution to the SALC:

$$E' : 2(2s_a) - 2s_b - 2s_c + 2(2s_a) - 2s_b - 2s_c = 4(2s_a) - 2(2s_b) - 2(2s_c).$$

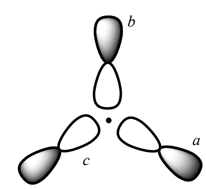
Reduction to the lowest common integer coefficient affords $2(2s_a) - (2s_b) - (2s_c)$, and $N = \left(\sqrt{(2)^2 + (-1)^2 + (-1)^2}\right)^{-1} = \frac{1}{\sqrt{6}}$. The normalized E' SALC is therefore

$$\frac{1}{\sqrt{6}}\left[2(\Psi(2s_a) - \Psi(2s_b) - \Psi(2p_c)\right].$$

The remaining E' SALC can be deduced by examination of the coefficients and the sums of their squares.

	Coefficients of Normalized SALCs			Squares of SALC Coefficients			Sum of the Squares = 1 for Normalization
	c_a	c_b	c_c	c_a^2	c_b^2	c_c^2	
A_1'	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	1
E'	$\frac{2}{\sqrt{6}}$	$-\frac{1}{\sqrt{6}}$	$-\frac{1}{\sqrt{6}}$	$\frac{2}{3}$	$\frac{1}{6}$	$\frac{1}{6}$	1
E'	0	$\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$	0	$\frac{1}{2}$	$\frac{1}{2}$	1
Sum of the squares for each 2s wavefunction must total 1 for an identical contribution of each atomic orbital to the group orbitals				1	1	1	

Since the sum of the squares of the coefficients for $2s_a$ equals 1 without any contribution from the second E' SALC, this SALC must have $c_a = 0$. The squares of c_b and c_c must equal $\frac{1}{2}$ to satisfy the normalization and identical contribution from each orbital requirements. Since E' matches the symmetry of the *x* and *y* axes, and the origin is the center of the group orbital (the boron atom), one of the coefficients must be positive and the other negative. The second E' SALC is therefore $\frac{1}{\sqrt{2}}\left[\Psi(2s_b) - \Psi(2s_c)\right]$.



The irreducible representation associated with the $2p_y$ set is also $\Gamma = A_1' + E'$. The atoms are labeled as shown. The fate of one of the fluorine $2p_y$ orbitals as the symmetry operations are carried out is:

	E	C_3	C_3^2	$C_{2(a)}$	$C_{2(b)}$	$C_{2(c)}$	σ_h	S_3	S_3^2	$\sigma_{v(a)}$	$\sigma_{v(b)}$	$\sigma_{v(c)}$
$2p_{y(a)}$ becomes…	$2p_{y(a)}$	$2p_{y(b)}$	$2p_{y(c)}$	$2p_{y(a)}$	$2p_{y(c)}$	$2p_{y(b)}$	$2p_{y(a)}$	$2p_{y(b)}$	$2p_{y(c)}$	$2p_{y(a)}$	$2p_{y(c)}$	$2p_{y(b)}$

Now we multiply these outcomes by the characters associated with each operation for A_1' in the D_{3h} character table. All of the characters are 1 for the A_1' irreducible representation. Therefore:

$$A_1' : 2p_{y(a)} + 2p_{y(b)} + 2p_{y(c)} + 2p_{y(a)} + 2p_{y(c)} + 2p_{y(b)} + 2p_{y(a)} + 2p_{y(b)} + 2p_{y(c)} + 2p_{y(a)} + 2p_{y(c)} + 2p_{y(b)}$$
$$= 4(2p_{y(a)}) + 4(2p_{y(b)}) + 4(2p_{y(c)}).$$

The lowest common integer coefficient is 1, and $N = \left(\sqrt{(1)^2 + (1)^2 + (1)^2}\right)^{-1} = \frac{1}{\sqrt{3}}$. The normalized A_1' SALC is therefore $\frac{1}{\sqrt{3}}\left[\Psi(2p_{y(a)}) + \Psi(2p_{y(b)}) + \Psi(2p_{y(c)})\right]$.

Next we multiply the terms in the table above by the characters of the E' irreducible representation. The characters for C_2 and σ_v are 0, so multiplication by these characters leads to no contribution to the SALC:

$$E':2(2p_{y(a)})-2p_{y(b)}-2p_{y(c)}+2(2p_{y(a)})-2p_{y(b)}-2p_{y(c)}=4(2p_{y(a)})-2(2p_{y(b)})-2(2p_{y(c)}).$$

Reduction to the lowest common integer coefficient affords $2(2p_{y(a)})-(2p_{y(b)})-(2p_{y(c)})$, and

$N=\left(\sqrt{(2)^2+(-1)^2+(-1)^2}\right)^{-1}=\dfrac{1}{\sqrt{6}}$. The normalized E' SALC is

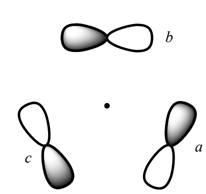
$$\frac{1}{\sqrt{6}}\left[2(\Psi(2p_{y(a)})-\Psi(2p_{y(b)})-\Psi(2p_{y(c)})\right].$$

The remaining E' SALC can be deduced by examination of the coefficients and the sums of their squares.

	Coefficients of Normalized SALCs			Squares of SALC Coefficients			Sum of the Squares = 1 for Normalization
	c_a	c_b	c_c	c_a^2	c_b^2	c_c^2	
A_1'	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	1
E'	$\frac{2}{\sqrt{6}}$	$-\frac{1}{\sqrt{6}}$	$-\frac{1}{\sqrt{6}}$	$\frac{2}{3}$	$\frac{1}{6}$	$\frac{1}{6}$	1
E'	0	$\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$	0	$\frac{1}{2}$	$\frac{1}{2}$	1
Sum of the squares for each $2p_y$ wavefunction must total 1 for an identical contribution of each atomic orbital to the group orbitals				1	1	1	

Since the sum of the squares of the coefficients for $2p_{y(a)}$ equals 1 without any contribution from the second E' SALC, this SALC must have $c_a = 0$. The squares of c_b and c_c must equal $\frac{1}{2}$ to satisfy the normalization and identical contribution from each orbital requirements. Since E' matches the symmetry of the *x* and *y* axes, and the origin is the center of the group orbital (the boron atom), one of the coefficients must be positive and the other negative. The second E' SALC is $\dfrac{1}{\sqrt{2}}\left[\Psi(2p_{y(b)})-\Psi(2p_{y(c)})\right]$.

The irreducible representation associated with the $2p_x$ set is $\Gamma = A_2' + E'$. The atoms are labeled as shown. The fate of one of the fluorine $2p_x$ orbitals as the symmetry operations are carried out is:



	E	C_3	C_3^2	$C_{2(a)}$	$C_{2(b)}$	$C_{2(c)}$	σ_h	S_3	S_3^2	$\sigma_{v(a)}$	$\sigma_{v(b)}$	$\sigma_{v(c)}$
$2p_{x(a)}$ becomes…	$2p_{x(a)}$	$2p_{x(b)}$	$2p_{x(c)}$	$-2p_{x(a)}$	$-2p_{x(c)}$	$-2p_{x(b)}$	$2p_{x(a)}$	$2p_{x(b)}$	$2p_{x(c)}$	$-2p_{x(a)}$	$-2p_{x(c)}$	$-2p_{x(b)}$

Now we multiply these outcomes by the characters associated with each operation for A_2' in the D_{3h} character table:

$$A_2' : 2p_{x(a)} + 2p_{x(b)} + 2p_{x(c)} + 2p_{x(a)} + 2p_{x(c)} + 2p_{x(b)} + 2p_{x(a)} + 2p_{x(b)} + 2p_{x(c)} + 2p_{x(a)} + 2p_{y(c)} + 2p_{x(b)}$$
$$= 4(2p_{x(a)}) + 4(2p_{x(b)}) + 4(2p_{x(c)})$$

The lowest common integer coefficient is 1, and $N = \left(\sqrt{(1)^2 + (1)^2 + (1)^2}\right)^{-1} = \frac{1}{\sqrt{3}}$. The normalized A_2' SALC is $\frac{1}{\sqrt{3}}\left[\Psi(2p_{x(a)}) + \Psi(2p_{x(b)}) + \Psi(2p_{x(c)})\right]$.

Next we multiply the terms in the table by the characters of the E' irreducible representation.

$$E' : 2(2p_{x(a)}) - 2p_{x(b)} - 2p_{x(c)} + 2(2p_{y(a)}) - 2p_{x(b)} - 2p_{x(c)} = 4(2p_{x(a)}) - 2(2p_{x(b)}) - 2(2p_{x(c)})$$

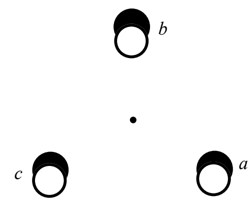
Reduction to the lowest common integer coefficient affords $2(2p_{x(a)}) - (2p_{x(b)}) - (2p_{x(c)})$, and $N = \left(\sqrt{(2)^2 + (-1)^2 + (-1)^2}\right)^{-1} = \frac{1}{\sqrt{6}}$. The normalized E' SALC is $\frac{1}{\sqrt{6}}\left[2(\Psi(2p_{x(a)}) - \Psi(2p_{x(b)}) - \Psi(2p_{x(c)})\right]$.

The remaining E' SALC can be deduced by examination of the coefficients and the sums of their squares.

	Coefficients of Normalized SALCs			Squares of SALC Coefficients			Sum of the Squares = 1 for Normalization Requirement
	c_a	c_b	c_c	c_a^2	c_b^2	c_c^2	
A_2'	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	1
E'	$\frac{2}{\sqrt{6}}$	$-\frac{1}{\sqrt{6}}$	$-\frac{1}{\sqrt{6}}$	$\frac{2}{3}$	$\frac{1}{6}$	$\frac{1}{6}$	1
E'	0	$\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$	0	$\frac{1}{2}$	$\frac{1}{2}$	1
Sum of the squares for each $2p_x$ wavefunction must total 1 for an identical contribution of each atomic orbital to the group orbitals				1	1	1	

Since the sum of the squares of the coefficients for $2p_{x(a)}$ equals 1 without any contribution from the second E' SALC, this SALC must have $c_a = 0$. The squares of c_b and c_c must equal $\frac{1}{2}$ to satisfy the normalization and identical contribution from each orbital requirements. Because E' matches the symmetry of the *x* and *y* axes, and the origin is the center of the group orbital (the boron atom), one of the coefficients must be positive and the other negative. The second E' SALC is $\frac{1}{\sqrt{2}}\left[\Psi(2p_{x(b)}) - \Psi(2p_{x(c)})\right]$.

The irreducible representation associated with the $2p_z$ set is $\Gamma = A_2'' + E''$. The atoms are labeled as shown. The fate of one of the fluorine $2p_z$ orbitals as the symmetry operations are carried out is:



	E	C_3	C_3^2	$C_{2(a)}$	$C_{2(b)}$	$C_{2(c)}$	σ_h	S_3	S_3^2	$\sigma_{v(a)}$	$\sigma_{v(b)}$	$\sigma_{v(c)}$
$2p_{z(a)}$ becomes…	$2p_{z(a)}$	$2p_{z(b)}$	$2p_{z(c)}$	$-2p_{z(a)}$	$-2p_{z(c)}$	$-2p_{z(b)}$	$-2p_{z(a)}$	$-2p_{z(b)}$	$-2p_{z(c)}$	$2p_{z(a)}$	$2p_{z(c)}$	$2p_{z(b)}$

Now we multiply these outcomes by the characters associated with each operation for A_2'' in the D_{3h} character table:

$$A_2'': 2p_{z(a)} + 2p_{z(b)} + 2p_{z(c)} + 2p_{z(a)} + 2p_{z(c)} + 2p_{z(b)} + 2p_{z(a)} + 2p_{z(b)} + 2p_{z(c)} + 2p_{x(a)} + 2p_{z(c)} + 2p_{z(b)}$$
$$= 4(2p_{z(a)}) + 4(2p_{z(b)}) + 4(2p_{z(c)})$$

The lowest common integer coefficient is 1, and $N = \left(\sqrt{(1)^2 + (1)^2 + (1)^2}\right)^{-1} = \frac{1}{\sqrt{3}}$. The normalized A_2'' SALC is $\frac{1}{\sqrt{3}}\left[\Psi(2p_{z(a)}) + \Psi(2p_{z(b)}) + \Psi(2p_{z(c)})\right]$.

Next we multiply the terms in the table by the characters of the E'' irreducible representation:

$$E'': 2(2p_{z(a)}) - 2p_{z(b)} - 2p_{z(c)} + 2(2p_{z(a)}) - 2p_{z(b)} - 2p_{z(c)} = 4(2p_{z(a)}) - 2(2p_{z(b)}) - 2(2p_{z(c)}).$$

Reduction to the lowest common integer coefficient affords $2(2p_{z(a)}) - (2p_{z(b)}) - (2p_{z(c)})$, and $N = \left(\sqrt{(2)^2 + (-1)^2 + (-1)^2}\right)^{-1} = \frac{1}{\sqrt{6}}$. The normalized E'' SALC is

$$\frac{1}{\sqrt{6}}\left[2(\Psi(2p_{z(a)}) - \Psi(2p_{z(b)}) - \Psi(2p_{z(c)})\right].$$

The remaining E'' SALC can be deduced by examination of the coefficients and the sums of their squares.

	Coefficients of Normalized SALCs			Squares of SALC Coefficients			Sum of the Squares = 1 for Normalization Requirement
	c_a	c_b	c_c	c_a^2	c_b^2	c_c^2	
A_2''	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	1
E''	$\frac{2}{\sqrt{6}}$	$-\frac{1}{\sqrt{6}}$	$-\frac{1}{\sqrt{6}}$	$\frac{2}{3}$	$\frac{1}{6}$	$\frac{1}{6}$	1
E''	0	$\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$	0	$\frac{1}{2}$	$\frac{1}{2}$	1
Sum of the squares for each $2p_z$ wavefunction must total 1 for an identical contribution of each atomic orbital to the group orbitals				1	1	1	

Since the sum of the squares of the coefficients for $2p_{z(a)}$ equals 1 without any contribution from the second E'' SALC, this SALC must have $c_a = 0$. The squares of c_b and c_c must equal $\frac{1}{2}$ to satisfy the normalization and identical contribution from each orbital requirements. Since E'' has the same symmetry as the xz and yz orbitals that have nodes defined by the yz and xz planes, respectively, one of the coefficients must be positive and the other negative. The second E' SALC is $\frac{1}{\sqrt{2}}\left[\Psi(2p_{z(b)}) - \Psi(2p_{z(c)})\right]$.

5.28 The point group is D_{4h}. The reducible representation that describes the symmetries of the group orbitals is:

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
	4	0	0	2	0	0	0	4	2	0

Reduction affords $\Gamma = A_{1g} + B_{1g} + E_u$. To deduce the SALCs, we need to track the fate of one of the 3*s* orbitals through each symmetry operation of the character table.

$3s(A)$ becomes…	E	C_4	C_4^3	C_2	$C_2'(x)$	$C_2'(y)$	$C_2''(1)$	$C_2''(2)$
	$3s(A)$	$3s(B)$	$3s(D)$	$3s(C)$	$3s(C)$	$3s(A)$	$3s(D)$	$3s(B)$
	i	S_4	S_4^3	σ_h	$\sigma_v(x)$	$\sigma_v(y)$	$\sigma_d(1)$	$\sigma_d(2)$
	$3s(C)$	$3s(B)$	$3s(D)$	$3s(A)$	$3s(C)$	$3s(A)$	$3s(D)$	$3s(B)$

Since all of the characters for A_{1g} are 1, the SALC for A_{1g} is:

$$A_{1g}: 3s(A)+3s(B)+3s(D)+3s(C)+3s(C)+3s(A)+3s(D)+3s(B)+3s(C)+3s(B)+3s(D)+3s(A)+$$
$$3s(C)+3s(A)+3s(D)+3s(B)=4(3s(A))+4(3s(B))+4(3s(C))+4(3s(D))$$

This simplifies to $3s(A)+3s(B)+3s(C)+3s(D)$, which provides a normalization constant of $N=\left(\sqrt{(1)^2+(1)^2+(1)^2+(1)^2}\right)^{-1}=\frac{1}{2}$ and the SALC $\frac{1}{2}\left[\Psi(3s(A))+\Psi(3s(B))+\Psi(3s(C))+\Psi(3s(D))\right]$.

Multiplication of the orbitals in the above table by the B_{1g} characters gives:

$$B_{1g}: 3s(A)-3s(B)-3s(D)+3s(C)+3s(C)+3s(A)-3s(D)-3s(B)+3s(C)-3s(B)-3s(D)+3s(A)+$$
$$3s(C)+3s(A)-3s(D)-3s(B)=4(3s(A))-4(3s(B))+4(3s(C))-4(3s(D))$$

This simplifies to $3s(A)-3s(B)+3s(C)-3s(D)$, which provides a normalization constant of

$N=\left(\sqrt{(1)^2+(-1)^2+(1)^2+(-1)^2}\right)^{-1}=\frac{1}{2}$ and $\frac{1}{2}\left[\Psi(3s(A))-\Psi(3s(B))+\Psi(3s(C))-\Psi(3s(D))\right]$

as the B_{1g} normalized SALC.

Multiplication of the orbitals in the above table by the E_u characters affords:

$$E_u: 2(3s(A))-2(3s(C))-2(3s(C))+2(3s(A))=4(3s(A))-4(3s(C))$$

This simplifies to $3s(A)-3s(C)$, which provides a normalization constant of

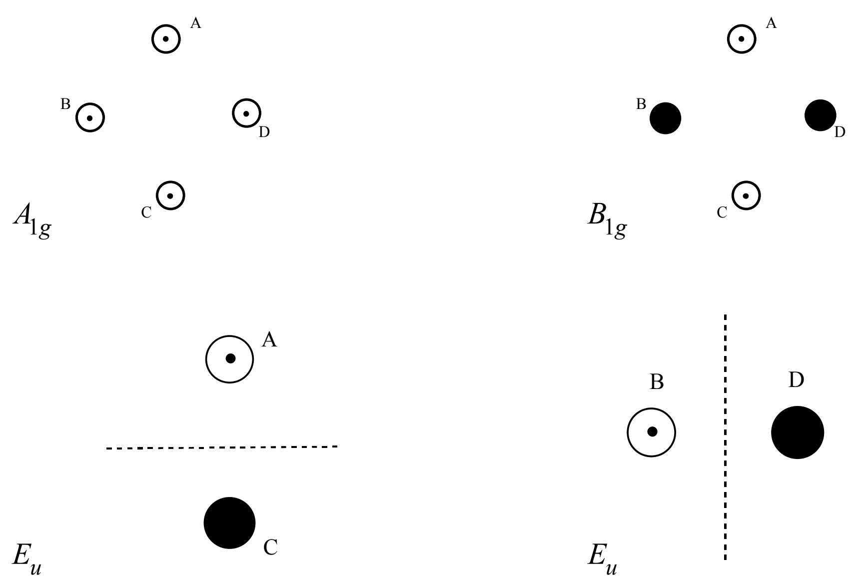
$N=\left(\sqrt{(1)^2+(-1)^2}\right)^{-1}=\frac{1}{\sqrt{2}}$ and $\frac{1}{\sqrt{2}}\left[\Psi(3s(A))-\Psi(3s(C))\right]$ as one of the normalized E_u SALCs.

The equation for the other E_u SALC can be deduced by consideration of the normalized SALC coefficients and their squares.

	Coefficients of Normalized SALCs				Squares of SALC Coefficients				Sum of the Squares = 1 for Normalization Requirement
	c_A	c_B	c_C	c_D	c_A^2	c_B^2	c_C^2	c_D^2	
A_{1g}	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	1
B_{1g}	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	1
E_u	$\frac{1}{\sqrt{2}}$	0	$-\frac{1}{\sqrt{2}}$	0	$\frac{1}{2}$	0	$\frac{1}{2}$	0	1
E_u	0	$\frac{1}{\sqrt{2}}$	0	$-\frac{1}{\sqrt{2}}$	0	$\frac{1}{2}$	0	$\frac{1}{2}$	1
Sum of the squares for each $3s$ wavefunction must total 1 for an identical contribution of each atomic orbital to the group orbitals					1	1	1	1	

The sum of $c_A^{\;2}$ and $c_C^{\;2}$ equals 1 without any contribution from the second E_u SALC; $c_A = c_C = 0$ for this second E_u SALC. A magnitude of $\frac{1}{\sqrt{2}}$ is required for both c_B and c_D of the second E_u SALC on the basis of the normalization requirement and equal contribution of each atomic orbital to the group orbital's requirement. The alternate signs are required since E_u has the symmetry of the *x* and *y* axes; these E_u group orbitals need to match the symmetry of the valence *p* orbitals of the central atom. The normalized equation for the second E_u SALC is $\frac{1}{\sqrt{2}}\left[\Psi(3s(B)) - \Psi(3s(D))\right]$.

Sketches of these group orbitals are below, using the coordinate system specified in this problem. Note the scaling of the orbitals to reflect the larger contribution of the $3s$ orbitals in the E_u SALCs compared to that in A_{1g} and B_{1g} SALCs.



5.29 For this question, we will label the $2p_z$ orbitals simply by their letters (A–F) for clarity. The first task is to track the fate of A through all of the D_{6h} symmetry operations:

A becomes…	E	C_6	$C_6^{\,5}$	C_3	$C_3^{\,2}$	C_2	$C_2'(1)$	$C_2'(2)$	$C_2'(3)$	$C_2''(1)$	$C_2''(2)$	$C_2''(3)$
	A	B	F	C	E	D	-A	-C	-E	-B	-D	-F
	i	S_3	$S_3^{\,2}$	S_6	$S_6^{\,5}$	σ_h	$\sigma_d(1)$	$\sigma_d(2)$	$\sigma_d(3)$	$\sigma_v(1)$	$\sigma_v(2)$	$\sigma_v(3)$
	-D	-C	-E	-B	-F	-A	B	D	F	A	C	E

Multiplication by the characters of *each* irreducible representation of the D_{6h} character table (and for each symmetry operation) is a tedious, but effective, method to deduce the SALCs.

$$A_{1g}: A+B+F+C+E+D-A-C-E-B-D-F-D-C-E-B-F-A+B+D+F+A+C+E=0$$

$$A_{2g}: A+B+F+C+E+D+A+C+E+B+D+F-D-C-E-B-F-A-B-D-F-A-C-E=0$$

$B_{1g}: A-B-F+C+E-D-A-C-E+B+D+F-D+C+E-B-F+A+B+D+F-A-C-E=0$

$B_{2g}: A-B-F+C+E-D+A+C+E-B-D-F-D+C+E-B-F+A-B-D-F+A+C+E$

$=4A-4B+4C-4D+4E-4F$

$E_{1g}: 2A+B+F-C-E-2D-2D-C-E+B+F+2A=4A+2B-2C-4D-2E+2F$

$E_{2g}: 2A-B-F-C-E+2D-2D+C+E+B+F-2A=0$

$A_{1u}: A+B+F+C+E+D-A-C-E-B-D-F+D+C+E+B+F+A-B-D-F-A-C-E=0$

$A_{2u}: A+B+F+C+E+D+A+C+E+B+D+F+D+C+E+B+F+A+B+D+F+A+C+E$

$=4A+4B+4C+4D+4E+4F$

$B_{1u}: A-B-F+C+E-D-A-C-E+B+D+F+D-C-E+B+F-A-B-D-F+A+C+E=0$

$B_{2u}: A-B-F+C+E-D+A+C+E-B-D-F+D-C-E+B+F-A+B+D+F-A-C-E=0$

$E_{1u}: 2A+B+F-C-E-2D+2D+C+E-B-F-2A=0$

$E_{2u}: 2A-B-F-C-E+2D+2D-C-E-B-F+2A=4A-2B-2C+4D-2E-2F$

The six group orbitals have the symmetries B_{2g}, A_{2u}, E_{1g}, and E_{2u}, expressed in simplified form below, with normalization constants shown at right.

$B_{2g}: A-B+C-D+E-F$ $\qquad B_{2g}: N=\left(\sqrt{(1)^2+(-1)^2+(1)^2+(-1)^2+(1)^2+(-1)^2}\right)^{-1}=\dfrac{1}{\sqrt{6}}$

$A_{2u}: A+B+C+D+E+F$ $\qquad A_{2u}: N=\left(\sqrt{(1)^2+(1)^2+(1)^2+(1)^2+(1)^2+(1)^2}\right)^{-1}=\dfrac{1}{\sqrt{6}}$

$E_{1g}: 2A+B-C-2D-E+F$ $\qquad E_{1g}: N=\left(\sqrt{(2)^2+(1)^2+(-1)^2+(-2)^2+(-1)^2+(1)^2}\right)^{-1}=\dfrac{1}{\sqrt{12}}$

$E_{2u}: 2A-B-C+2D-E-F$ $\qquad E_{2u}: N=\left(\sqrt{(2)^2+(-1)^2+(-1)^2+(2)^2+(-1)^2+(-1)^2}\right)^{-1}=\dfrac{1}{\sqrt{12}}$

The first four SALC equations are:

$$B_{2g}: \frac{1}{\sqrt{6}}\left[\Psi(2p_{z(A)})-\Psi(2p_{z(B)})+\Psi(2p_{z(C)})-\Psi(2p_{z(D)})+\Psi(2p_{z(E)})-\Psi(2p_{z(F)})\right]$$

$$A_{2u}: \frac{1}{\sqrt{6}}\left[\Psi(2p_{z(A)})+\Psi(2p_{z(B)})+\Psi(2p_{z(C)})+\Psi(2p_{z(D)})+\Psi(2p_{z(E)})+\Psi(2p_{z(F)})\right]$$

$$E_{1g}: \frac{1}{\sqrt{12}}\left[2\Psi(2p_{z(A)})+\Psi(2p_{z(B)})-\Psi(2p_{z(C)})-2\Psi(2p_{z(D)})-\Psi(2p_{z(E)})+\Psi(2p_{z(F)})\right]$$

$$E_{2u}: \frac{1}{\sqrt{12}}\left[2\Psi(2p_{z(A)})-\Psi(2p_{z(B)})-\Psi(2p_{z(C)})+2\Psi(2p_{z(D)})-\Psi(2p_{z(E)})-\Psi(2p_{z(F)})\right]$$

The remaining two SALCs (E_{1g} and E_{2u}) can be deduced by examination of the coefficients of the normalized equations.

	Coefficients of Normalized SALCs						Squares of SALC Coefficients						Sum of the Squares = 1 for Normalization Requirement
	c_A	c_B	c_C	c_D	c_E	c_F	c_A^2	c_B^2	c_C^2	c_D^2	c_E^2	c_F^2	
B_{2g}	$\frac{1}{\sqrt{6}}$	$-\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{6}}$	$-\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{6}}$	$-\frac{1}{\sqrt{6}}$	$\frac{1}{6}$	$\frac{1}{6}$	$\frac{1}{6}$	$\frac{1}{6}$	$\frac{1}{6}$	$\frac{1}{6}$	1
A_{2u}	$\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{6}}$	$\frac{1}{\sqrt{6}}$	$\frac{1}{6}$	$\frac{1}{6}$	$\frac{1}{6}$	$\frac{1}{6}$	$\frac{1}{6}$	$\frac{1}{6}$	1
E_{1g}	$\frac{2}{\sqrt{12}}$	$\frac{1}{\sqrt{12}}$	$-\frac{1}{\sqrt{12}}$	$-\frac{2}{\sqrt{12}}$	$-\frac{1}{\sqrt{12}}$	$\frac{1}{\sqrt{12}}$	$\frac{1}{3}$	$\frac{1}{12}$	$\frac{1}{12}$	$\frac{1}{3}$	$\frac{1}{12}$	$\frac{1}{12}$	1
E_{1g}	0	$\frac{1}{2}$	$\frac{1}{2}$	0	$-\frac{1}{2}$	$-\frac{1}{2}$	0	$\frac{1}{4}$	$\frac{1}{4}$	0	$\frac{1}{4}$	$\frac{1}{4}$	1
E_{2u}	$\frac{2}{\sqrt{12}}$	$-\frac{1}{\sqrt{12}}$	$-\frac{1}{\sqrt{12}}$	$\frac{2}{\sqrt{12}}$	$-\frac{1}{\sqrt{12}}$	$-\frac{1}{\sqrt{12}}$	$\frac{1}{3}$	$\frac{1}{12}$	$\frac{1}{12}$	$\frac{1}{3}$	$\frac{1}{12}$	$\frac{1}{12}$	1
E_{2u}	0	$-\frac{1}{2}$	$\frac{1}{2}$	0	$\frac{1}{2}$	$-\frac{1}{2}$	0	$\frac{1}{4}$	$\frac{1}{4}$	0	$\frac{1}{4}$	$\frac{1}{4}$	1
Sum of the squares for each $2p_z$ wavefunction must total 1 for an identical contribution of each atomic orbital to the group orbitals							1	1	1	1	1	1	

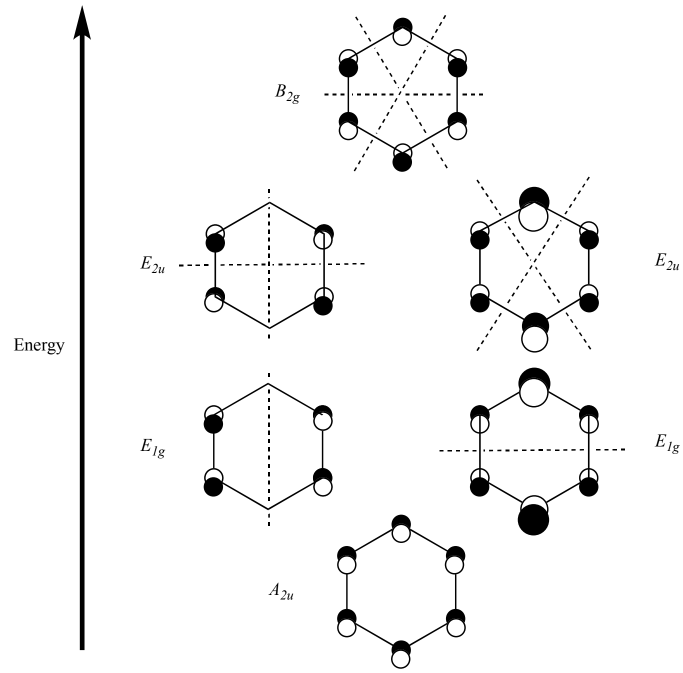
The sum of the squares of the SALC coefficients for A and D equal 0 without any contribution from the second E_{1g} and E_{2u} SALCs; therefore, c_A and c_D are zero for these two SALCs. The sum of the squares of the coefficients for B, C, E, and F equal $\frac{1}{2}$ without contributions from the second E_{1g} and E_{2u} SALCs. This suggests that c_B^2, c_C^2, c_D^2, and c_E^2 equal $\frac{1}{4}$ for these two SALCs, and that c_C, c_D, c_E, and c_F equal $\pm\frac{1}{2}$. The choice of signs in the table above are those required for the SALCs to satisfy the symmetry requirements of the functions associated with the E_{1g} and E_{2u} representations, and to obtain the number of nodes expected (see sketches below).

The last two normalized SALCs are:

$$E_{1g} : \frac{1}{2}\left[\Psi(2p_{z(B)}) + \Psi(2p_{z(C)}) - \Psi(2p_{z(E)}) - \Psi(2p_{z(F)})\right]$$

$$E_{2u} : \frac{1}{2}\left[-\Psi(2p_{z(B)}) + \Psi(2p_{z(C)}) - \Psi(2p_{z(E)}) + \Psi(2p_{z(F)})\right]$$

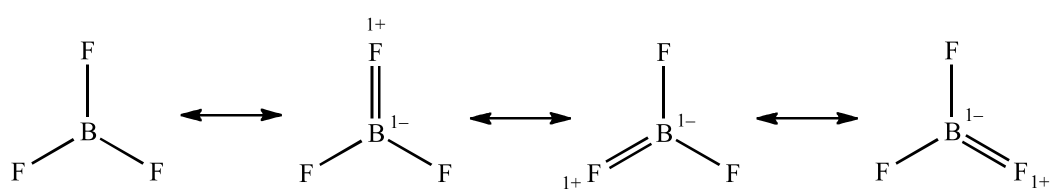
The six group orbitals are sketched below, ranked by their relative energy. The number of nodes increases from zero to three with orbital energy. These orbitals, and a discussion of their energies, are in Section 13.4.4.



5.30 **a.** Cl_2^+ has one fewer electron than Cl_2, so the π* levels have three, rather than four, electrons. As a result, Cl_2^+ has a bond order of 1.5, and the bond is shorter and stronger than that of of Cl_2 (189 pm, compared with 199 pm for Cl_2).

b. Cl_4^+ has such an elongated rectangular shape (194 pm by 294 pm) that it must be essentially a Cl_2 and a Cl_2^+ side by side, with only a weak attraction between them through the π* orbitals. The Cl–Cl bond in Cl_2 is 199 pm long; apparently, the weak side-to-side bond draws off some of the antibonding electron density, strengthening and shortening the other two shorter Cl–Cl bonds.

5.31 **a.**

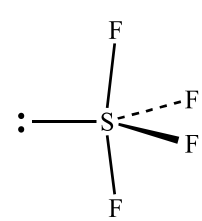


b. The $1a_2''$ orbital near the middle of the figure is the π-bonding orbital.

c. The LUMO, $2a_2''$, is the best orbital for accepting a lone pair.

d. The $1a_2''$ orbital is formed by adding all the p_z orbitals together. The $2a_2''$ orbital is formed by adding the B p_z orbital and subtracting the three F p_z orbitals.

5.32 SF_4 has C_{2v} symmetry. Treating the four F atoms as simple spherical orbitals, the reducible representation Γ_σ can be found and reduced to



$\Gamma_\sigma = 2A_1 + B_1 + B_2$. Overall, the bonding orbitals can be dsp^2 or d^2sp, with the s and p_z or d_{z^2} orbital with A_1 symmetry, p_x or d_{xy} with B_1 symmetry, and p_y or d_{yz} with B_2 symmetry. The p_z or d_{z^2} orbital remaining accounts for the lone pair. (The use of the trigonal bipyramidal hybrids dsp^3 or d^3sp include the lone pair as one of the five locations.)

C_{2v}	E	C_2	$\sigma(xz)$	$\sigma(yz)$	
Γ_σ	4	0	2	2	
A_1	1	1	1	1	z, z^2
A_2	1	1	–1	–1	
B_1	1	–1	1	–1	x, xz
B_2	1	–1	–1	1	y, yz

5.33 A square pyramidal molecule has the reducible representation $\Gamma = E + 2A_1 + B_1$.

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$	
Γ_σ	5	1	1	3	1	
E	2	0	–2	0	0	(x, y) (xz, yz)
A_1	1	1	1	1	1	z, z^2, x^2+y^2
B_1	1	–1	1	1	–1	$x^2–y^2$

There appear to be three possibilities for combining orbitals, depending on the details of their relative energies: dsp^3 (p_x and p_y for E, s and p_z for A_1, $d_{x^2-y^2}$ for B_1), d^2sp^2 (substituting d_{z^2} for p_z), and d^3sp (substituting d_{xz} and d_{yz} for p_x and p_y). Although d_{xz} and d_{yz} appear to work, they actually have their electron concentration between the B atoms, and therefore do not participate in σ bonding, so d^3sp or d^2sp^2 fit better.

5.34 Square planar compounds have D_{4h} symmetry.

D_{4h}	E	$2C_4$	C_2	C_2'	C_2''	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	
Γ	4	0	0	2	0	0	0	4	2	0	
E_u	2	0	–2	0	0	–2	0	2	0	0	(x,y)
A_{1g}	1	1	1	1	1	1	1	1	1	1	z^2
B_{1g}	1	–1	1	1	–1	1	–1	1	1	–1	$x^2–y^2$

$$\Gamma_\sigma = \underset{s,\ d_{z^2}}{\underset{\downarrow}{A_{1g}}} + \underset{d_{x^2-y^2}}{\underset{\downarrow}{B_{1g}}} + \underset{p_x,\ p_y}{\underset{\downarrow}{E_u}}$$

dsp^2 hybrids are the usual ones used for square planar compounds, although d^2p^2 is also possible. Since the d_{z^2} orbital does not extend far in the xy plane, it is less likely to participate in σ bonding.

5.35 **a.** PCl_5 has D_{3h} symmetry.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	
Γ	5	2	1	3	0	3	
E'	2	–1	0	2	–1	0	(x, y) $(x^2–y^2, xy)$
A_1'	1	1	1	1	1	1	z^2
A_2''	1	1	–1	–1	–1	1	z

$\Gamma = E' + 2A_1' + A_2''$, so the hybrids are dsp^3 or d^3sp.

b. This could also be analyzed separately for the axial and the equatorial positions. The p_z and d_{z^2} orbitals can bond to the axial chlorines ($A_1' + A_2''$) and the s, p_x, and p_y orbitals or the s, $d_{x^2-y^2}$, and d_{xy} orbitals can bond to the equatorial chlorines (E').

c. The d_{z^2} orbital extends farther than the p orbitals, making the axial bonds a bit longer.

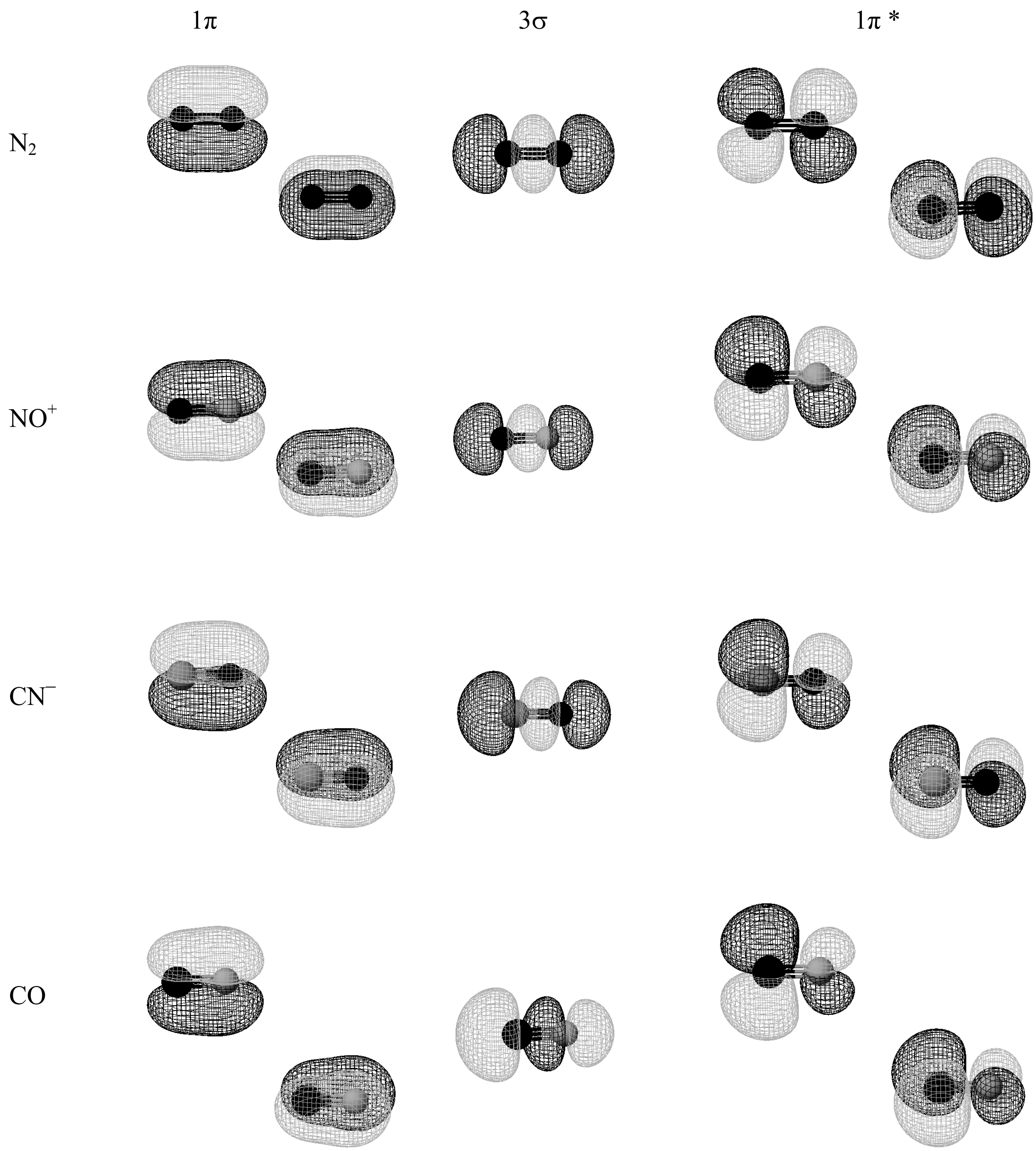
5.36

	Ignoring Orbital Lobe Signs	Including Orbital Lobe Signs
$1a_2''$	D_{3h}	C_{3v}
$2a_2''$	D_{3h}	C_{3v}
$1a_2'$	D_{3h}	C_{3h}
$1e''$	C_{2v}	C_1

Results should be similar to Figure 5.32. The energies of some of the orbitals in the middle of the diagram are similar, and the order may vary with different calculation methods. In addition, the locations of the nodes in degenerate orbitals (e'' and e') may vary depending on how the software assigns orientations of atomic orbitals. If nodes cut through atomic nuclei, $1e''$ orbitals may have C_2 symmetry, matching the symmetry of the first E'' group orbital shown in Figure 5.31. The table of orbital contributions for each of the orbitals should show the same orbitals as in Figure 5.32. There may be some differences in contributions with different calculation methods, but they should be minor. Assignments to p_x, p_y, and p_z will also differ, depending on how the software defines orientations of orbitals. Semi-empirical calculation AM1 gives these as the major contributors to the specified orbitals:

	$3a_1'$	$4a_1'$	$1a_2''$	$1a_2'$	$2a_2''$
B	$2s$	$2s$	$2p_z$		$2p_z$
F	$2s$	$2s$, $2p_y$	$2p_z$	$2p_x$	$2p_z$

5.37 **a.** The shapes of the orbitals, generated using one of the simplest computational methods, Extended Hückel Theory, are shown below, with the most electronegative element shown at right in the heteronuclear cases.



b. In the 1π orbitals (bonding), the lobes are increasingly concentrated on the more electronegative atom as the difference in electronegativity between the two atoms increases. This effect is seen most significantly in CO, where the difference in electronegativity is the greatest.

In the $1\pi^*$ orbitals, the antibonding partners of the 1π orbitals, the effect is reversed, with the largest lobes now concentrated on the *less* electronegative atoms. The greatest effect is again shown in CO, with the lobes on carbon much

larger than those on oxygen.
The 3σ orbitals also show the influence of electronegativity, this time with the lobe extending to the left from the less electronegative atom being the largest, with CO once more showing the greatest effect. This can be viewed in part as a consequence of the 3 σ orbital being a better match for the energy of the less electronegative atom's 2*s* orbital which, together with the $2p_z$ orbital of the same atom, interacts with the $2p_z$ orbital of the more electronegative atom (the atom shown on the right).

c. The results vary greatly depending on the software used. The results using one approach, AM1, are shown below (numerical values are energies in electron volts).

	σ*	π*	σ	π	σ*	σ
		LUMO	HOMO			
CN^-	14.7	0.13	–3.13	–5.10	–9.37	–28.0
CO	5.28	0.94	–13.31	–16.30	–22.00	–41.2
N_2	6.03	1.00	–14.32	–16.19	–21.43	–41.39
NO^+	–4.42	–9.62	–26.13	–28.80	–35.80	–56.89

In this table, the energies decrease as the atomic numbers increase (with CO and N_2 giving mixed results). There is considerable mixing of the σ orbitals, a phenomenon that may raise the energy of the σ (HOMO) orbital above the energy of the π orbitals– as is the case in each of these examples.

5.38 Among the trends that should be observed is the effect on the shapes of the π and π* orbitals (see orbitals of CO labeled as 1π and 1π* in Figure 5.13) as the difference in electronegativity between the atoms increases (this trend is also observed in Problem 37). For BF and BeNe, the lobes of the π orbitals should become increasingly concentrated on the more electronegative atoms, and the lobes of the π* orbitals should become increasingly concentrated on the less electronegative atoms (a pattern that has begun with CO, if the orbital shapes for CO are compared with those of the isoelectronic N_2).

An additional effect is that the size of the protruding orbital lobe of the less electronegative atom should increase as the difference in electronegativity between the atoms increases; this can be see in the 3σ orbital of CO in Figure 5.13. Additional trends in the other molecular orbitals can also be noted.

5.39 In one bonding orbital, the H *s* orbitals have the same sign and add to the Be *s* orbital in the HOMO–1 orbital. Subtracting the Be *s* orbital results in the antibonding LUMO. The difference between the two H *s* orbitals added to the Be p_z orbital results in the HOMO; subtracting the Be p_z results in the LUMO+3 orbital. LUMO+1 and LUMO+2 are the Be p_x and p_y orbitals and are nonbonding (and degenerate) in BeH_2. For an energy level diagram, see the solution to Exercise 5.8 in Appendix A.

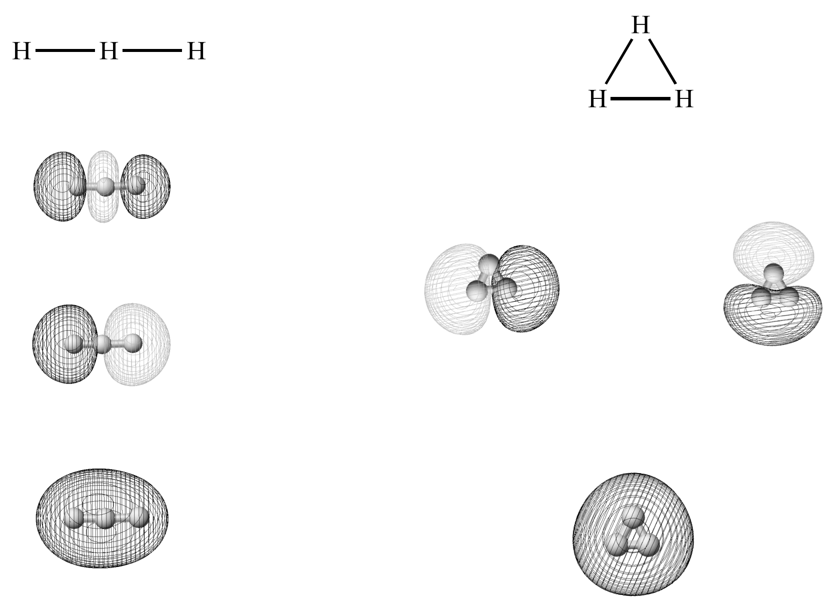
5.40 BeF_2 is similar to BeH_2, with the addition of π and π* orbitals from the p_x and p_y orbitals, extending over all three atoms. The F p_x orbitals with opposite signs do not combine with the Be orbitals, and neither do the p_y orbitals; the p_x and p_y orbitals form the HOMO and HOMO+1 pair.

The answer to Problem 5.16 shows more details.

5.41 The azide orbitals are similar to the CO_2 orbitals, with some differences in contributions from the atomic orbitals because the CO_2 atomic orbitals do not have the identical energies as the nitrogen atoms do. The two highest occupied orbitals of CO_2, BeF_2, and N_3^- all consist of p_x or p_y orbitals of the outer atoms with opposite signs, essentially nonbonding orbitals. The third orbital down has more *s* orbital contribution from the outer atoms than either of the other two; in those cases, the lower orbital energies of the atoms reduce that contribution. See also the solution to Exercise 5.7 in Appendix A.

5.42 One aspect of ozone's molecular orbitals that should be noted is its π system. For reference, it is useful to compare the bonding π orbital that extends over all three atoms (the atomic orbitals that are involved are shown as molecular orbital 6 in the solution to Problem 5.19); this orbital is the lowest in energy of the 3-orbital bonding/nonbonding/antibonding set (orbitals 6, 9, and 10 in Problem 5.19) involving the 2*p* orbitals that are not involved in σ bonding. Another bonding/nonbonding/antibonding set can be seen in the molecular orbitals derived from 2*s* orbitals (orbitals 1, 2, and 3 in Problem 5.19).

5.43 **a.** Linear Cyclic



In the linear arrangement, the molecular orbitals shown, from bottom to top, are bonding, nonbonding, and antibonding, with only the bonding orbital occupied. In the cyclic geometry, the lowest energy orbital is bonding, and the other two orbitals are degenerate, each with a node slicing through the center; again, only the lowest energy orbital is occupied.

b. Cyclic H_3^+ is slightly more stable than linear H_3^+, based on the energy of the lowest orbital in an AM1 calculation (–28.4 eV versus –26.7 eV).

5.44 **a.** The full group theory treatment (D_{2h} symmetry), shown in Section 8.5.1, uses the two bridging hydrogens as one set for group orbitals and the four terminal hydrogens as another set; these sets are shown in Figure 8.11. The representations for these sets can be reduced as follows:

The bridging hydrogens have $\Gamma = A_g + B_{3u}$.

The boron *s* orbitals have $\Gamma = A_g + B_{1u}$.

The p_x orbitals (in the plane of the bridging hydrogens) have $\Gamma = B_{2g} + B_{3u}$.

The p_z orbitals (perpendicular to the plane of the bridging hydrogens) have $\Gamma = A_g + B_{1u}$.

The boron A_g and B_{3u} orbitals combine with the bridging hydrogen orbitals, resulting in two bonding and two antibonding orbitals. Electron pairs in each of the bonding orbitals result in two bonds holding the molecule together through hydrogen bridges.

b. Examples of diborane molecular orbitals are in Figure 8.14.