corners of a trigonal bipyramid (as in  $PF_5$ ). The three lone pairs will be in the equatorial plane, to minimize lone pair-lone pair repulsions. The resulting shape of the molecule, shown at the right, is linear (i.e., the F-Xe-F bond angle is 180°).



- **S2.8** Electron configurations for  $S_2^{2^-}$  and  $Cl_2^{-2}$ . The first of these two anions has the same Lewis structure as peroxide,  $O_2^{2^-}$ . It also has a similar electron configuration to that of peroxide, except for the use of sulfur atom valence 3s and 3p atomic orbitals instead of oxygen atom 2s and 2p orbitals. There is no need to use sulfur atom 3d atomic orbitals, which are higher in energy than the 3s and 3p orbitals, since the 2(6) + 2 = 14 valence electrons of  $S_2^{2^-}$  will not completely fill the stack of molecular orbitals constructed from sulfur atom 3s and 3p atomic orbitals. Thus, the electron configuration of  $S_2^{2^-}$  is  $1\sigma_g^{-2}2\sigma_u^{-3}3\sigma_g^{-1}\pi_u^{-4}2\pi_g^{-4}$ . The  $Cl_2^{-}$  anion contains one more electron than  $S_2^{2^-}$ , so its electron configuration is  $1\sigma_g^{-2}2\sigma_u^{-3}3\sigma_g^{-1}\pi_u^{-4}2\pi_g^{-4}4\sigma_u^{-1}$ .
- **S2.9** Molecular orbitals of CIO<sup>-</sup>? Study Section 2.9, *Heteronuclear diatomic molecules*, again. After that, you should conclude that the bonding molecular orbitals of CIO<sup>-</sup> are predominantly oxygen in character, since oxygen is more electronegative than chlorine. Similarly, the antibonding molecular orbitals are predominantly chlorine in character. A chlorine atom uses its 3s and 3p valence-shell orbitals for bonding. An oxygen atom uses its 2s and 2p orbitals. The MO diagram for CIO<sup>-</sup> will look very similar to Figure 2.24 except that Cl, with its 3s and 3p orbitals, will replace iodine on the left-hand side of the figure and O, with its 2s and 2p orbitals, will replace chlorine on the right-hand side of the figure.
- S2.10 Predict the order of bond strength and bond length for C-N, C=N, and C=N? In general, the more bonds you have between two atoms, the shorter the bond length and the stronger the bond. Therefore, the ordering for bond length going from shortest to longest is C=N, C=N, and C-N. For bond strength, going from strongest to weakest, the order is C=N > C=N.
- **S2.11** Is any XH<sub>2</sub> molecule linear? According to Figure 2.35, a XH<sub>2</sub> molecule is expected to be linear if it contains four or fewer electrons. This is because the bottom two orbitals, which can contain up to four electrons, are lowest in energy when the H-X-H bond angle is 180°. Based on this analysis, both NaH<sub>2</sub> and MgH<sub>2</sub> should be linear, because they contain three and four valence electrons, respectively. The molecule A1H<sub>2</sub> contains five electrons and so is not expected to be linear.
- 2.1 Lewis structures and VSEPR theory? (a) GeCl<sub>3</sub>? The Lewis structure is shown below. Only one resonance structure is important (each atom has an octet).



(b)  $FCO_2$ ? The Lewis structure is shown above, with two resonance contributors to account for the equivalence of the two C-O bonds. Each atom has an octet.

(c)  $CO_3^{2-2}$ ? Three resonance structures are necessary to account for the fact that the three C–O bonds in the carbonate anion are equivalent, and these are shown below. Each atom has an octet in all three resonance structures.







(e) FNO? The least electronegative atom is likely to be the central atom. The Lewis structure of this molecule is shown above, requiring only one resonance structure to achieve an octet around all three atoms.

Lewis structures and formal charges? (a) ONC? With one O atom, one N atom, one C atom, and a -1 charge, the ONC anion has 16 valence electrons. You can arrange them in two resonance forms as follows:



The nonzero formal charges for the atoms are given. These were calculated using the formula in Section 2.1(b), *Formal charges*. The number of lone pair electrons (not the number of lone pairs) and half the number of shared electrons are subtracted from the number of valence electrons on the parent atom. The resonance structure on the left is likely to be the dominant one, since it contains smaller formal charges. In addition, the resonance structure on the right is probably not very important because it puts a high *negative* formal charge on the least electronegative atom.

(b) NCO<sup>-</sup>? This ion also has 16 electrons, and the two most important resonance structures are shown below. The nonzero formal charges are given. The resonance structure on the left is likely to be the dominant one, since it puts the negative formal charge on O, the most electronegative atom.

$$:N \equiv C - \ddot{O}: \overrightarrow{\phantom{0}} \longrightarrow \qquad \ddot{N} \equiv C = \ddot{O}^{-1}$$



2.2

Formal charges and oxidation numbers of  $NO_2^-$ ? The resonance structures, nonzero formal charges, and oxidation numbers for nitrite ion are shown below:



The two structures shown are similar in that they both contain a N–O single bond and a N=O double bond. Therefore, they each contribute equally. The nitrogen atom in nitrite ion can be oxidized or reduced, since it is in the +3 oxidation state and since nitrogen can have oxidation numbers that range from -3 to +5. Both the oxidation number (+3) and the formal charge of zero on the nitrogen atom fail to give an accurate picture of its actual charge, which is slightly negative (that is, the negative charge is shared by all three atoms).

2.4

2.5

More Lewis structures? (a)  $XeF_4$ ? There is a straightforward way to draw Lewis structures with a central atom and some number of atoms. In this case, start with the Lewis structure of a xenon atom. Then consider how many fluorine atoms there are in the molecule, and use one of xenon's electrons for each Xe–F bond. The complete Lewis structure of XeF<sub>4</sub> is shown below.



(b) **PF**<sub>5</sub>? The Lewis structure, above, shows that the central P atom is surrounded by five bonding electron pairs.

(c)  $BrF_3$ ? The Lewis structure for this molecule is also shown above. Like the P atom in  $PF_5$ , the Br atom in  $BrF_3$  is surrounded by five electron pairs, three bonding pairs, and two lone pairs.

(d) TeCl<sub>4</sub>? The Lewis structure for this molecule is shown below.



(e) ICI2? The Lewis structure is shown above. The central I atom has five electron pairs.

What shape would you expect for (a)  $H_2S$ ? The Lewis structure for hydrogen sulfide is shown below. The shape would be expected to be bent with the H–S–H angle less than 109°. However, the angle is actually close to 90°, indictative of considerable *p* character in the bonding between S and H.

(b) BF<sub>4</sub>? The Lewis structure is shown below. The shape is tetrahedral with all angles 109.5°.

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(c)  $NH_4^+$ ? The Lewis structure of the ammonium ion is shown below. Again, the shape is tetrahedral with all angles 109.5°.



2.6

What shape would you expect for (a) SO<sub>3</sub>? The Lewis structure of sulfur trioxide is shown below. With three  $\sigma$  bonds and no lone pairs, you should expect a trigonal-planar geometry (like BF<sub>3</sub>). The shape of SO<sub>3</sub> is also shown below.

(b)  $SO_3^{2-2}$  The Lewis structure of sulfite ion is shown below. With three  $\sigma$  bonds and one lone pair, you should expect a trigonal-pyramidal geometry such as NH<sub>3</sub>. The shape of  $SO_3^{2-}$  is also shown below.

(c) IF<sub>5</sub>? The Lewis structure of iodine pentafluoride is shown below. With five  $\sigma$  bonds and one lone pair, you should expect a square-pyramidal geometry. The shape of IF<sub>5</sub> is also shown below.



2.7 The shapes of ClF<sub>3</sub>, ICl<sub>4</sub>, and I<sub>3</sub>? (a) The Lewis structure of ClF<sub>3</sub> is shown below. The chlorine atom in ClF<sub>3</sub> is bonded to the three fluorine atoms through sigma bonds and has two nonbonding electron lone pairs. Both lone pairs occupy equatorial positions (the largest angles in a trigonal bipyramid), resulting in a T shape for the molecule.



(b) The Lewis structure for ICl<sub>4</sub><sup>-</sup> is shown below. The iodide atom is bonded to the four chlorine atoms through sigma bonds and has two sets of lone pairs. The lone pairs are opposite each other, occupying the axial sites of an octahedron. The overall shape of the molecule is square planar.



(c) The Lewis structure for  $I_3^-$  is shown below. The iodide atom is bonded to two other iodide atoms through sigma bonds and has three sets of lone pairs. The lone pairs occupy the equatorial sites of a trigonal bipyramid. The overall shape of the molecule is linear.



2.8 The shapes of PCl<sub>4</sub><sup>+</sup> and PCl<sub>6</sub><sup>-</sup>? The Lewis structures of these two ions are shown below. With four  $\sigma$  bonds and no lone pairs for PCl<sub>4</sub><sup>+</sup>, and six  $\sigma$  bonds and no lone pairs for PCl<sub>6</sub><sup>-</sup>, the expected shapes are tetrahedral (like CCl<sub>4</sub>) and octahedral (like SF<sub>6</sub>), respectively. In the tetrahedral PCl<sub>4</sub><sup>+</sup> ion, all P–Cl bonds are the same length and all Cl–P–Cl bond angles are 109.5°. In the octahedral PCl<sub>6</sub><sup>-</sup> ion, all P–Cl bonds are the same length and all Cl–P–Cl bond angles are either 90° or 180°. The P–Cl bond distances in the two ions would not necessarily be the same length.



2.9 Calculate bond lengths. (a) CCl<sub>4</sub> (observed value = 1.77 Å)? From the covalent radii values given in Table 2.4, 0.77 Å for C and 0.99 Å for Cl, the C-Cl bond length in CCl<sub>4</sub> is predicted to be 0.77 Å + 0.99 Å = 1.76 Å. The agreement with the experimentally observed value is excellent.

(b) SiCl<sub>4</sub> (observed value = 2.01 Å)? The covalent radius for Si is 1.18 Å. Therefore, the Si–Cl bond length in SiCl<sub>4</sub> is predicted to be 1.18 Å + 0.99 Å = 2.17 Å. This is 8% longer than the observed bond length, so the agreement is not as good in this case.

(c) GeCl<sub>4</sub> (observed value = 2.10 Å)? The covalent radius for Ge is 1.22 Å. Therefore, the Ge–Cl bond length in GeCl<sub>4</sub> is predicted to be 2.21 Å. This is 5% longer than the observed bond length.

2.10 Si=O or Si-O in silicon-oxygen compounds? You need to consider the enthalpy difference between one mole of Si=O double bonds and two moles of Si-O single bonds. The difference is:

2(Si-O) - (Si=O) = 2(466 kJ) - (640 kJ) = 292 kJ

- 2.14 Place the compounds AB, AD, BD, and AC in order of increasing covalent character? Difference in electronegativities are AB 0.5, AD 2.5, BD 2.0, and AC 1.0. The increasing covalent character is AD < BD < AC < AB.
- 2.15 What type of bonding for BCl<sub>3</sub>, KCl, and BeO? (a) Using the electronegativity values in Table 1.8 and the Ketelaar triangle in Figure 2.2, the  $\Delta \chi$  for BCl<sub>3</sub> = 3.16 2.04 = 1.12 and  $\chi_{mean}$  = 2.60. This value places BCl<sub>3</sub> in the covalent region of the triangle.

(b)  $\Delta \chi$  for KCl = 3.16 - 0.82 = 2.34 and  $\chi_{mean} = 1.99$ . This value places KCl in the ionic region of the triangle.

(c)  $\Delta \chi$  for BeO = 3.44 - 1.57 = 1.87 and  $\chi_{mean} = 2.51$ . This value places BeO in the ionic region of the triangle. prefly close to the correlation

2.16 How many unpaired electrons? (a)  $O_2^{-?}$  You must write the electron configurations for each species, using Figure 2.14, and then apply the Pauli exclusion principle to determine the situation for incompletely filled degenerate orbitals. In this case the electron configuration is  $1\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 2\pi_g^3$ . With three electrons in the pair of  $2\pi_g$  molecular orbitals, one electron must be unpaired. Thus, the superoxide anion has a single unpaired electron.

(b)  $O_2^+$ ? The configuration is  $1\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 2\pi_g^1$ , so the oxygenyl cation also has a single unpaired electron.

(c) BN? You can assume that the energy of the  $3\sigma_g$  molecular orbital is *higher* than the energy of the  $1\pi_u$  orbitals, since that is the case for CO (see Figure 2.22). Therefore, the configuration is  $1\sigma_g^{2}2\sigma_u^{2}1\pi_u^{4}$ , and, as observed, this diatomic molecule has no unpaired electrons. If the configuration were  $1\sigma_g^{2}2\sigma_u^{2}3\sigma_g^{2}1\pi_u^{2}$ , the molecule would have two unpaired electrons since each of the  $1\pi_u$  orbitals would contain an unpaired electron, in accordance with the Pauli exclusion principle.

(d) NO<sup>-</sup>? The exact ordering of the  $3\sigma_g$  and  $1\pi_u$  energy levels is not clear in this case, but it is not relevant either as far as the number of unpaired electrons is concerned. The configuration is either  $1\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2 2\pi_g^2$  or it is  $1\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 2\pi_g^2$ . In either case, this anion has two unpaired electrons, and these electrons occupy the set of antibonding  $2\pi_g$  molecular orbitals.

2.17 Writing electron configurations using Figure 2.17? (a) Be<sub>2</sub>? Having only four valence electrons for two Be atoms gives the electron configuration  $1\sigma_g^2 2\sigma_u^2$ . The HOMO for Be<sub>2</sub> is a  $\sigma$  antibonding orbital, shown below.







(c)  $C_2$ ? The electron configuration is  $1\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^1$ . The HOMO for  $C_2^+$  is a  $\sigma$  bonding MO formed from mixing two 2p atomic orbitals, shown below.



(d)  $F_2^+$ ? The electron configuration is  $1\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 2\pi_g^3$ . The HOMO for  $F_2^+$  is a  $\pi$  antibonding MO, shown below.



2.18

**Determining bond orders?** The Lewis structures for the three species are shown below:

 $\ddot{\mathbf{s}} = \ddot{\mathbf{s}}:$   $\ddot{\mathbf{c}}_{l} - \ddot{\mathbf{c}}_{l}:$   $\ddot{\mathbf{N}} = \ddot{\mathbf{o}}:$ 

(a) S<sub>2</sub>? The electron configuration of this diatomic molecule is  $1\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 2\pi_g^2$ . The bonding molecular orbitals are  $1\sigma_g$ ,  $1\pi_u$ , and  $3\sigma_g$ , while the antibonding molecular orbitals are  $2\sigma_u$ , and  $2\pi_g$ . Therefore, the bond order is (1/2)((2 + 4 + 2) - (2 + 2)) = 2, which is consistent with the double bond between the S atoms suggested by the Lewis structure.

(b) Cl<sub>2</sub>? The electron configuration is  $1\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 2\pi_g^4$ . The bonding and antibonding orbitals are the same as for S<sub>2</sub>, above. Therefore, the bond order is (1/2)((2+4+2)-(2+4)) = 1, which is in harmony with the single bond between the Cl atoms indicated by the Lewis structure.

(c) NO? The electron configuration of NO<sup>-</sup>,  $1\sigma_{\rm g}^2 2\sigma_{\rm u}^2 1\pi_{\rm u}^4 3\sigma_{\rm g}^2 2\pi_{\rm g}^2$ , is the same as the configuration for S<sub>2</sub>, shown above. Thus, the bond order for NO<sup>-</sup> is 2, as for S<sub>2</sub>, once again in harmony with the conclusion based on the Lewis structure.

Changes in bond order and bond distance? (a)  $O_2 \rightarrow O_2^+ + e^?$  The molecular orbital electron configuration of O<sub>2</sub> is  $1\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 2\pi_g^2$ . The two  $2\pi_g$  orbitals are  $\pi$  antibonding orbitals, so when one of the  $2\pi_{\rm g}$  electrons is removed, the oxygen-oxygen bond order increases from 2 to 2.5. Since the bond in  $O_2^+$ becomes stronger, it should become shorter as well.

(b)  $N_2 + e^- \rightarrow N_2^-$ ? The molecular orbital electron configuration of  $N_2$  is  $1\sigma_p^2 2\sigma_u^2 1\pi_u^4 3\sigma_p^2 2\pi_p^4$ . The next electron must go into the  $4\sigma_u$  orbital, which is  $\sigma$  antibonding (refer to Figures 2.13 and 2.14). This will decrease the nitrogen-nitrogen bond order from 3 to 2.5. Therefore,  $N_2^-$  has a weaker and longer bond than  $N_2$ .

(c) NO  $\rightarrow$  NO<sup>+</sup> + e<sup>-</sup>? The configuration of the NO molecule is either  $1\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2 2\pi_g^4 4\sigma_u^1$  or  $1\sigma_{g}^{2}2\sigma_{u}^{2}3\sigma_{g}^{2}1\pi_{u}^{4}2\pi_{g}^{4}4\sigma_{u}^{1}$ . Removal of the  $4\sigma_{u}$  antibonding electron will increase the bond order from 2.5 to 3. Therefore,  $NO^+$  has a stronger and shorter bond than NO. Notice that  $NO^+$  and  $N_2$  are isoelectronic.

2.20 Linear H4 MOs? Four atomic orbitals can yield four independent linear combinations. The four relevant ones in this case, for a hypothetical linear  $H_4$  molecule, are shown at the right in order of increasing energy. The most stable orbital has the fewest nodes (i.e., the electrons in this orbital are not excluded from the internuclear regions), the next orbital in energy has only one node, and so on to the fourth and highest energy orbital, with three nodes (a node between each of the four H atoms).



Molecular orbitals of linear [HHeH]<sup>2+</sup>? By analogy to linear H<sub>3</sub>, the three atoms of [HHeH]<sup>2+</sup> will form a 2.21 set of three molecular orbitals; one bonding, one nonbonding, and one antibonding. They are shown below.

2.19

The forms of the wavefunctions are also shown, without normalizing coefficients. You should conclude that He is more electronegative than H because the ionization energy of He is nearly twice that of H. Therefore, the bonding MO has a larger coefficient (larger sphere) for He than for H, and the antibonding MO has a larger coefficient for H than for He. The bonding MO is shown at lowest energy, since it has no nodes. The nonbonding and antibonding orbitals follow at higher energies, since they have one and two nodes, respectively. Since  $[HHeH]^{2+}$  has four electrons, only the bonding and nonbonding orbitals are filled. However, the species is probably not stable in isolation because of +/+ repulsions. In solution it would be unstable with respect to proton transfer to another chemical species that can act as a base, such as the solvent or counterion. *Any* substance is more basic than helium.



- 2.22 Average bond order in NH<sub>3</sub>? The molecular orbital energy diagram for ammonia is shown in Figure 2.30. The interpretation given in the text was that the  $2a_1$  molecular orbital is almost nonbonding, so the electron configuration  $1a_1^{-2}1e^42a_1^{-2}$  results in only three bonds ((2 + 4)/2 = 3). Since there are three N-H "links," the average N-H bond order is 1 (3/3 = 1).
- **2.23** Describe the character of the HOMOs and LUMOs of  $SF_6$ ? The molecular orbital energy diagram for sulfur hexafluoride is shown in Figure 2.31. The nonbonding *e* HOMOs are pure F atom symmetry-adapted orbitals, and they do not have any S atom character whatsoever. They could only have S atom character if they were bonding or antibonding orbitals composed of atomic orbitals of both types of atoms in the molecule. On the other hand, the antibonding *t* orbitals have both a sulfur and a fluorine character. Since sulfur is less electronegative than fluorine, its valence orbitals lie at higher energy than the valence orbitals of fluorine (from which the *t* symmetry-adapted combinations were formed). Thus, the *t* bonding orbitals lie closer in energy to the F atom *t* combinations and hence they contain more F character; the *t* antibonding orbitals, the LUMOs, lie closer in energy to the S atom 3*p* orbitals and hence they contain more S character.
- 2.24 Electron precise or electron deficient? (a) Square  $H_4^{2+}$ ? The drawing below shows a square array of four hydrogen atoms. Clearly, each line connecting any two of the atoms is not a (2c,2e) bond, because this molecular ion has only two electrons. Instead, this is a hypothetical example of (4c,2e) bonding. We cannot write a Lewis structure for this species. It is not likely to exist; it should be unstable with respect to two separate  $H_2^+$  diatomic species with (2c,1e) bonds.



(b) Bent  $O_3^{2-2}$  A proper Lewis structure for this 20-electron ion is shown above. Therefore, it is electron precise. It could very well exist.

**2.25** Find isolobal fragments? (a) CH<sub>3</sub>? The fragment CH<sub>3</sub><sup>-</sup> has a pyramidal structure with a single lone pair of electrons in the carbon atom. Ammonia, NH<sub>3</sub>, has exactly the same molecular and electronic structure (see below), and hence is isolobal with CH<sub>3</sub><sup>-</sup>.

Problems

2.1 Covalent radii take into account attractive (e=⇒nuclei) forces and repulsive (e=⇔e= & nuclei ⇒nuclei) forces. As you move → (across a period) shelding of nuclei becomes more effective. Covalent radii shortens, because nuclei can get closer to cach other. As you go down the table, radial function predicts electrons move out. Thus covalent radii moves out as well.

