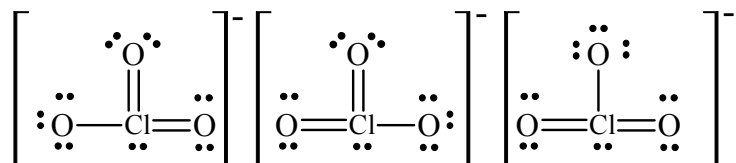


CHAPTER 3

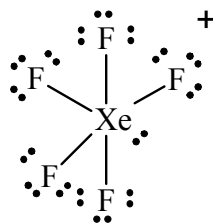
MOLECULAR SHAPE AND STRUCTURE

3.2



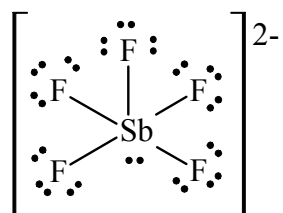
(a) The chlorate ion is trigonal pyramidal. (b) All the oxygen atoms are equivalent (resonance forms) so there should be only one O—Cl—O bond angle with a value close to 109.5° .

3.4



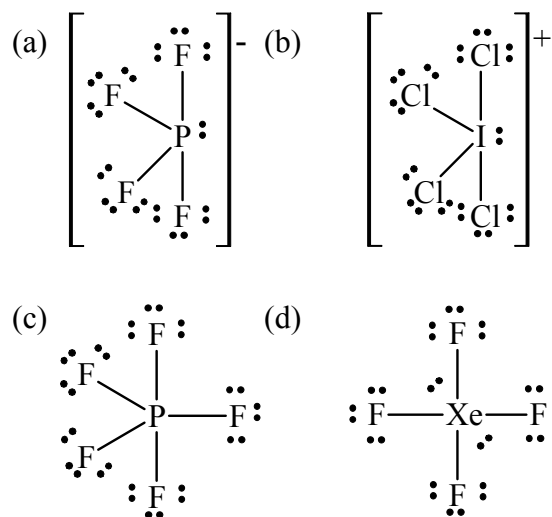
(a) The shape of the XeF_5^{+} ion is square pyramidal based upon an octahedral arrangement of electrons about the Xe atom. (b) There are two types of F—Xe—F bond angles. (c) The F—Xe—F bond angles are approximately 90° or 180° .

3.6



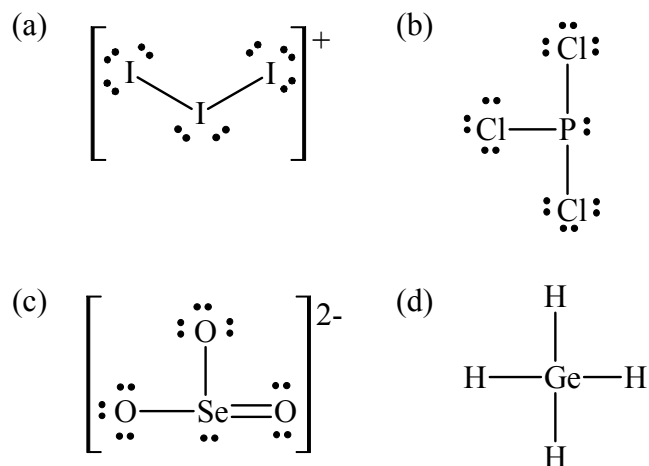
(a) Square pyramidal; (b) two; (c) 90° (adjacent), 180° (opposite)

3.8



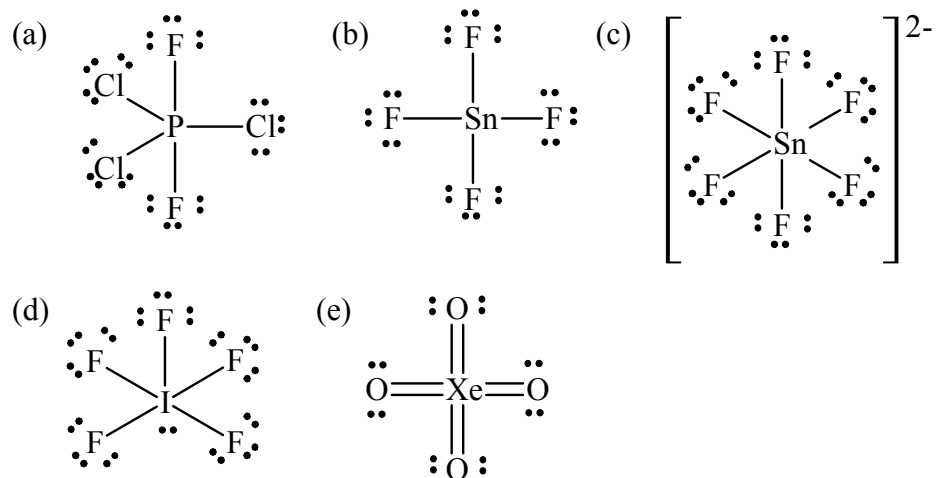
(a) The phosphorus atom in PF_4^- will have five pairs of electrons about it. There will be four bonding pairs and one lone pair. The arrangement of electron pairs will be trigonal bipyramidal with the lone pair occupying an equatorial position in order to minimize e-e repulsions. The name of the shape ignores the lone pairs, so the molecule is described best as having a seesaw structure. AX_4E ; (b) The number and types of lone pairs is the same for $[\text{ICl}_4]^+$ as it is for PF_4^- . The structural arrangement of electron pairs and name are the same as in (a). AX_4E ; (c) As in (a), the central P atom has five pairs of electrons about it, but this time they all are bonding pairs. The arrangement of pairs is still trigonal bipyramidal, but this time the name of the molecular shape is the same as the arrangement of electron pairs. The molecule is, therefore, a trigonal bipyramid. AX_5 ; (d) Xenon tetrafluoride will have six pairs of electrons about the central atom, of which two are lone pairs and four are bonding pairs. These pairs will adopt an octahedral geometry, but because the name of the molecule ignores the lone pairs, the structure will be called square planar. The lone pairs are placed opposite each other rather than adjacent, in order to minimize e-e repulsions between the lone pairs. AX_4E_2

3.10 The Lewis structures are



(a) I_3^+ should be bent with a bond angle of slightly less than 109.5° . AX_2E_2 ; (b) PCl_3 is pyramidal with $\text{Cl}-\text{P}-\text{Cl}$ bond angles of slightly less than 109.5° . AX_3E ; (c) SeO_3^{2-} is pyramidal with $\text{O}-\text{Se}-\text{O}$ angles of slightly less than 109.5° . AX_3E ; (d) GeH_4 is tetrahedral with $\text{H}-\text{Ge}-\text{H}$ angles of 109.5° . Note that GeH_4 has the same electronic structure as CH_4 because Ge lies in the same group as C. AX_4

3.12 The Lewis structures are



(a) PCl_3F_2 is trigonal bipyramidal with angles of 120° , 90° , and 180° . The most symmetrical structure is shown with all Cl atoms in equatorial positions. Phosphorus pentahalide compounds with more than one type of

halogen atom like this have several possible geometrical arrangements of the halogen atoms. These different arrangements are known as isomers. For this type of compound, the energy differences between the different isomers are low, so that the compounds exist as mixtures of different isomers that are rapidly interconverting. AX_5 (or $AX_3X'_2$);

(b) SnF_4 is tetrahedral with $F-Sn-F$ bond angles of 109.5° . AX_4 ; (c)

SnF_6^{2-} is octahedral with $F-Sn-F$ bond angles of 90° and 180° . AX_6 ;

(d) IF_5 is square pyramidal with $F-I-F$ angles of approximately

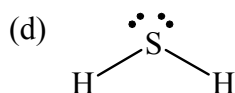
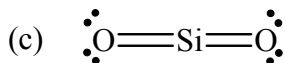
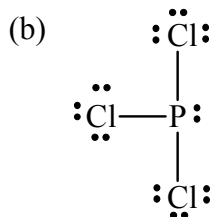
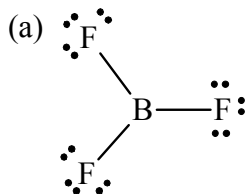
90° and 180° . AX_5E ; (e) XeO_4 is tetrahedral with angles equal to

109.5° . AX_4

3.14 Angles a and c are expected to be approximately 120° . Angle b is expected to be around 109.5° .

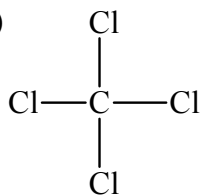
3.16 (a) slightly less than 109.5° ; (b) slightly less than 109.5° ; (c) slightly less than 120°

3.18 The Lewis structures are



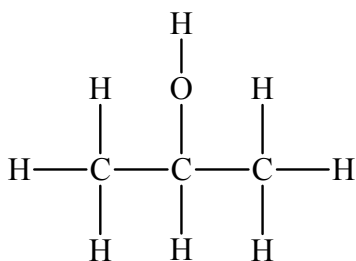
Molecules (b) and (d) will be polar; (a) and (c) will be nonpolar.

3.20 (a)



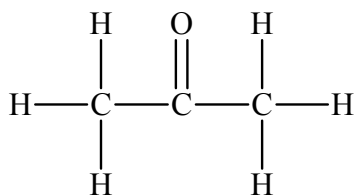
tetrachloromethane
nonpolar

(b)



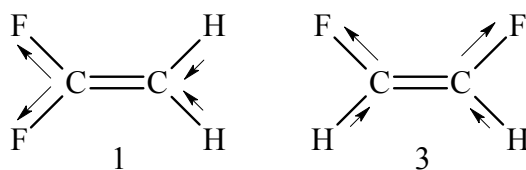
2-propanol
polar

(c)

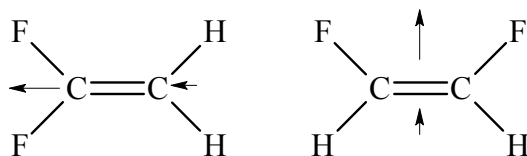


acetone
polar

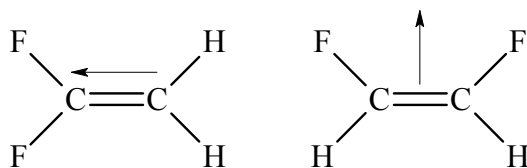
3.22 (a) In **2** the C—H and C—F bond vectors oppose identical bonds on opposite ends of the molecule; the individual dipole moments will cancel so that **2** will be nonpolar. This is not true for either **1** or **3**, which will both be expected to be polar. (b) Assuming the C—F and C—H polarities are the same in molecules **1** and **3**, one can carry out a vector addition of the individual dipole moments. It is perhaps easiest to look at the resultant of the two F—C dipoles and the two C—H dipoles in each molecule. The dipoles will sum as shown:



Addition of 2 C-F and 2 C-H dipoles in **1** and **3** give:

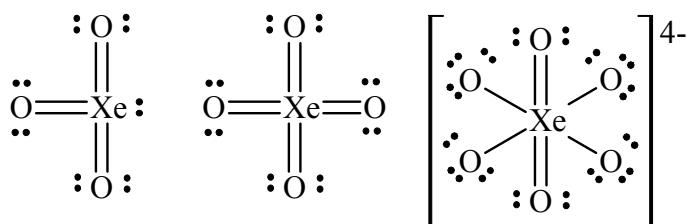


Net dipoles:



The net C—F and C—H dipoles reinforce in both these molecules, but because the F—C—F and H—C—H angles in **3** are more acute, the magnitude of the resultant will be slightly larger for **3**.

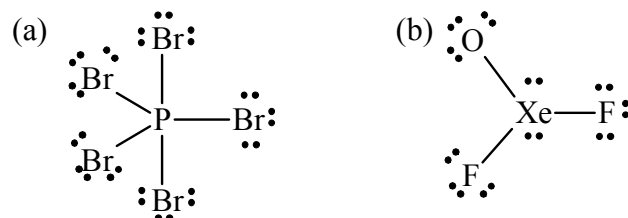
3.24



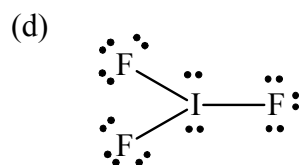
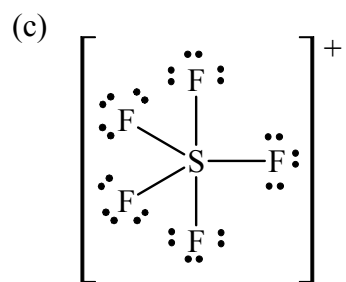
The first two molecules have four groups around the central atom, leading to tetrahedral dispositions of the bonds and lone pairs. XeO_3 is of the AX_3E type and will be pyramidal, whereas XeO_4 will be of the AX_4 type and will be tetrahedral. The XeO_6^{4-} ion will be octahedral. The hybridizations will be sp^3 , sp^3 , and sp^3d^2 , respectively.

The Xe—O bonds should be longest in XeO_6^{2-} because each of those bonds should have a bond order of ca. $(4 \times 1 + 2 \times 2)/6 = 1.5$, whereas the bond orders in XeO_3 and XeO_4 will be about 2. This agrees with experiment: XeO_3 , 174 pm; XeO_4 , 176 pm; XeO_6^{2-} , 186 pm.

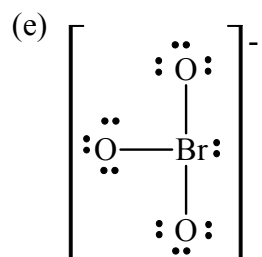
3.26



no lone pairs on central atom; trigonal bipyramidal; 90° , 120° two lone pairs on central atom; trigonal planar; 120°

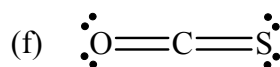
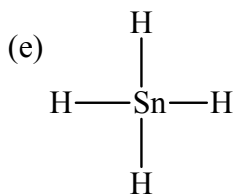
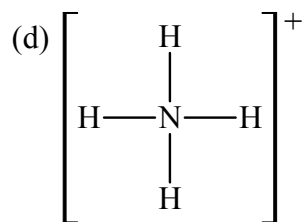
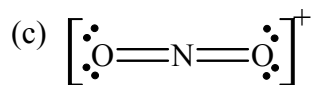
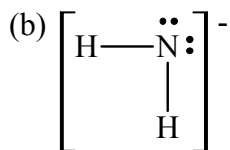
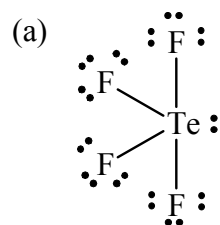


no lone pairs on central atom; two lone pairs on central atom
 tribonalbipyramidyl; 90° , 120° trigonal planar; 120°



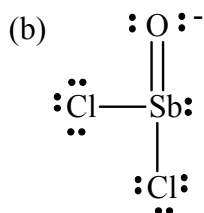
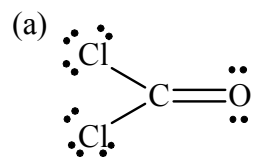
one lone pair on central atom
 trigonal pyramidyl; 107°

3.28



(a) seesaw; (b) angular; (c) linear; (d) tetrahedral;
 (e) tetrahedral; (f) linear

3.30



(a) trigonal planar; (b) pyramidal

3.32 (a) sp^3 ; (b) sp^3d ; (c) sp^3d^2 ; (d) sp

3.34 (a) sp^3d^2 ; (b) sp^3 ; (c) sp^3 ; (d) sp^2

3.36 (a) sp ; (b) sp^2 ; (c) sp^2 ; (d) sp^3

3.38 (a) sp ; (b) sp^2 ; (c) sp ; (d) sp^2

3.40 (a) In the NH_2^+ molecule, there is a single lone pair of electrons on the central N atom and as a result, the hybridization about the N atom is sp^2 . In NH_2^- , there are two lone pairs of electrons on the central N atom and the hybridization about this atom is best described as sp^3 . (b) The $\text{N}2p_x$ orbital contributes to bonding in the NH_2^- molecule (all p -orbitals participate in the hybrid orbitals) but the $\text{N}2p_x$ orbital does not contribute to bonding in NH_2^+ . In this molecule, the $\text{N}2p_x$ orbital lies normal to the plane containing the bonds and the lone pair, i.e. there is no overlap between the $\text{N}2p_x$ and the orbitals responsible for bonding and the orbital containing the lone pair of electrons.

3.42 If we take the hybrid orbital to be $\text{N} \cdot h_1$, then normalization requires that:

$$\int (\text{N} \cdot h_1)^2 d\tau = 1$$

solving for N:

$$\text{N}^2 \cdot \int h_1^2 d\tau = \text{N}^2 \cdot \int (s + p_x + p_y + p_z)^2 d\tau = 1$$

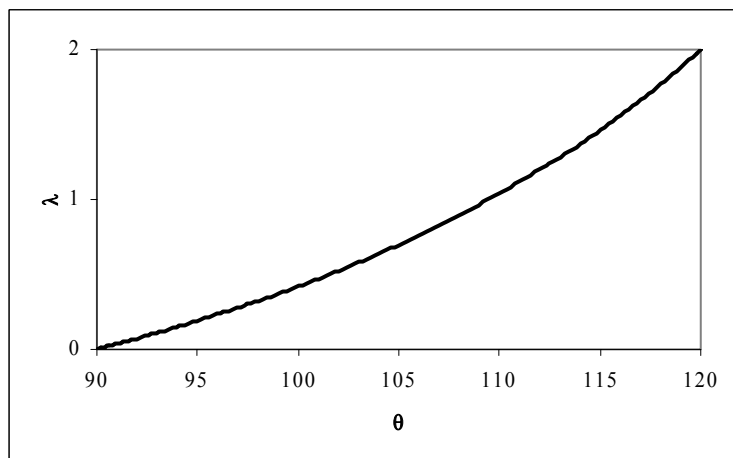
Expanding this expression we find that the only terms that are not zero are:

$$N^2 \cdot \int s^2 + p_x^2 + p_y^2 + p_z^2 d\tau = N^2 \cdot 4 = 1$$

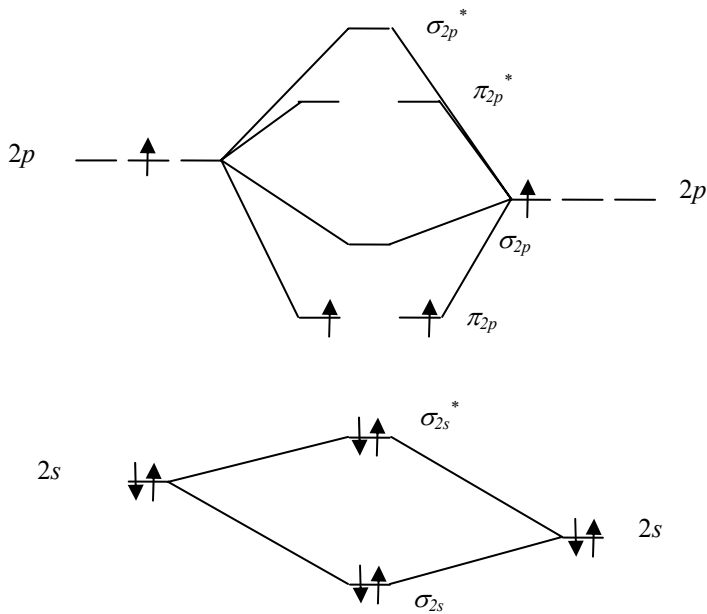
$$\text{Therefore, } N = \sqrt{\frac{1}{4}}$$

and the normalized wavefunction is $\sqrt{\frac{1}{4}}h_1$

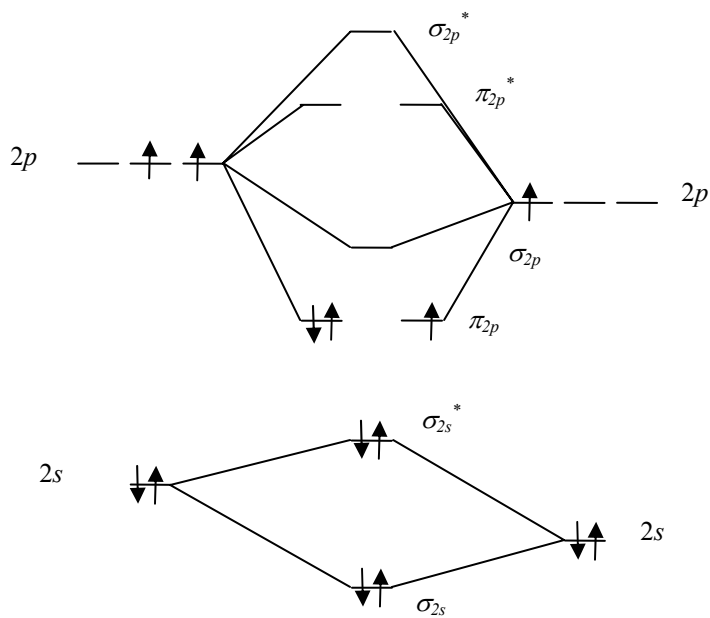
3.44



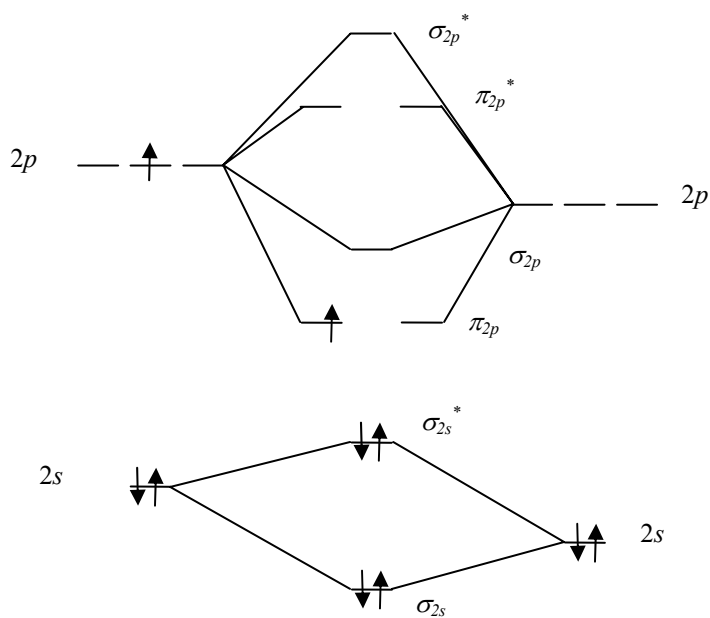
3.46 (a) B_2 $BO = \frac{1}{2}(2 - 0) = 1$ Paramagnetic, 2 unpaired electrons



(b) B_2^- $BO = \frac{1}{2}(2 + 3 - 2) = 3/2$ Paramagnetic, one unpaired electron



(c) B_2^+ $BO = \frac{1}{2} (2 + 4 - 2) = 2$ Paramagnetic, one unpaired electron



3.48 (a) (1) $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p_x})^2 (\pi_{2p_y})^2 (\sigma_{2p})^1$
 (2) $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p_x})^2 (\pi_{2p_y})^2$

$$(3) (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p_x})^2 (\pi_{2p_y})^2 (\sigma_{2p})^2 (\pi_{2p_x}^*)^1 (\pi_{2p_y}^*)^1$$

(b) (1) 2.5

(2) 2

(3) 2

(c) (1) and (3) are paramagnetic

(d) (1) σ

(2) π

(3) π

- 3.50** (a) In molecular orbital theory, ionic and covalent bonding are extremes of the same phenomenon. According to molecular orbital theory, bonding occurs when at least one orbital on each of two atoms combines to form a bonding and antibonding set of molecular orbitals. If the orbitals on each atom that are used to make the molecular orbital are similar in energy, the resultant molecular orbitals will be composed almost equally of contributions from the two atoms. The result is a covalent bond. On the other hand, if the two orbitals that make up the molecular orbitals are quite different in energy, the bond will be highly polarized. The more electronegative atom will contribute more to the bonding orbital, and the more electropositive atom will contribute more to the antibonding orbital.
- (b) The electronegativity of an atom is reflected in the energy of its atomic orbitals. The more electronegative the atom, the lower the orbitals. As the electronegativity difference becomes larger, the atomic orbitals on the two atoms being combined to form the molecular orbitals become farther apart in energy, so that the bond becomes more polarized.

- 3.52** (a) NO^+ (10 valence electrons): $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p})^2 (\pi_{2p_x})^2 (\pi_{2p_y})^2$, bond order = 3;
- (b) N_2^+ (9 valence electrons): $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p_x})^2 (\pi_{2p_y})^2 (\sigma_{2p})^1$, bond

order = 2.5; (c) C_2^{2+}

(6 valence electrons): $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p_x})^1(\pi_{2p_y})^1$, bond order = 1.

3.54 N_2^- and F_2^+ have an odd number of electrons and must, therefore, be paramagnetic. Referring to the molecular orbital diagram for N_2 (51), we see that adding one electron will place it in a π_{2p}^* orbital. This will give one unpaired electron and a bond order of 2.5. The removal of an electron from F_2 to give F_2^+ will produce one unpaired electron in the π_{2p}^* orbital (see 52). O_2^{2+} will be diamagnetic, as the removal of two electrons from O_2 will eliminate the two unpaired electrons (see 53).

3.56 (a) C_2^+ (7 valence electrons): $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p_x})^2(\pi_{2p_y})^1$, bond order = 1.5; C_2 (8 valence electrons): $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p_x})^2(\pi_{2p_y})^2$, bond order = 2. C_2 will have the stronger bond. (b) O_2 (12 valence electrons): $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p_x})^2(\pi_{2p_y})^2(\pi_{2p_x}^*)^1(\pi_{2p_y}^*)^1$, bond order = 2; O_2^+ (11 valence electrons): $(\sigma_{2s})^2(\sigma_{2s}^*)^2(\sigma_{2p})^2(\pi_{2p_x})^2(\pi_{2p_y})^2(\pi_{2p_x}^*)^1$, bond order = 2.5. O_2^+ will have the stronger bond.

3.58 (a) and (b) The valence band is mostly filled with electrons although a small percentage of holes is present, due to electrons being promoted into the conduction band from the valence band or due to the presence of p -type dopants. When an electron moves from one location to a hole, the hole appears to move in the other direction, i.e., the hole is now located where the electron was. As a consequence, in semiconductor materials, holes move in the opposite direction of electrons, so if current is moving from left to right, the holes will be moving from right to left.

3.60 In order to produce an *n*-type semiconductor, we need to introduce an additional valence electron into the material. Selenium would be the element appropriate for this purpose because it has one more valence electron than arsenic. Substituting phosphorus for arsenic would not change the number of valence electrons present. Silicon would result in the formation of a *p*-type semiconductor.

3.62 Given the overlap integral $S = \int \Psi_{A1s} \Psi_{B1s} d\tau$, the bonding orbital $\Psi = \Psi_{A1s} - \Psi_{B1s}$, and the fact that the individual atomic orbitals are normalized, we are asked to find the normalization constant N which will normalize the bonding orbital Ψ such that:

$$\begin{aligned} \int N^2 \Psi^2 d\tau &= N^2 \int (\Psi_{A1s} - \Psi_{B1s})^2 d\tau = 1 \\ N^2 \int (\Psi_{A1s} - \Psi_{B1s})^2 d\tau &= N^2 \int (\Psi_{A1s}^2 - 2\Psi_{A1s} \Psi_{B1s} + \Psi_{B1s}^2) d\tau = \\ N^2 \left(\int \Psi_{A1s}^2 d\tau - 2 \int \Psi_{A1s} \Psi_{B1s} d\tau + \int \Psi_{B1s}^2 d\tau \right) \end{aligned}$$

Given the definition of the overlap integral above and the fact that the individual orbitals are normalized, this expression simplifies to:

$$N^2(1 - 2S + 1) = 1$$

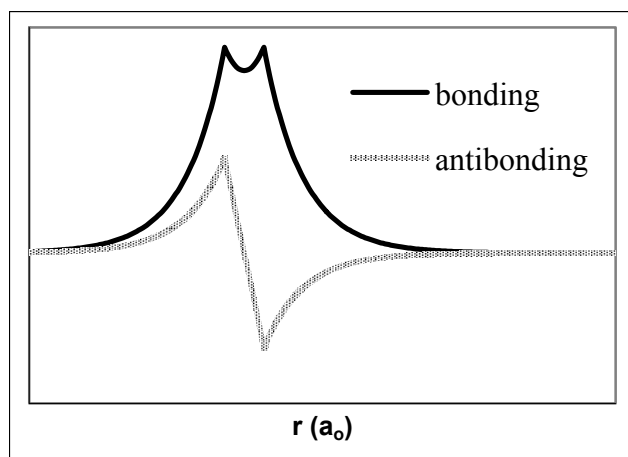
$$\text{Therefore, } N = \sqrt{\frac{1}{2 - 2S}}$$

To confirm that these two orbitals are orthogonal we evaluate the integral:

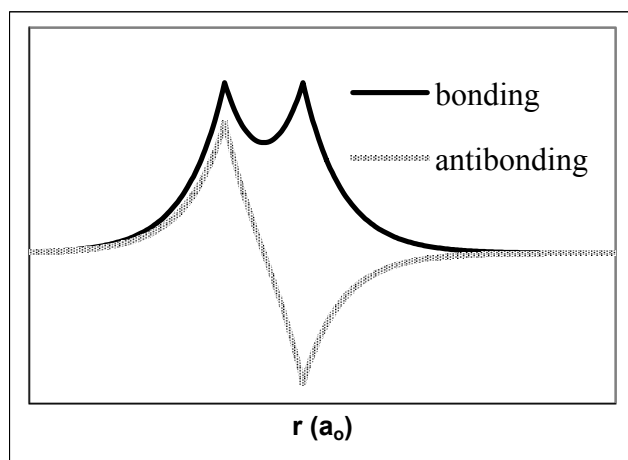
$$\begin{aligned} &\int (\Psi_{A1s} - \Psi_{B1s}) \cdot (\Psi_{A1s} + \Psi_{B1s}) d\tau \\ &= \int \Psi_{A1s}^2 + \Psi_{A1s} \cdot \Psi_{B1s} - \Psi_{A1s} + \Psi_{B1s} - \Psi_{B1s}^2 d\tau \\ &= 1 - 1 = 0 \end{aligned}$$

The overlap integral is zero. Therefore, the two wavefunctions are orthogonal.

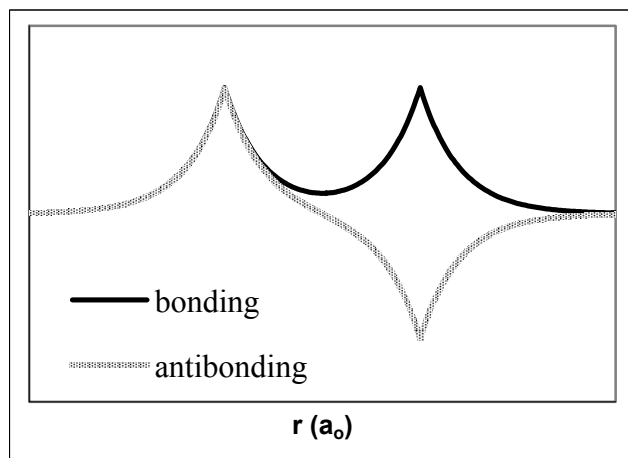
3.64 (a)



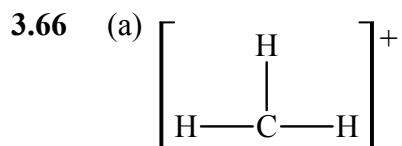
(b)



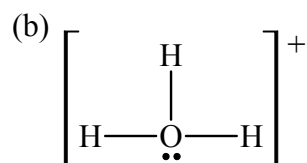
(c)



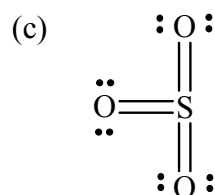
$1a_0$ is most likely closest to the real bond length as the orbital overlap integral will be greatest at this separation.



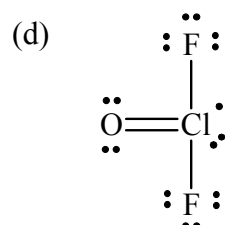
trigonal planar, sp^2 , H—C—H bond angles = 120° , nonpolar



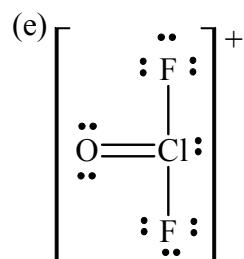
trigonal pyramidal, sp^3 , H—O—H bond angles are slightly less than 109.5° , polar



trigonal planar, sp^2 , O—S—O bond angles = 120° , nonpolar



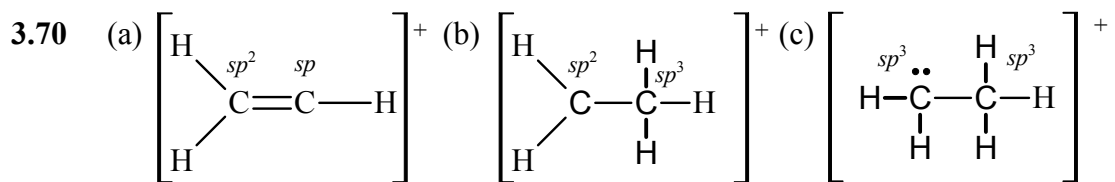
T-shaped, sp^3d , F—Cl—C, O—Cl—F bond angles are 90° and 180° , polar



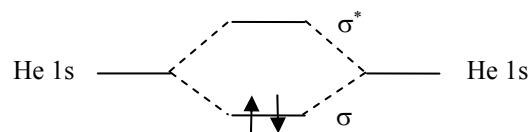
trigonal pyramidal, sp^3 , bond angles are all slightly less than 109.5° , polar

- 3.68** (a) The XX' molecules will be simple diatomic molecules with an X—X' single bond. The XX'_3 molecules will have a central atom that is of the

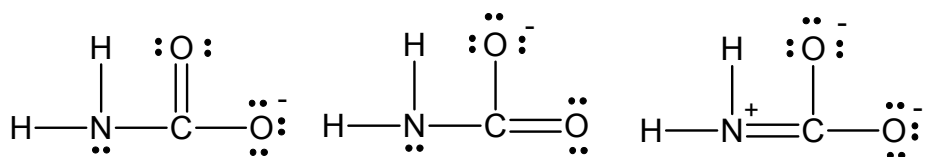
VSEPR type AX_3E_2 . The molecule will, therefore, be T-shaped. The $X'-X-X'$ bond angles will be slightly less than 90° and 180° . The XX'_5 molecules will have central atoms of the type AX_5E , which will be a square pyramidal structure with bond angles of ca. 90° and 180° . All three types will be polar. (b) only the XX' molecules will be polar (c) The central atom is the one that is the least electronegative. A consideration of the oxidation numbers shows that the central atom is the one that is positive, and the atoms around it are negative. Thus, the central atom will be the one that retains its electrons less effectively.



- 3.72 (a) The helium and hydrogen atoms have only their $1s$ orbitals available for bonding. Combination of these two will lead to a σ and a σ^* pair of orbitals. The most stable species will be one in which only the σ orbital is filled. Thus we need a species that has only two electrons. The charge on this species will be +1.
- (b) The maximum bond order will be 1. (c) Adding one electron will decrease the bond order by $1/2$ because an antibonding orbital will be populated. Taking an electron away will also decrease the bond order by $1/2$ because it will remove one bonding electron.



- 3.74 The Lewis structures that contribute to the structure of the carbamate ion are

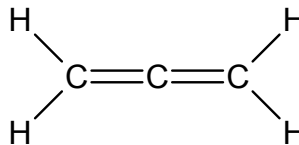
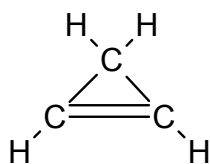


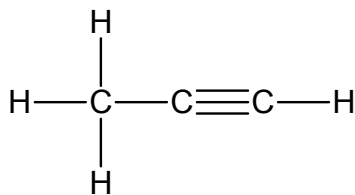
The charges show the location of the formal charges on the atoms in the Lewis structure. Note that the form that has a double bond to N is what we call a zwitterion, a structure that contains a + and a – charge in the same molecule. We might expect this structure to have a higher energy and contribute less to the overall structure than the other two forms, which have less separation of charge and which are equivalent in energy. To get insight into this question, we can compare the observed bond distances (C—O, 128 pm C—N, 136 pm) to those expected for various C—O and C—N bond orders. We can estimate these values using the data given in Table 2.3 and Figure 2.19. The following values are obtained:

| Bond | Expected Bond Length, pm |
|------|--------------------------|
| C—O | 151 |
| C=O | 112, 127 |
| C—N | 152 |
| C=N | 127 |

The C—O bond distance is very close to what we would expect for a C=O, although the average of experimental data gives a value closer to 112 pm. The second value is probably more reliable and indicates that the C—O bonds in the carbamate ion are intermediate between a double and single bond. The same is true of the C—N bond (Experimental values of C=N double bonds are close to 127 pm). It appears then that the resonance form with a C=N double bond does contribute substantially to the structure.

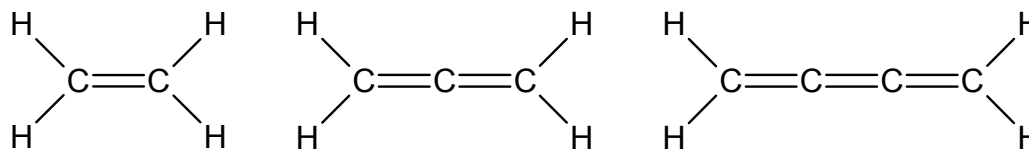
3.76 The three possible forms that maintain a valence of 4 at carbon are cyclopropene, allene, and propyne, which have the structures





The C—C—C bond angles in cyclopropene are restricted by the cyclic structure to be approximately 60°, which is far from the ideal value of 109.47° for an sp^3 hybridized carbon atom, or 120° for an sp^2 hybridized C atom. Consequently, cyclopropene is a very strained molecule that is extremely unstable. The H—C—H bond angle at the CH₂ group would be expected to be 109.47°, but it is actually larger due to the narrow C—C—C bond angle. The carbon of the CH₂ group is sp^3 hybridized, whereas the other two carbon atoms are sp^2 . Likewise the C=C—H angles, which would normally be expected to be 120° due to sp^2 hybridization at C, are somewhat larger. In allene, the middle carbon atom is sp hybridized; the two end carbons are sp^2 hybridized. The C—C—C bond angle is expected to be 180°; the H—C—H bond angles should be close to 120°. In propyne, one end carbon is sp^3 hybridized (109.5° angles); the other two C atoms are sp hybridized, with 180° bond angles. The three structures are not resonance structures of each other as they have a different spatial arrangement of atoms. For two structures to be resonance forms of each other, only the positions of the electrons may be changed. These two compounds would be known as *isomers* (see section 18.3).

3.78 (a)



- (b) The hybridization at the atoms attached to two hydrogen atoms is sp^2 , whereas that at the carbon atoms attached only to two other carbon atoms is sp .
- (c) Double bonds connect all of the carbon atoms to each other.
- (d) The H—C—H and C—C—H angles should all be ca. 120°. The C—C—C angles will all be 180°.

(e) The hydrogen atoms in H_2CCH_2 and H_2CCCCH_2 lie in the same plane, whereas the planes that are defined by the two end CH_2 groups lie perpendicular to each other in H_2CCCH_2 . This is because the p orbitals that are used by the central carbon atom to form the double bonds to the end carbon atoms are perpendicular to each other as shown.

Diagram of the interaction of the p orbitals used in making the $\text{C}=\text{C}$ double bonds:

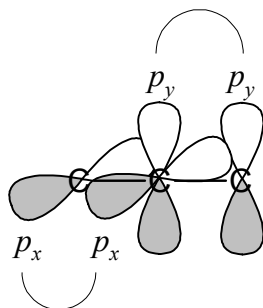
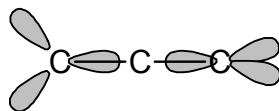


Diagram showing the orientation of the sp^2 orbitals used for bonding to the H atoms:



The three different p orbitals are commonly labeled p_x , p_y , and p_z to distinguish them. They may be thought of as pointing in the x , y , and z directions on a set of Cartesian axes that intersect at the carbon atom. The three p orbitals on a given carbon atom will be oriented 90° apart. Thus, if the central carbon atom is sp hybridized, the sp hybrid orbitals will be 180° apart (not shown) and will form the σ bonds to the other carbon atoms. This arrangement will use the p orbitals on the end carbon atoms that are oriented in the same direction (as shown here, the p_z orbitals on all three carbons have been used). The p_x and p_y orbitals on the middle carbon will be used in forming the bonds. This means that the bond to one carbon atom will be made from p_x , p_x interactions and the bond to the other will be p_y , p_y . One end carbon will be using the s , p_z , and p_x orbitals for forming the sp^2 hybrids and the other will be using the s , p_z , and p_y

orbitals. This change will result in the sp^2 orbitals on the end carbons being oriented 90° away from each other. This orientation effect will occur only if there is an odd number of carbons in the chain. If there is an even number of carbon atoms, the end C atoms will be required to use the same type of p orbitals as each other for forming the sp^2 hybrid orbitals. Thus $H_2CCCCCH_2$ should have all the hydrogen atoms in the same plane, and in $H_2CCCCCH_2$ the planes of the end CH_2 groups will again be perpendicular to each other.

(f) If x is odd, the hydrogens will point toward the same side of the molecule. If x is even, they will point toward different sides of the molecule.

3.80 Dyes get their color from the absorption of visible light. This absorption cannot take place unless there are bonding and antibonding orbitals available that have the correct energy spacing in order to absorb this visible light. The presence of a number of multiple bonds in molecules may lead to a delocalized set of orbitals. It is these delocalized orbitals that often absorb light in the visible region, giving rise to the desired color.

3.82 To show that two π orbitals taken together are cylindrically symmetric, we assume that the z axis is the bonding axis and show that net probability distribution (the sum of the two molecular orbitals squared) is not a function of ϕ . (Refer to Figure 1.24 on page 20 to confirm that, looking down the z axis, a cylindrically symmetric orbital will not be a function of ϕ).

$$x \cdot f(z) = f(z) \cdot C \cdot \sin \theta \cdot \cos \phi$$

$$y \cdot f(z) = f(z) \cdot C \cdot \sin \theta \cdot \sin \phi$$

where $C = \left(\frac{3}{4\pi}\right)^{\frac{1}{2}}$, and $f(z)$ is not a function of x or y

(and, therefore, $f(z)$ is not a function of ϕ). Squaring the two wavefunctions and summing them:

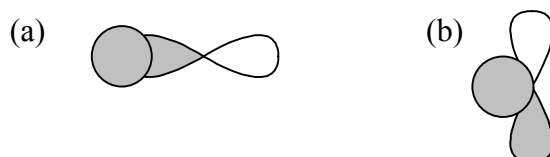
$$\begin{aligned} & f(z)^2 C^2 \sin^2 \theta \cos^2 \phi + f(z)^2 C^2 \sin^2 \theta \sin^2 \phi \\ &= f(z)^2 C^2 \sin^2 \theta (\cos^2 \phi + \sin^2 \phi) \end{aligned}$$

Using the identity $\cos^2 x + \sin^2 x = 1$ this becomes

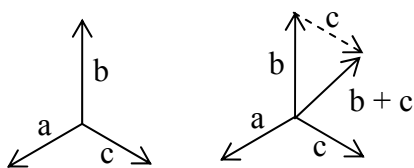
$$= f(z)^2 C^2 \sin^2 \theta$$

With two electrons in each π orbital, the electron distribution is not a function of ϕ and is, therefore, cylindrically symmetric about the bonding axis.

- 3.84** The overlap can be end-to-end or side-on. In the side-on overlap situation, the net overlap is zero because the areas of the wave function that are negative will cancel with the areas of the wave function that are positive. These will be equal in area and opposite in sign, giving no net overlap.

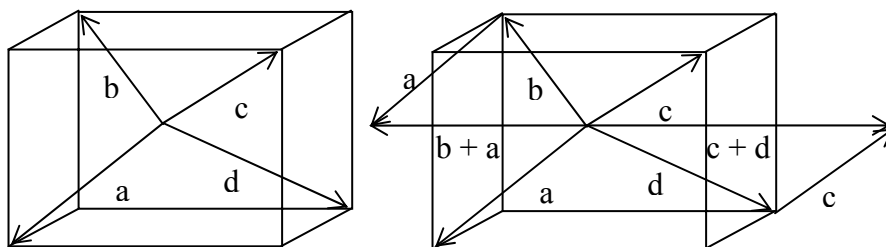


3.86



For the trigonal planar molecule, we first construct the vectors representing the individual dipole moments and then add them. This can be done most easily by combining two of the vectors first and then adding that to the third. Let's first add b and c . In order to add the vectors, we need to position them head to tail. Because the original angle where b and c come together in the AX_3 molecule is 120° , the angle between them when the origin of c is shifted to the end of b will be 60° . Because that

angle is 60° and b is the same length as c , the resultant of $b + c$ must also have the same length as a (and b and c). As can be seen from the diagram, the original vector a points in exactly the opposite direction from the summed vector $b + c$. Because the angle between b and $b + c$ is 60° and the angle between a and b is 120° , it follows that the angle between a and $b + c$ must be 180° . Because $b + c$ has exactly the same magnitude as a , they will exactly cancel each other.



For the tetrahedron, which can be inscribed inside a cube as shown, the vectors can be added in pairs to give resultants as shown. Starting with original vectors a , b , c , and d , we can add $a + b$ and $c + d$. (For an ideal tetrahedron in which all the atoms bonded to the central atom are identical, the choice of which vector is a , b , c , or d is arbitrary because they are all equivalent.) An examination of the tetrahedron will show that the vectors a and b lie in a plane that is perpendicular to the plane in which vectors c and d lie. The resultant $c + d$ will be equal in magnitude to the resultant $a + b$ because the vectors a , b , c , and d all have the same magnitude, and the angle between them is the same. It is easy to see that the vectors $a + b$ and $c + d$ lie exactly opposite each other and will add to zero.

- 3.88** (a) There are many, many structural reports in which the sulfate ion is the counterion. (b) The errors in terms of σ will vary, depending on the quality of the x-ray diffraction data, but generally data with three or four significant figures will be obtained. (c) Many structural reports will give results in which all the S—O distances and O—S—O angles will be the same within experimental error (within 3σ of each other). Some

structural data, however, will give values that are significantly different from each other. This will be obvious if compared for a large number of compounds. Distances will be near 149 pm. (d) If the sulfate ions were well isolated from other species, as in the gas phase at low pressure, you would expect the values to be identical. However, in the solid state, there are interactions between other species in the crystal lattice and the sulfate ion. The result is that the environment around the sulfate ion is often not symmetrical, and different bond distances and angles may result. Even so, the distances will fall within a fairly close range of values.

- 3.90** If we assume that the size of the lanthanum atom inside a C_{60} molecule is given by the atomic radius of the lanthanum atom, then we find that the diameter of a lanthanum atom would be $2 \times 188 \text{ pm} = 376 \text{ pm}$ (from Appendix 2D). For the C_{60} molecule to encapsulate more than one lanthanum atom, it would have to have a diameter at least twice the size of a lanthanum atom ($2 \times 376 \text{ pm} = 752 \text{ pm}$). Because the diameter of C_{60} is approximately 100 pm, two lanthanum atoms could not fit inside. (c) The radius of a La^{3+} ion is 122 pm so that its diameter would be 244 pm. Two La^{3+} ions could possibly fit inside a C_{60} molecule (or C_{60}^{6-} ion) because $2 \times 244 \text{ pm}$ is substantially smaller than the diameter of the C_{60} structure; however, placing two +3 ions in such close proximity would be electrostatically very unfavorable, and it would be unlikely to occur.
- 3.92** Yes. The color is due to absorption of light, which causes an electron to move from one d orbital to another d orbital ($d-d$ transition).
- 3.94** (a) Doping silicon with P will form an n-type semiconductor. However, to make an LED one must provide a junction between an n-type semiconductor and a p-type semiconductor. Si has a completely full valence band. Electrons arriving in the conduction band of pure silicon can

not fall down to the valence band, giving a photon, because the valence band in pure silicon is full.

(b) and (c) If the flow of electrons is reversed, electrons from the valence band of the p-type material would be “forced” into the conduction band of the n-type material as the valence band of the n-type material is full. One would not expect any light to be produced as electrons placed in the conduction band of the n-type material cannot fall down to the conduction band as the conduction band in an n-type semiconductor is full.