

## Chapter 7

### Covalent Bonding and Molecular Orbitals

*Some seventy years ago, the physicist P. A. M. Dirac declared-with no small degree of overstatement-that the whole of chemistry had been reduced to a solved problem: that the explanation of all things chemical lay in the Schrödinger equation and its solutions, and that chemists needed only to do the calculations.*

*Chemists today are still doing those calculations and, more important, they continue to seek physical meaning in the numbers and equations. For in all but the simplest of systems, an exact solution is beyond reach. As it was with atoms, so it is with molecules: Approximations and models, not simply raw equations, pave the road to understanding.*

*The classical electron-pair bond thus gives way to the bonding orbital, but the notion of chemical bonds between atoms stubbornly remains. "Satisfied octets" and otherwise mysterious "expanded" or "deficient" octets find explanation in the quantization of molecular energy levels. Localized valence bond pictures coexist fruitfully with full-dress molecular orbital theories. The old notions of single, double, and triple bonds persist in the concept of bond order. Classical resonance structures blend together into systems of delocalized orbitals. And, for a certain class of molecule, the purely electrostatic arguments of VSEPR theory continue to give the right answer.*

*The discussion and exercises of Chapter 7 aim to convey a sense, at least, of how the practical chemist chooses from among a number of simple models-a sense of what is possible, a sense of how best to develop a rigorous chemical understanding without sacrificing chemical intuition.*

*The first dozen or so exercises recapitulate the most basic assumptions of molecular quantum mechanics. Essential ingredients such as wave functions and interference (Chapter 4), the one-electron atom and its special solutions (Chapter 5), and the orbital model of many-electron atoms (Chapter 6) come to the fore.*

1. Mutual electrostatic attraction, understood quantum mechanically, holds a molecule together: All of the nuclei are attracted to all of the electrons, and all of the electrons are attracted to all of the nuclei. The attractive influence of more than one nucleus greatly lowers the electrostatic energy, despite the electron-electron and nucleus-nucleus repulsions always present. Stabilization of the electronic energy is optimal at the equilibrium bond distance.

2. A molecule will survive if it proves stronger, more stable, and hence lower in energy than the component atoms existing apart. The stronger the bonds, the better a structure can withstand the impacts of collisions and thermal buffeting. Bond strength is measured thermodynamically (Chapters 12 through 14) and explained quantum mechanically (this chapter).

3. An electron, although particle-like in many ways, also displays the property most characteristic of a wave: interference. Passing through a crystal, a beam of electrons will produce a diffraction pattern; and, merging into a molecule, the electronic wave functions in two atoms will combine constructively and destructively-like waves.

When the atoms combine constructively, as in a bonding interaction, *more* electron density is concentrated between the nuclei than otherwise. The total energy of the system decreases.

When the atoms combine destructively, as in an antibonding interaction, the shared density is less. Electrons are forced into closer quarters on each atom, further raising the total energy.

4. Molecular wave functions. See pages 219-224 in *PoC* and the brief comments below.

(a) The whereabouts of an electron are described quantum mechanically by a wave function  $\psi(x, y, z)$ , which we interpret as a probability amplitude: The square of the wave function,  $\psi^2(x, y, z)$ , gives the probability that the electron will be found within an infinitesimal volume around the point  $(x, y, z)$ .

(b) When atoms form chemical bonds, their individual wave functions appear to combine just as ordinary waves do. They interfere. They produce a joint probability density different from  $\psi_A^2 + \psi_B^2$ , either more or less. The amplitudes may mix *constructively*, adding with matching phases as

$$\Psi = \psi_A + \psi_B$$

to enhance the combined probability (electron density) by  $2\psi_A \psi_B$ :

$$\Psi^2 = \psi_A^2 + \psi_B^2 + 2\psi_A \psi_B$$

Or they may combine *destructively*, adding with opposite phases as

$$\Psi = \Psi_A - \Psi_B$$

to diminish the combined probability by  $2\Psi_A\Psi_B$  :

$$\Psi^2 = \Psi_A^2 + \Psi_B^2 - 2\Psi_A\Psi_B$$

The constructive combination produces a *bonding* interaction; the destructive combination produces *an antibonding* interaction.

5. Atomic versus molecular orbitals. See *PoC*, pages 225-228.

(a) Atomic and molecular orbitals share the following characteristics: (1) They are one-particle wave functions, specified for a single electron in a many-electron system. The exact solutions derived for a hydrogen atom serve as prototypes. (2) They are *approximate* wave functions. A single-particle wave function presupposes that each electron interacts, in turn, with a repulsive field averaged over all the other electrons at once.

Atomic and molecular orbitals differ mostly in their symmetry and mathematical construction. For an atomic orbital, the potential produced by the nucleus is the same in all directions; and, as a result, an atom is spherical. Reflecting the  $1/r$  Coulomb symmetry, atomic wave functions fall into subshells characterized by angular momentum quantum numbers  $\ell$  (with values 0, 1, 2, . . .  $n - 1$ ). Each subshell contains  $2\ell + 1$  orbitals.

In a molecule, by contrast, there is no single center of nuclear attraction, and the structure is not necessarily a sphere. Molecular orbitals are characterized by angular quantum numbers different from those pertaining to atomic orbitals.

(b) If molecules are built from atoms, then we may reasonably suppose that molecular wave functions can be built from atomic wave functions. Addition and subtraction of  $n$  atomic orbitals in various proportions—in effect, a simulation of constructive and destructive interference—produces  $n$  molecular orbitals.

6. Hybrid orbitals. See *PoC*, pages 247-253.

(a) A hybrid orbital is *an atomic* orbital, centered on a single nucleus in a molecule. Formed by combination of two or more simpler atomic orbitals, the hybrid has direction and shape different from the usual  $s$ ,  $p$ ,  $d$ , and  $f$  functions. Examples include the  $sp$  hybrid (linear), the  $sp^2$  hybrid (trigonal planar), and the  $sp^3$  hybrid (tetrahedral).

Hybrid orbitals, combined further with orbitals contributed by other atoms, offer a way to account for the shapes of molecules. They serve mainly as an organizing tool, a summary of experimental and theoretical observations.

(b) Unlike a molecular orbital, a hybrid orbital is built around a single center-one nucleus, not two or more. As such, it serves as an “atomic orbital” available for combination within a molecule, entering into bonding and antibonding combinations with orbitals centered on other nuclei.

7. A homonuclear diatomic molecule is constructed from two identical atoms, utterly indistinguishable. Everything about the participating atoms is the same.

(a) Each of the two atoms exercises the same potential on the bonded electrons, and consequently the electron distribution proves to be symmetric up, down, and around the bond. The symmetry is that of a cylinder cut by a mirror plane passing perpendicularly through the center of the axis.

(b) The bonded atoms are indistinguishable, neither of them more likely than the other to attract an electron. Symmetry prevents any excess charge from clustering permanently at one end or the other. All homonuclear diatomic molecules are nonpolar,

8. See Exercise 1 l(b) in this manual as well as Figures 7-4, 7-7, and 7-8 in *PoC*, among others, for correlation diagrams showing the mixing of *s* atomic orbitals into  $\sigma$  molecular orbitals. One combination (bonding) goes down in energy; the other combination (antibonding) goes up.

See also Figures 7-3 and 7-6 in *PoC* for the shape and angular symmetry of the *s*-derived  $\sigma$  orbitals.

9. Overlapping head-on, two atomic *p* orbitals form bonding and antibonding molecular orbitals of  $\sigma$  symmetry. Overlapping side by side, they form bonding and antibonding orbitals of  $\pi$  symmetry. Schematic correlation diagrams are shown in the solution to Exercise 12(b), where they are compared with similar diagrams for heteronuclear systems.

For angular views of homonuclear-*p* sigma orbitals, see Figure 7-9 on page 230 of *PoC*. For *p*-*p* pi combinations, see Figure 7-10.

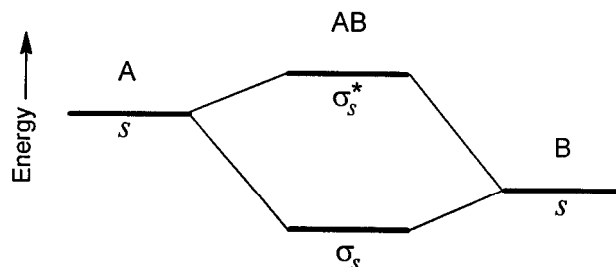
10. A heteronuclear diatomic molecule is built from two distinct atoms, each with its own set of properties.

(a) One of the atoms, more electronegative than the other, will accumulate excess electron density. The resulting distribution is cylindrically symmetric (as in a homonuclear system), but the molecule no longer enforces reflection symmetry through a mirror perpendicular to the bond axis.

(b) The two atoms are demonstrably different, and thus there is no barrier toward skewing the charge to one side. A heteronuclear diatomic molecule possesses a permanent dipole moment to the extent that the two atoms differ in electronegativity. One side is partially positive, and the other side is partially negative.

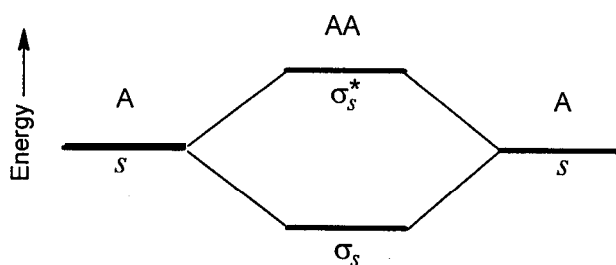
11. See pages 236-240 in *PoC* for a discussion of heteronuclear diatomic molecules.

(a) Atomic orbitals  $s_A$  and  $s_B$  mix to form molecular orbitals  $\sigma_s$  and  $\sigma_s^*$  in AB:



The axial symmetry of the  $\sigma$  orbitals is preserved in a heteronuclear combination, but the more electronegative site (here, B) contributes an atomic orbital of lower energy. The bonding orbital that results is overweighted toward B in composition and electron density.

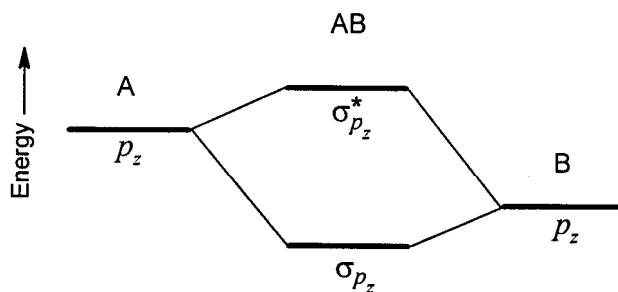
(b) Mixing of  $s$  orbitals in the homonuclear molecule AA:



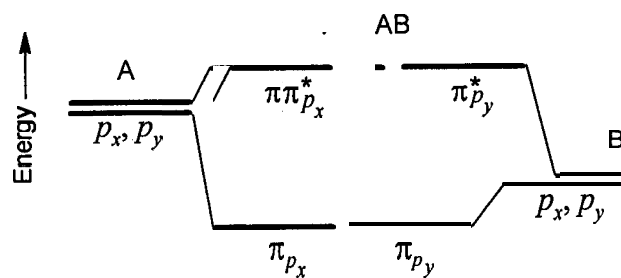
The molecular orbitals are equally weighted. Neither of the two sites is favored.

12. Similar to the preceding exercise, but this time with  $p$  orbitals.

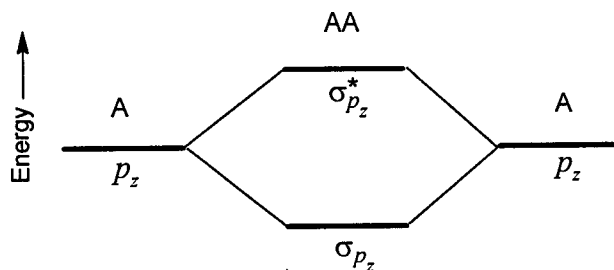
(a)  $p$ - $p$  sigma orbitals in AB:



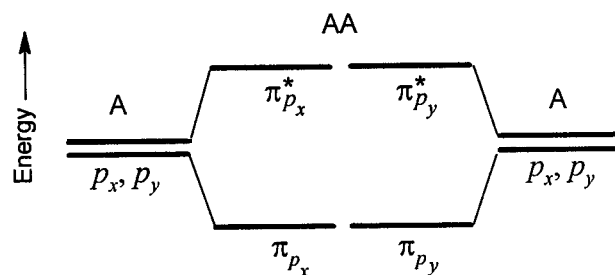
$p$ - $p$  pi orbitals in AB:



(b)  $p$ - $p$  sigma orbitals in AA:



$p$ - $p$  pi orbitals in AA:



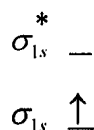
13. This exercise and the next three explore the unique status of  $H_2^+$ . For a similar treatment of  $He_2^+$ , see Example 7-1 in *PoC* (page R7.5).

(a) The hydrogen molecule ion is a one-electron system, free from any electron-electron repulsion. All molecules outside this class have at least two electrons.

(b) Unencumbered by electron-electron repulsion, the wave functions for  $H_2^+$  need not be based on a smoothed-out, average interelectronic potential-as is otherwise required for molecules and many-electron atoms (see *PoC*, pages 178-181). In that sense, the hydrogen molecule ion is similar to the hydrogen atom.

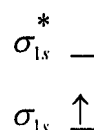
In contrast to the hydrogen atom, however, the lone electron in  $H_2^+$  is attracted simultaneously to two nuclei, not one. The resulting distribution of electron density is cylindrically symmetric rather than spherically symmetric.

14. The configuration of  $H_2^+$  is  $(\sigma_{1s})^1$ :



A bonding arrangement is thereby produced, and the ion is stable. See the next exercise.

15. Built up to the minimal configuration  $(a_{1g})^1$ , the hydrogen molecule ion has but one bonding orbital:



The energy of this molecular orbital,  $\sigma_{1s}$ , is lower than the energy of a  $1s$  atomic orbital in H alone.

(a) One electron occupies the bonding orbital. The antibonding orbital,  $\sigma_{1s}^*$ , remains vacant.

(b) With one bonding electron and zero antibonding electrons, the ion has a bond order of  $\frac{1}{2}$ :

$$\begin{aligned} \text{Bond order} &= \frac{1}{2}(\text{no. of bonding electrons} - \text{no. of antibonding electrons}) \\ &= \frac{1}{2}(1 - 0) \\ &= \frac{1}{2} \end{aligned}$$

(c) The lone electron makes  $H_2^+$  paramagnetic-unlike  $H_2$ , in which two electrons are paired in the  $\sigma_{1s}$  orbital.

16. Neutral  $H_2$  has the configuration (a,,)' and hence a bond order of 1:

$$\begin{aligned}\text{Bond order} &= \frac{1}{2}(\text{no. of bonding electrons} - \text{no. of antibonding electrons}) \\ &= \frac{1}{2}(2 - 0) \\ &= 1\end{aligned}$$

The molecular ion, with only one electron, has a bond order of  $\frac{1}{2}$ . See the preceding exercise.

(a) The extra bonding electron in  $H_2$  enhances the attraction and helps pull the two nuclei closer together. The linkage (a classic electron-pair bond) is shorter than the corresponding "half-bond" in  $H_2^+$ .

Experimental results show the following bond lengths:

H-H	0.74 Å
H-H <sup>+</sup>	1.06 Å

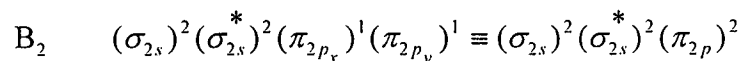
(b) The shorter bond is a stronger bond, as evidenced by the experimental dissociation energies:

H-H	436 kJ mol <sup>-1</sup>
H-H <sup>+</sup>	255 kJ mol <sup>-1</sup>

*Having briefly explored  $H_2^+$ , a molecule unique among molecules, we go on to review the building-up of diatomic structures in the second row (Section 7-2 of PoC). Connections between orbital populations, bond order, bond strength, bond length, and magnetism are demonstrated for various molecular systems. The exercises that follow are similar to Example 7-2 in PoC (beginning on page R7.5).*

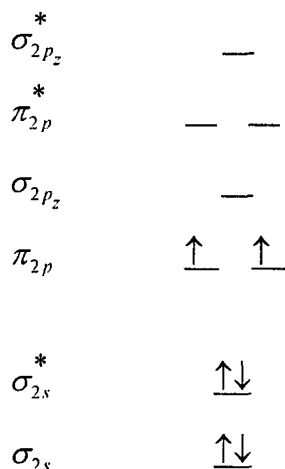
17. Molecular orbitals in  $B_2$  adopt the pattern shown in Figure 7-1 l(b) of PoC (page 232).

(a) Six valence electrons are distributed over four orbitals in the ground-state configuration:



Spin alignment in the degenerate  $\pi_{2p}$  orbitals is determined by Hund's rule (see PoC, pages 188-191):



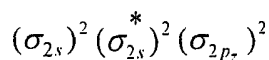


(b) Since there are two unpaired electrons in the ground state, the molecule is expected to be paramagnetic.

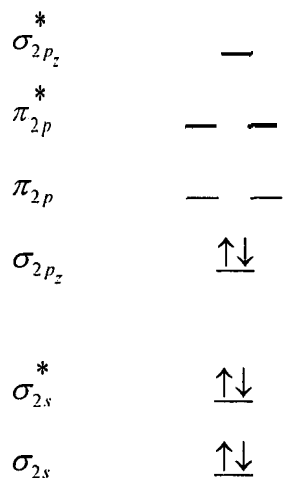
(c) Two bonding electrons-net-give  $B_2$  a bond order of 1:

$$\begin{aligned}
 \text{Bond order} &= \frac{1}{2}(\text{no. of bonding electrons} - \text{no. of antibonding electrons}) \\
 &= \frac{1}{2}(4 - 2) \\
 &= 1
 \end{aligned}$$

18. If the  $\sigma_{2p_z}$  and  $\pi_{2p}$  orbitals in  $B_2$  were interchanged, the configuration would become



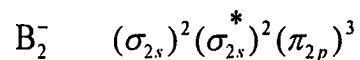
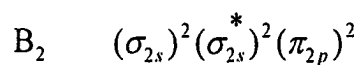
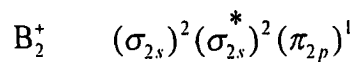
(a) The resulting distribution of electrons would leave none unpaired. The system would be diamagnetic, not paramagnetic:



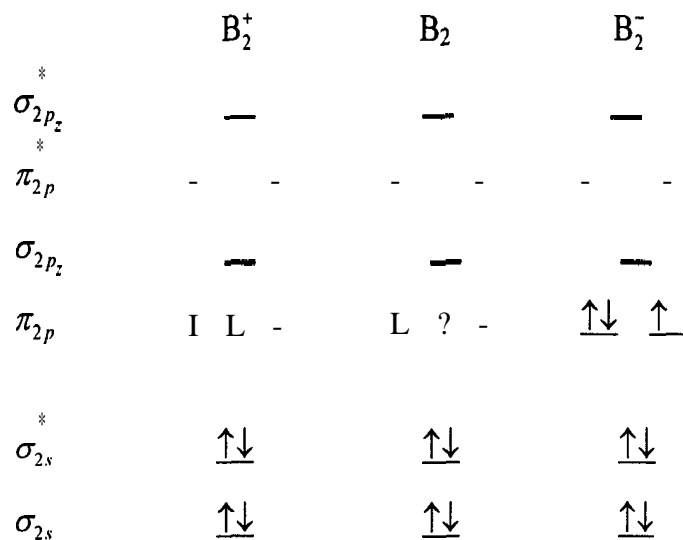
(b) Such a structure, with two net bonding electrons, would still have a bond order of 1:

$$\begin{aligned}\text{Bond order} &= \frac{1}{2}(\text{no. of bonding electrons} - \text{no. of antibonding electrons}) \\ &= \frac{1}{2}(4 - 2) \\ &= 1\end{aligned}$$

19. Count five, six, and seven valence electrons in the cation, neutral molecule, and anion, respectively:



Where two electrons must occupy the two degenerate  $\pi_{2p}$  orbitals, as in  $\text{B}_2$ , Hund's rule predicts parallel spins:



Bond order is lowest in the cation and highest in the anion:

$$\text{B}_2^+ \quad \text{Bond order} = \frac{1}{2}(3 - 2) = \frac{1}{2}$$

$$\text{B}_2 \quad \text{Bond order} = \frac{1}{2}(4 - 2) = 1$$

$$\text{B}_2^- \quad \text{Bond order} = \frac{1}{2}(5 - 2) = \frac{3}{2}$$

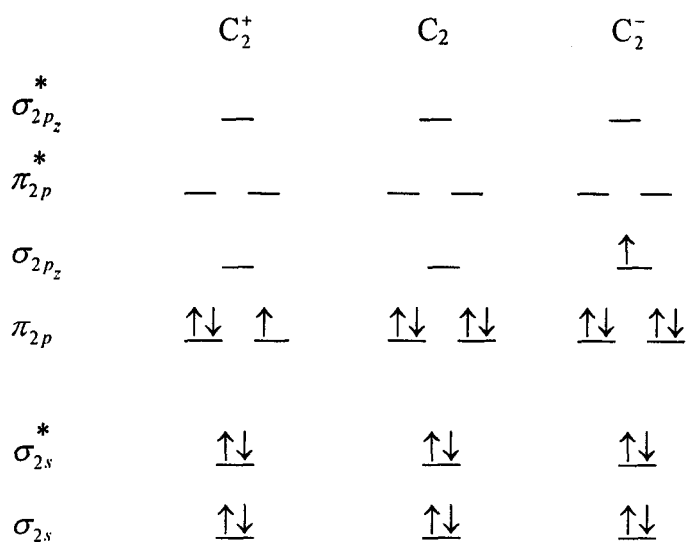
Strong bonds (characterized by high bond order) are short bonds, and therefore bond energy increases and bond length *decreases* in the same order:

$$\text{Bond energy: } B_2^+ < B_2 < B_2^-$$

$$\text{Bond length: } B_2^+ > B_2 > B_2^-$$

Note, finally, that all three structures are paramagnetic. The ions each have one unpaired electron; the neutral molecule has two.

20. The neutral molecule  $C_2$  contains eight valence electrons. The cation has seven. The anion has nine:



$C_2^-$  is bound the strongest;  $C_2^+$  is bound the weakest.  $C_2$  is diamagnetic.

CONFIGURATION	BOND ORDER	UNPAIRED ELECTRONS	COMMENT
$C_2^+$ $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^3$	$\frac{3}{2}$	1	longest and weakest bond
$C_2$ $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^4$	2	0	intermediate length/strength
$C_2^-$ $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p})^4 (\sigma_{2p_z})^1$	$\frac{5}{2}$	1	shortest and strongest bond

21. Beginning with  $O_2$ , the  $\sigma_{2p_z}$  orbital falls below the  $\pi_{2p}$ . The neutral molecule has 12 valence electrons; the cation has 11; the anion has 13.

Filling of the degenerate  $\pi_{2p}^*$  orbitals proceeds according to Hund's rule:

	$O_2^+$	$O_2$	$O_2^-$
$\sigma_{2p_z}^*$	—	—	—
$\pi_{2p}^*$	$\uparrow$ —	$\uparrow$ $\uparrow$	$\uparrow\downarrow$ $\uparrow$
$\pi_{2p}$	$\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$	$\uparrow\downarrow$ $\uparrow\downarrow$
$\sigma_{2p_z}$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
$\sigma_{2s}^*$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
$\sigma_{2s}$	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$

The anion, with three antibonding  $\pi$  electrons, has the weakest and longest bond. The cation, with only one antibonding  $\pi$  electron, has the strongest and shortest. All three species are paramagnetic:

	CONFIGURATION	BOND ORDER	UNPAIRED ELECTRONS	COMMENT
$O_2^-$	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p_z})^2(\pi_{2p})^4(\pi_{2p}^*)^3$	$\frac{3}{2}$	1	longest/weakest
$O_2$	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p_z})^2(\pi_{2p})^4(\pi_{2p}^*)^2$	2	2	intermediate
$O_2^+$	$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p_z})^2(\pi_{2p})^4(\pi_{2p}^*)^1$	$\frac{5}{2}$	1	shortest/strongest

22. Verify (for  $Z < 8$ ) that molecular orbitals are filled in the order

$$\sigma_{2s} < \sigma_{2s}^* < \pi_{2p} < \sigma_{2p_z} < \pi_{2p}^* < \sigma_{2p_z}^*$$

and then simply count the valence electrons.

Of the three structures considered,  $N_2$  (with bond order = 3) exhibits the highest dissociation energy and the shortest bond.  $Be_2$  (bond order = 0) has the weakest and longest bond.  $Li_2$  (bond order = 1) is intermediate. See the detailed explanation in the succeeding paragraphs.

(a) The valence configuration  $(\sigma_{2s})^2 (\sigma_{2s}^*)^2$  corresponds to  $\text{Be}_2$ , which contains four electrons outside the  $1s$  core orbitals. Each beryllium atom ( $Z = 4$ ) contributes two electrons to the valence and two to the core (not shown):



With two bonding electrons canceled by two antibonding electrons, the bond order is 0:

$$\begin{aligned} \text{Bond order} &= \frac{1}{2}(\text{no. bonding electrons} - \text{no. antibonding electrons}) \\ &= \frac{1}{2}(2 - 2) \\ &= 0 \end{aligned}$$

All the electrons are paired.  $\text{Be}_2$  is diamagnetic, not paramagnetic.

The molecule, although very weakly bound, has been observed experimentally. Its bond energy is less than  $10 \text{ kJ mol}^{-1}$ . See *PoC*, page 229.

(b) The configuration  $(\sigma_{2s})^2$  matches  $\text{Li}_2$ , with six electrons overall and two in the valence orbitals. Each lithium atom ( $Z = 3$ ) supplies one of the valence electrons:

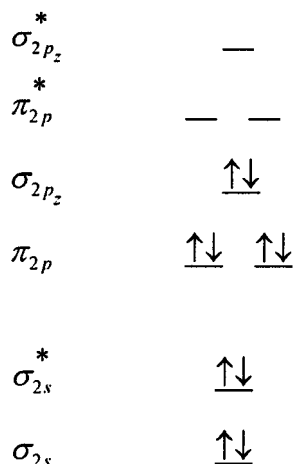


The bonding pair, unopposed by any antibonding electrons, produces a bond order of 1

$$\begin{aligned} \text{Bond order} &= \frac{1}{2}(\text{no. bonding electrons} - \text{no. antibonding electrons}) \\ &= \frac{1}{2}(2 - 0) \\ &= 1 \end{aligned}$$

The molecule is diamagnetic. There are no unpaired electrons,

(c) A nitrogen atom ( $Z = 7$ ) contains two electrons in its core  $1s$  orbital and five in its valence shell. The diatomic molecule  $\text{N}_2$  thus has 10 valence electrons to distribute:



With a net of six bonding electrons, the nitrogen molecule displays a bond order of 3—a triple bond:

$$\begin{aligned}
 \text{Bond order} &= \frac{1}{2}(\text{no. bonding electrons} - \text{no. antibonding electrons}) \\
 &= \frac{1}{2}(8 - 2) \\
 &= 3
 \end{aligned}$$

No electrons remain unpaired. The molecule is not paramagnetic.

*At issue in Exercises 23 through 26 is the arbitrariness inherent in distinctions between “ionic bonds” and “covalent bonds.” Throughout, the electronegativity scale (Figure 7-18 in PoC) serves as a useful-if empirical-predictor of bond polarity*

*For demonstration problems, see Examples 7-3 and 7-4 (beginning on page R7.7).*

23. An atom high on the electronegativity scale tends to attract a disproportionate share of negative charge. Strongly electronegative species lie toward the right-hand side and top of the periodic table.

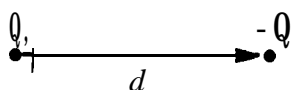
(a) Consult Figure 7-18 in *PoC* (page 244) to establish the trend in polarity. The greater the difference in electronegativity, the more polar is the bond:

AB	$EN_A$	$EN_B$	$EN_B - EN_A$	BOND POLARITY
NO	3.0	3.5	0.5	$N^{\delta+}O^{\delta-}$ (lowest)
PN	2.1	3.0	0.9	$P^{\delta+}N^{\delta-}$ (intermediate)
BeN	1.5	3.0	1.5	$Be^{\delta+}N^{\delta-}$ (highest)

(b) Bond polarities are  $\text{Be}^{\delta+}\text{N}^{\delta-}\text{P}$ ,  $\text{N}^{\delta-}$ , and  $\text{N}^{\delta+}\text{O}^{\delta-}$ , as indicated above. Note that nitrogen gives electrons to oxygen, a highly electronegative atom, but takes electrons from both beryllium and phosphorus.

The bond of highest polarity is between a metal (beryllium) and a nonmetal (nitrogen). The least polar bond is between nonmetals with similar electronegativities, nitrogen and oxygen.

24. Imagine the bond to consist of equal but opposite charges separated by a distance  $d$ ,



and further specify  $Q$  as a fraction ( $\delta$ ) of one full electronic charge ( $e = 1.602 \times 10^{-19} \text{ C}$ ):

$$Q = \delta e$$

The magnitude of the dipole moment is then

$$\mu = Qd = \delta ed$$

with the assumed fractional point charge,  $\delta$ , given as follows:

$$\delta = \frac{\mu}{ed}$$

Beginning with HF, for example,

$$d = 0.917 \text{ \AA} = 9.17 \times 10^{-11} \text{ m}$$

$$\mu = 1.826 \text{ D}$$

$$1 \text{ D} = 3.336 \times 10^{-30} \text{ C m}$$

we obtain a value of 0.415 for  $\delta$ —effectively the fractional ionic character in our simple model of the bond:

$$\delta = \frac{\mu}{ed} = \frac{1.826 \text{ D}}{(1.602 \times 10^{-19} \text{ C})(9.17 \times 10^{-11} \text{ m})} \times \frac{3.336 \times 10^{-30} \text{ C m}}{\text{D}} = 0.415$$

Values for all four molecules are tabulated in (a). See Example R7.4 in *PoC* (page R7.8).

(a) Note how the “covalent” bonds contain varying amounts of ionic character. The effect is especially pronounced in HF, where the fluorine atom is both small and highly electronegative:

	DIPOLE MOMENT (D)	BOND LENGTH (Å)	$\delta$
HF	1.826	0.917	0.415
HCl	1.109	1.275	0.181
HBr	0.827	1.415	0.122
HI	0.448	1.609	0.0580

(b) All four halogens (X = F, Cl, Br, HI) are more electronegative than hydrogen and thus bear the partial negative charge. The hydrogen is partially positive in each molecule:



25. Use the same method as in the preceding exercise.

(a) Even nominally ionic compounds like alkali bromides may contain sizable amounts of *covalent* character-between 20% and 30% in LiBr, NaBr, and KBr:

	DIPOLE MOMENT (D)	BOND LENGTH (Å)	$\delta$
I <sub>2</sub>	0.726	2.469	0.0612
BrO	1.76	1.717	0.213
TlBr	4.49	2.618	0.357
LiBr	7.268	2.170	0.6975
NaBr	9.118	2.502	0.7589
KBr	10.628	2.821	0.7845

(b) Consult Figure 7-1 8 on page 244 of *PoC* to establish the electronegativities. Bromine (more electronegative than I, Tl, Li, Na, and IS) is partially negative in all of these compounds except for BrO.

26. Similar.

(a) Hydrogen, usually +1, takes a -1 oxidation state in combination with an alkali metal:

	DIPOLE MOMENT (D)	BOND LENGTH (Å)	$\delta$
HI	0.448	1.609	0.0580
NH	1.39	1.036	0.279
LiH	5.884	1.595	0.7682



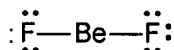
(b) Hydrogen is less electronegative than both iodine and nitrogen, but more electronegative than lithium (a metal). H is partially negative in LiH, lithium hydride.

*With all of our models in hand-Lewis, VSEPR, molecular quantum mechanics, localized valence bond and hybrid orbitals, resonance, delocalized molecular orbitals-we conclude by surveying a number of polyatomic systems,*

*Relevant material will be found in Sections 7-3 through 7-5 of PoC, as well as in Example 7-5 ( $sp^3$  hybridization), Example 7-6 ( $sp^2$  hybridization), Example 7-7 ( $d^2sp^3$  and  $dsp^3$  hybridization), and Example 7-8 (delocalization).*

27. The VSEPR model is treated in Chapter 2. See pages 62-66 of *PoC* and also Examples 2-4 and 2-5 (beginning on page R2.8).

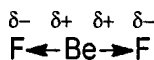
(a) Beryllium contributes two valence electrons, and each fluorine contributes seven to make a total of 16 valence electrons in  $\text{BeF}_2$ . Note that Be remains octet-deficient in the Lewis structure:



Since only two electron pairs surround the central atom, VSEPR theory predicts a linear structure to minimize electrostatic repulsion. The prediction is consistent with the experimental evidence.

(b) Beryllium, an alkaline earth metal, is considerably less electronegative than fluorine (the most electronegative element of all). Each of the two bonds is polarized as  $\text{Be}^{\delta+}-\text{F}^{\delta-}$ .

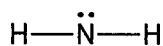
(c) The molecule has no dipole moment overall, because the two  $\text{Be}^{\delta+}-\text{F}^{\delta-}$  bond dipole moments are diametrically opposed in the linear molecule:



28. The linear structure of  $\text{BeF}_2$  is consistent with  $sp$  hybridization around the beryllium atom.

Each of the two  $sp$  orbitals on Be contains a single electron. Overlap of one such orbital with a singly occupied  $sp^3$  orbital on fluorine then produces a Be-F bond-one on the left and one on the right. Two unhybridized  $p$  orbitals stay vacant on beryllium.

29. Eight valence electrons (five from nitrogen, one each from three hydrogens) are distributed in the Lewis structure of ammonia:



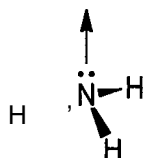
H

(a) With four electron pairs around the central nitrogen atom, VSEPR theory predicts a tetrahedral arrangement for the electrons and a trigonal pyramidal arrangement for the atoms. One hydrogen sits at each of three vertices of the tetrahedron, thereby forming a trigonal pyramid capped by nitrogen. A lone pair occupies the fourth vertex of the electronic tetrahedron.

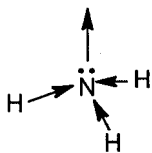
The prediction is consistent with the observed geometry.

(b) Nitrogen ( $EN = 3.0$ ) is more electronegative than hydrogen ( $EN = 2.1$ ). Each nitrogen-hydrogen bond is polarized as  $N^{\delta-}-H^{\delta+}$ .

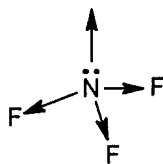
(c) A net dipole moment persists in the molecule, directed along the central axis of the pyramid. Nitrogen is negative, and the hydrogens are positive:



30. In  $NH_3$ , the N-H bond dipoles all point toward the nitrogen-which is partially negative and has, moreover, a lone pair to furnish additional electron density to the site:



In  $NF_3$ , by contrast, the bonds are polarized in the opposite direction—from partially positive  $N^{\delta+}$  to partially negative  $F^{\delta-}$ . The combined nitrogen-to-fluorine dipole moment that results, coming from the three bonding pairs, is largely counterbalanced by the lone pair on nitrogen:

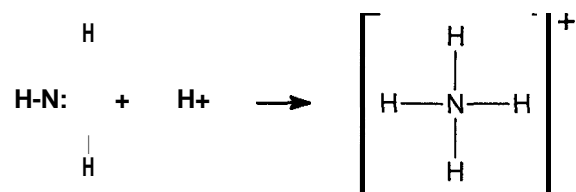


Directed opposite to the bonding-pair contribution, the lone-pair contribution shrinks the net dipole moment to only 0.2 D.

Incidentally, the large electronegativity of fluorine is subordinate here to the *direction* of bond polarity in  $NF_3$  compared with  $NH_3$ . The difference in electronegativity between N ( $EN = 3.0$ ) and F ( $EN = 4.0$ ) is, after all, only slighter greater than the difference between N ( $EN = 3.0$ ) and H ( $EN = 2.1$ ). What matters is the relative orientation of the bonding-pair and lone-pair contributions to the dipole moment. In  $NH_3$ , they point in the same direction. In  $NF_3$ , they point in opposite directions.

31. The nearly tetrahedral bond angles in  $\text{NH}_3$  are consistent with  $sp^3$  hybridization around the nitrogen. Three  $sp^3$  orbitals on N overlap, in turn, with the  $1s$  orbitals on each of three H atoms to form three N-H  $\sigma$  bonds. A lone pair resides in the fourth  $sp^3$  hybrid orbital on nitrogen.

32. The ammonium ion is formed by attachment of  $\text{H}^+$  to  $\text{NH}_3$ :

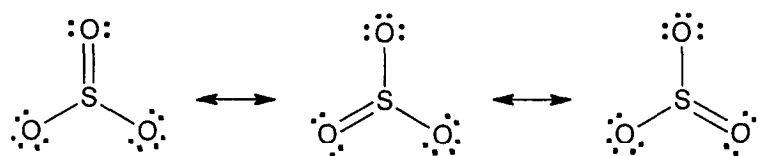


(a) There are eight valence electrons, just as in  $\text{NH}_3$ , but now each of the four pairs is a *bonding* pair. VSEPR predicts tetrahedral geometry for the atoms and electron pairs alike.

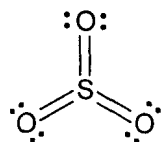
(b) A valence bond approach, based on  $sp^3$  hybridization of the nitrogen atom in ammonia, also predicts tetrahedral geometry. The lone pair in the fourth  $sp^3$  orbital of  $:\text{NH}_3$  provides a basic site for attack by  $\text{H}^+$  to produce  $\text{NH}_4^+$ .

There are four  $\sigma$  bonds in the ion, each coming from the overlap of an  $sp^3$  orbital on nitrogen with a  $1s$  orbital on hydrogen. No lone pairs remain.

33. A total of 24 valence electrons (six from sulfur, six from each of three oxygens) must be distributed throughout the molecule  $\text{SO}_3$ . Three equivalent resonance forms, each containing one double bond and two single bonds, will provide octets for all four atoms:



An alternative Lewis structure,



allows sulfur to expand beyond an octet and also leaves the four atoms with zero formal charges.

(a) In either choice of Lewis structure, only three atoms are bonded to the central sulfur site—with no lone pairs. The VSEPR model therefore predicts, correctly, a trigonal planar geometry for both the electron pairs and the atoms.

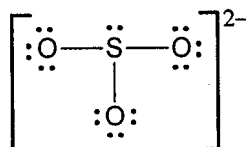
The sulfur-oxygen distances are all equal, too. If sulfur is deemed to have an octet, then each of the three equivalent resonance forms (see above) contributes equally to the molecule. If sulfur is surrounded instead by 12 electrons, then the three double bonds are symmetric and equal as well.

(b) Each sulfur-oxygen bond is polarized as  $S^{\delta+}-O^{\delta-}$ . Oxygen ( $EN = 3.5$ ) is more electronegative than sulfur ( $EN = 2.5$ ).

(c) No net dipole moment emerges from the trigonal planar structure. Spaced at  $120^\circ$ , the three bond dipole moments cancel out.

34. The trigonal planar structure of  $SO_3$  is consistent with  $sp^2$  hybridization around the sulfur. Each  $sp^2$  orbital forms a sigma bond with one of the oxygens, leaving an unhybridized  $p$  orbital perpendicular to the atomic plane and available for pi bonding.

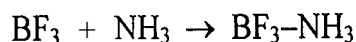
35. The sulfite ion,  $SO_3^{2-}$ , contains 26 valence electrons (two more than  $SO_3$ ):



(a) Here there are electrons coming off sulfur in four directions, compared with only three in  $SO_3$  (as determined in Exercise 33). VSEPR predicts a tetrahedral geometry for the electron pairs and a trigonal pyramidal geometry for the atoms. The structure is similar to  $NH_3$ .

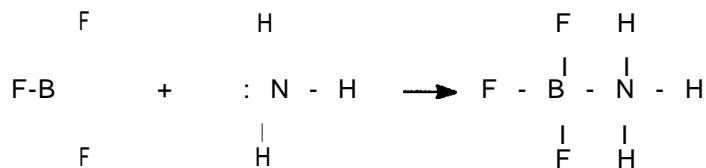
(b) The tetrahedral arrangement of four electron pairs demands  $sp^3$  hybridization around the sulfur atom. Each oxygen atom, surrounded by three lone pairs and one bonding pair, is presumably  $sp^3$  as well. Single bonds between sulfur and oxygen are formed by  $sp^3-sp^3$  overlap, and a nonbonding pair of electrons occupies the fourth  $sp^3$  hybrid orbital on sulfur.

36. The reaction between boron trifluoride and ammonia,



is described on pages 63-65 and page 80 of *POC*. See also Example 7-6 (beginning on page R7.10) for a valence bond description of  $BF_3$ .

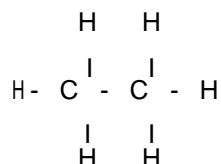
For simplicity, we suppress the lone pairs on fluorine and write the process as follows:



Thus we see that boron and nitrogen are each surrounded by four bonding pairs in the product, with no lone pairs. The geometry is tetrahedral all around, and the hybridization is  $sp^3$ . All of the bonds are single bonds.

The boron atom, with four bonding pairs, bears a formal charge of -1. The nitrogen atom, also surrounded by four bonding pairs, has a formal charge of +1.

37. Ethane contains 14 valence electrons, and each carbon is surrounded by four bonding pairs:



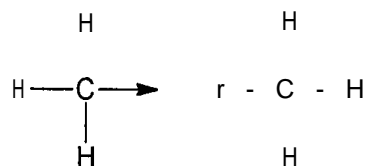
There are no lone pairs.

(a) The geometry is tetrahedral, and the hybridization is  $sp^3$ . The hydrogen atoms, as usual, contribute one electron apiece from their  $1s$  atomic orbitals. All of the bonds are single bonds.

(b) The carbon-hydrogen bonds are polarized as  $\text{C}^{\delta-}-\text{H}^{\delta+}$ . Carbon (EN = 2.5) is slightly more electronegative than hydrogen (EN = 2.1).

The carbon-carbon bond is nonpolar, of course, because the two atoms are identical.

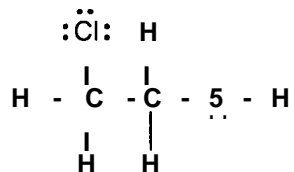
(c) Individually, each of the two methyl fragments ( $\text{CH}_3$ ) forms a trigonal pyramid and displays a dipole moment along its axis (as in the two-dimensional projection below):



These opposing moments, however, are equal in magnitude and thus cancel along the C-C bond axis. The molecule as a whole is nonpolar. It has no net dipole moment.

38. The molecule  $\text{CH}_2\text{ClCH}_2\text{OH}$  is a derivative of ethane,  $\text{CH}_3\text{CH}_3$ .

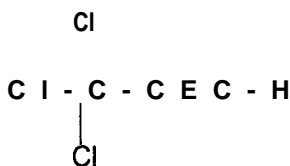
(a) Cl replaces H on one carbon of ethane, and OH replaces H on the other:



(b) Both the oxygen atom and the two carbon atoms are surrounded by four electron pairs each, consistent with a tetrahedral  $sp^3$  system. The chlorine, with three lone pairs and one bonding pair, is also hybridized as  $sp^3$ . All of the bonds are single bonds.

(c) Oxygen (EN = 3.5) and chlorine (EN = 3.0) are both more electronegative than carbon (EN = 2.5). The polar  $\text{C}^{\delta+}-\text{Cl}^{\delta-}$  and  $\text{O}^{\delta-}-\text{H}^{\delta+}$  bonds, incompletely canceled in the structure, leave the molecule with a net dipole moment.

39. The Lewis structure for  $\text{CCl}_3\text{CCH}$  is shown below:



There are three C-Cl single bonds, one C-C single bond, one  $\text{C}\equiv\text{C}$  triple bond, and one C-H single bond. For simplicity, the three lone pairs on each chlorine atom are omitted from the diagram. Altogether, there are 34 valence electrons.

The triple-bonded carbons are hybridized as  $sp$ , consistent with  $180^\circ$  bond angles throughout the  $-\text{C}\equiv\text{C}-$  segment. Since each of these two carbon atoms has only two attached groups and no lone pairs, the VSEPR model predicts that electron-electron repulsion will be minimized in a linear structure. Within the  $-\text{C}\equiv\text{C}-$  group itself, there is a carbon-carbon  $\sigma$  bond ( $sp-sp$ ) and two  $\pi$  bonds ( $p-p$ ). H ( $1s$ ) is joined to  $-\text{C}\equiv\text{C}-$  on one end by a single  $\sigma$  bond ( $sp-1s$ ).

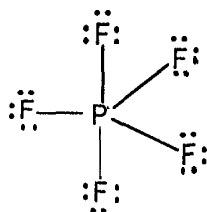
The third carbon is hybridized as  $sp^3$  in the group  $-\text{CCl}_3$ , corresponding to a tetrahedral arrangement of its four bonding pairs. A single  $\sigma$  bond ( $sp^3-sp$ ) connects the chlorinated methyl group with the remaining  $sp$  orbital in the  $-\text{C}\equiv\text{C}-$  unit.

Each of the three attached chlorine atoms, bringing with it seven valence electrons, is also hybridized as  $sp^3$  and thus forms a single  $\sigma$  bond ( $sp^3-sp^3$ ) with the carbon. According to VSEPR theory, three lone pairs and one bonding pair are configured tetrahedrally about each chlorine.

Note that  $\text{Cl}_3\text{C}-\text{C}\equiv\text{C}-\text{H}$  is a derivative of acetylene,  $\text{H}-\text{C}\equiv\text{C}-\text{H}$ , described on pages 252-253 of *PoC*.

40. See Example 7-7 in *PoC* (beginning on page R7.12) for a treatment of  $\text{PCl}_5$ , a direct analog of  $\text{PF}_5$ .

(a) Phosphorus contributes five electrons, and each of the five fluorine atoms contributes seven for a total of 40 valence electrons in  $\text{PF}_5$ :



There are five pairs of electrons around phosphorus, consistent with a trigonal bipyramidal geometry for both atoms and electrons.

(b) Neither  $sp$  hybridization ( $180^\circ$  bond angles) nor  $sp^2$  hybridization ( $120^\circ$  bond angles) nor  $sp^3$  hybridization ( $109.5^\circ$  bond angles) can account for the trigonal bipyramidal structure. *Five* orbitals—not two, not three, not four—must be present to hold the five bonding pairs of electrons.

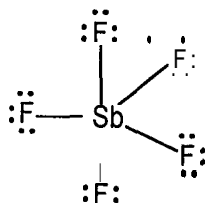
(c) The shape of the molecule calls for  $sp^3d$  hybridization: one  $3s$  orbital, three  $3p$  orbitals, and one  $3d$  orbital combined into five  $sp^3d$  hybrids. Each  $sp^3d$  function points to one of the vertices of a trigonal bipyramid.

41. Nitrogen, a second-row element, lacks the  $d$  orbitals it would need to support  $sp^3d$  hybridization. The nearest source of “ $d$  character” (the  $3d$  subshell) lies too high above the  $2s$  and  $2p$  orbitals of the valence shell. Orbitals mix best when their energies are similar.

42. Yes, both arsenic and antimony can form **pentafluoride** compounds. Like phosphorus, each of these two atoms has access to low-lying vacant  $d$  orbitals: in arsenic, the  $4d$  subshell; in antimony, the  $5d$ . Combined into  $sp^3d$  hybrids, these  $d$  orbitals allow As and Sb to expand beyond an octet and bond to five groups.

43.  $\text{SbF}_5$  is isoelectronic with  $\text{PF}_5$  (Exercise 40) and  $\text{PCl}_5$  (Example 7-7 in *PoC*).

(a) The Lewis structure contains 40 valence electrons:



Each fluorine atom has three lone pairs and forms one bond to antimony. Antimony, with five bonded fluorine atoms and no lone pairs, adopts a trigonal bipyramidal configuration according to VSEPR theory.

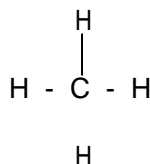
A valence bond approach requires construction of five  $sp^3d$  hybrid orbitals (also called  $dsp^3$ ). See part (b), immediately below.

(b) Hybridized as  $sp^3d$ , the antimony atom supports five fluorine atoms in a trigonal bipyramidal arrangement. The orbital mixture consists of one  $5s$  function, three  $5p$  functions, and one  $5d$  function drawn from the valence shell of the fifth-row element. Remember, it is the closed  $4d$  subshell in antimony—not the  $5d$ —that becomes part of the core. The  $5d$  orbitals remain open and available for bonding.

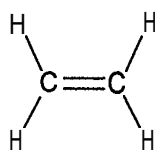
Each fluorine atom, contributing seven valence electrons, is hybridized as  $sp^3$ . Three of the  $sp^3$  orbitals contain lone pairs, and the remaining  $sp^3$  orbital furnishes one electron for bonding with antimony. With five valence electrons, the Sb atom then forms  $\sigma$  bonds with each of the five F atoms in turn.

44. The existence of symmetric resonance forms is often a symptom of delocalization.

(a) Methane is described satisfactorily by just one Lewis structure:

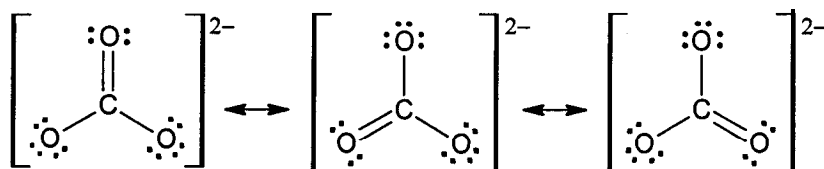


So is ethylene:



But not the carbonate ion. Three equivalent forms are needed to account for the bonding in  $\text{CO}_3^{2-}$ . These resonance structures (see below, part b) are demanded by the symmetry of the ion—a sign that a molecular orbital treatment is perhaps appropriate.

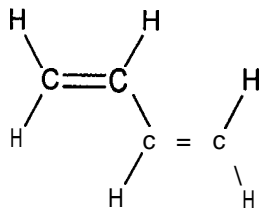
(b) Each resonance form contains 24 valence electrons:





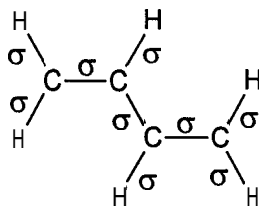
45. The following treatment of delocalization in 1,3-butadiene, a conjugated molecule, is only slightly more elaborate than the discussion of allylic systems in Example 7-8.

(a) Start with the Lewis structure,



and note that each carbon is bonded to three other atoms. From there, assume that the hybridization is  $sp^2$  and the angles are  $120^\circ$ . One unhybridized  $p$  orbital juts up from each carbon perpendicular to the plane of the nuclei.

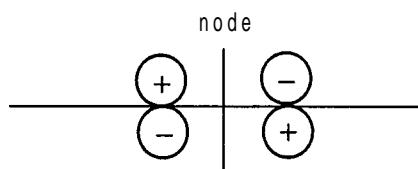
Thus of the 22 valence electrons, fully 18 are taken up by the  $sp^2$  framework of sigma bonds,



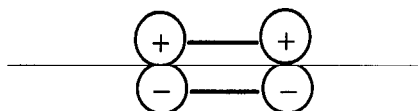
while the remaining four electrons are shunted into the pi system. Four unhybridized  $p$  orbitals, in various combinations, will form four  $\pi$  orbitals.

(b) Recall that one-dimensional standing waves are quantized according to the patterns shown in Figure 5-1 of *POC* (page 149). The fundamental mode,  $n = 1$ , contains zero nodes. The second harmonic,  $n = 2$ , contains one node. The third harmonic, two. The fourth harmonic, three. Energy increases with the number of nodes.

(c) These same nodal patterns, observe, are also generated when the four orbitals are mixed as shown in Figure 7.1. Electron density vanishes at any of the  $n - 1$  nodes,



since here the lobes combine with opposite phases (+ to - and - to +). Density increases, however, between any pair of orbitals with matching phases (+ to + and - to -):



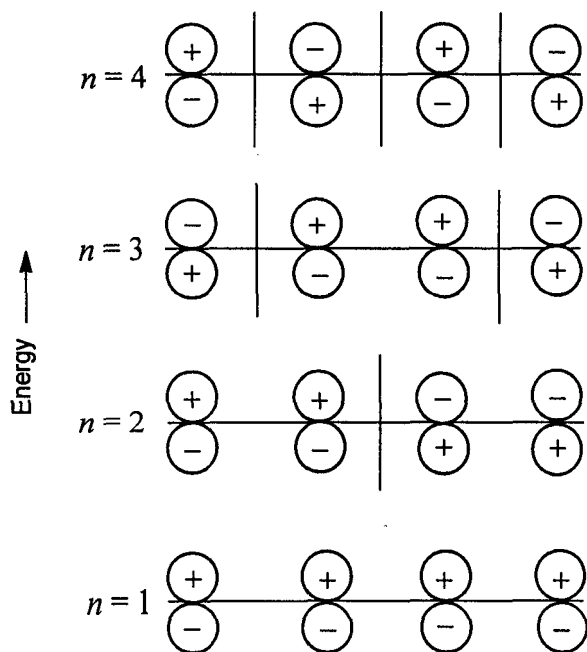
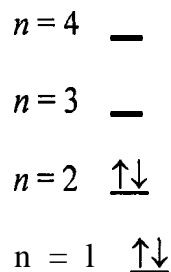
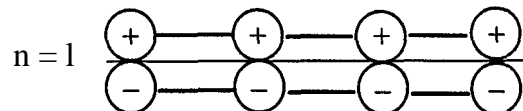


FIGURE 7.1 Linear combinations of four **atomic**  $p$  orbitals into four molecular orbitals, analogous to the four lowest standing waves on a string. Nodal planes are indicated by vertical lines.

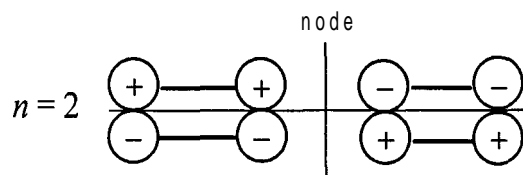
(d) The four  $\pi$  electrons occupy the lowest two orbitals:



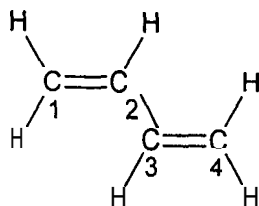
(e) Now look specifically at the wave function for each of these two occupied orbitals. The lowest level shows matching phases and enhanced bonding density throughout,



whereas the second orbital concentrates electrons only between the pairs of carbons at either end:



A perpendicular nodal plane in the  $n = 2$  function cuts through the midpoint of the molecule, and the effect is to produce more bonding density overall in the outlying segments,  $C_1-C_2$  and  $C_3-C_4$ . Bonding is weakest between  $C_2$  and  $C_3$ :



The stronger bonds are predicted to be shorter bonds as well, in accord with the experimentally observed structure.