Learning Objective

- To explain resonance structures using molecular orbitals.

So far in our molecular orbital descriptions we have not dealt with polyatomic systems with multiple bonds. To do so, we can use an approach in which we describe σ bonding using localized electron-pair bonds formed by hybrid atomic orbitals, and π bonding using molecular orbitals formed by unhybridized np atomic orbitals.

Multiple Bonds

We begin our discussion by considering the bonding in ethylene (C₂H₄). Experimentally, we know that the H–C–H and H–C–C angles in ethylene are approximately 120°. This angle suggests that the carbon atoms are sp² hybridized, which means that a singly occupied sp² orbital on one carbon overlaps with a singly occupied s orbital on each H and a singly occupied sp² lobe on the other C. Thus each carbon forms a set of three σ bonds: two C–H (sp² + s) and one C–C (sp² + sp²) (part (a) in Figure 5.4.1). The sp² hybridization can be represented as follows:

![Diagram of sp² hybridization](image)
Figure 5.4.1 Bonding in Ethylene (a) The \( \sigma \)-bonded framework is formed by the overlap of two sets of singly occupied carbon \( sp^2 \) hybrid orbitals and four singly occupied hydrogen 1s orbitals to form electron-pair bonds. This uses 10 of the 12 valence electrons to form a total of five \( \sigma \) bonds (four C–H bonds and one C–C bond). (b) One singly occupied unhybridized \( 2p_z \) orbital remains on each carbon atom to form a carbon–carbon \( \pi \) bond. (Note: by convention, in planar molecules the axis perpendicular to the molecular plane is the \( z \)-axis.)

After hybridization, each carbon still has one unhybridized \( 2p_z \) orbital that is perpendicular to the hybridized lobes and contains a single electron (part (b) in Figure 5.4.1). The two singly occupied \( 2p_z \) orbitals can overlap to form a \( \pi \) bonding orbital and a \( \pi^* \) antibonding orbital, which produces the energy-level diagram shown in Figure 5.4.2. With the formation of a \( \pi \) bonding orbital, electron density increases in the plane between the carbon nuclei. The \( \pi^* \) orbital lies outside the internuclear region and has a nodal plane perpendicular to the internuclear axis. Because each \( 2p_z \) orbital has a single electron, there are only two electrons, enough to fill only the bonding (\( \pi \)) level, leaving the \( \pi^* \) orbital empty. Consequently, the C–C bond in ethylene consists of a \( \sigma \) bond and a \( \pi \) bond, which together give a C=C double bond. Our model is supported by the facts that the measured carbon–carbon bond is shorter than that in ethane (133.9 pm versus 153.5 pm) and the bond is stronger (728 kJ/mol versus 376 kJ/mol in ethane). The two \( \text{CH}_2 \) fragments are coplanar, which maximizes the overlap of the two singly occupied \( 2p_z \) orbitals.

![Figure 5.4.2 Molecular Orbital Energy-Level Diagram for \( \pi \) Bonding in Ethylene](image)

As in the diatomic molecules discussed previously, the singly occupied \( 2p_z \) orbital in ethylene can overlap to form a bonding/antibonding pair of \( \pi \) molecular orbitals. The two electrons remaining are enough to fill only the bonding \( \pi \) orbital. With one \( \sigma \) bond plus one \( \pi \) bond, the carbon–carbon bond order in ethylene is 2.

Triple bonds, as in acetylene (\( \text{C}_2\text{H}_2 \)), can also be explained using a combination of hybrid atomic orbitals and molecular orbitals. The four atoms of acetylene are collinear, which suggests that each carbon is \( sp \) hybridized. If one \( sp \) lobe on each carbon atom is used to form a C–C \( \sigma \) bond and one is used to form the C–H \( \sigma \) bond, then each carbon will still have two unhybridized \( 2p \) orbitals (a \( 2p_{x,y} \) pair), each with one electron (part (a) in Figure 5.4.4).
The two 2p orbitals on each carbon can align with the corresponding 2p orbitals on the adjacent carbon to simultaneously form a pair of π bonds (part (b) in Figure 5.4.4). Because each of the unhybridized 2p orbitals has a single electron, four electrons are available for π bonding, which is enough to occupy only the bonding molecular orbitals. Acetylene must therefore have a carbon–carbon triple bond, which consists of a C–C σ bond and two mutually perpendicular π bonds. Acetylene does in fact have a shorter carbon–carbon bond (120.3 pm) and a higher bond energy (965 kJ/mol) than ethane and ethylene, as we would expect for a triple bond.

Figure 5.4.4 Bonding in Acetylene (a) In the formation of the σ-bonded framework, two sets of singly occupied carbon sp hybrid orbitals and two singly occupied hydrogen 1s orbitals overlap. (b) In the formation of two carbon–carbon π bonds in acetylene, two singly occupied unhybridized 2p_x,y orbitals on each carbon atom overlap. With one σ bond plus two π bonds, the carbon–carbon bond order in acetylene is 3.

Note the Pattern

In complex molecules, hybrid orbitals and valence bond theory can be used to describe σ bonding, and unhybridized π orbitals and molecular orbital theory can be used to describe π bonding.

Example 5.4.1

Describe the bonding in HCN using a combination of hybrid atomic orbitals and molecular orbitals. The HCN molecule is linear.

Given: chemical compound and molecular geometry

Asked for: bonding description using hybrid atomic orbitals and molecular orbitals

Strategy:

A From the geometry given, predict the hybridization in HCN. Use the hybrid orbitals to form the σ-bonded framework of the molecule and determine the number of valence electrons that are used for σ bonding.

B Determine the number of remaining valence electrons. Use any remaining unhybridized p orbitals to form π and π* orbitals.

C Fill the orbitals with the remaining electrons in order of increasing energy. Describe the bonding in HCN.
Solution:

A Because HCN is a linear molecule, it is likely that the bonding can be described in terms of \( sp \) hybridization at carbon. Because the nitrogen atom can also be described as \( sp \) hybridized, we can use one \( sp \) hybrid on each atom to form a C–N \( \sigma \) bond. This leaves one \( sp \) hybrid on each atom to either bond to hydrogen (C) or hold a lone pair of electrons (N). Of 10 valence electrons (5 from N, 4 from C, and 1 from H), 4 are used for \( \sigma \) bonding:

B We are now left with 2 electrons on N (5 valence electrons minus 1 bonding electron minus 2 electrons in the lone pair) and 2 electrons on C (4 valence electrons minus 2 bonding electrons). We have two unhybridized \( 2p \) atomic orbitals left on carbon and two on nitrogen, each occupied by a single electron. These four \( 2p \) atomic orbitals can be combined to give four molecular orbitals: two \( \pi \) (bonding) orbitals and two \( \pi^* \) (antibonding) orbitals. C With 4 electrons available, only the \( \pi \) orbitals are filled. The overall result is a triple bond (1 \( \sigma \) and 2 \( \pi \)) between C and N.

Exercise

Describe the bonding in formaldehyde (H₂C=O), a trigonal planar molecule, using a combination of hybrid atomic orbitals and molecular orbitals.

Answer:

\( \sigma \)-bonding framework: Carbon and oxygen are \( sp^2 \) hybridized. Two \( sp^2 \) hybrid orbitals on oxygen have lone pairs, two \( sp^2 \) hybrid orbitals on carbon form C–H bonds, and one \( sp^2 \) hybrid orbital on C and O forms a C–O \( \sigma \) bond.

\( \pi \) bonding: Unhybridized, singly occupied \( 2p \) atomic orbitals on carbon and oxygen interact to form \( \pi \) (bonding) and \( \pi^* \) (antibonding) molecular orbitals. With two electrons, only the \( \pi \) (bonding) orbital is occupied.

Molecular Orbitals and Resonance Structures

In Chapter 4, we used resonance structures to describe the bonding in molecules such as ozone (O₃) and the nitrite ion (NO₂⁻). We showed that ozone can be represented by either of these Lewis electron structures:

![Lewis structures for ozone (O₃)](image)

Although the VSEPR model correctly predicts that both species are bent, it gives no information about their bond orders.
Figure 5.4.5 Bonding in Ozone (a) In the formation of the σ-bonded framework, three sets of oxygen sp$^2$ hybrid orbitals overlap to give two O–O σ bonds and five lone pairs, two on each terminal O and one on the central O. The σ bonds and lone pairs account for 14 of the 18 valence electrons of O$_3$. (b) One unhybridized 2$p_z$ orbital remains on each oxygen atom that is available for π bonding. The unhybridized 2$p_z$ orbital on each terminal O atom has a single electron, whereas the unhybridized 2$p_z$ orbital on the central O atom has 2 electrons.

Experimental evidence indicates that ozone has a bond angle of 117.5°. Because this angle is close to 120°, it is likely that the central oxygen atom in ozone is trigonal planar and sp$^2$ hybridized. If we assume that the terminal oxygen atoms are also sp$^2$ hybridized, then we obtain the σ-bonded framework shown in Figure 5.4.5. Two of the three sp$^2$ lobes on the central O are used to form O–O sigma bonds, and the third has a lone pair of electrons. Each terminal oxygen atom has two lone pairs of electrons that are also in sp$^2$ lobes. In addition, each oxygen atom has one unhybridized 2$p$ orbital perpendicular to the molecular plane. The σ bonds and lone pairs account for a total of 14 electrons (five lone pairs and two σ bonds, each containing 2 electrons). Each oxygen atom in ozone has 6 valence electrons, so O$_3$ has a total of 18 valence electrons. Subtracting 14 electrons from the total gives us 4 electrons that must occupy the three unhybridized 2$p$ orbitals.

With a molecular orbital approach to describe the π bonding, three 2$p$ atomic orbitals give us three molecular orbitals, as shown in Figure 5.4.6. One of the molecular orbitals is a π bonding molecular orbital, which is shown as a banana-shaped region of electron density above and below the molecular plane. This region has no nodes perpendicular to the
O$_{3}$ plane. The molecular orbital with the highest energy has two nodes that bisect the O–O σ bonds; it is a π* antibonding orbital. The third molecular orbital contains a single node that is perpendicular to the O$_{3}$ plane and passes through the central O atom; it is a nonbonding molecular orbital. Because electrons in nonbonding orbitals are neither bonding nor antibonding, they are ignored in calculating bond orders.

![Diagram of π bonding in Ozone](image)

**Figure 5.4.6 π Bonding in Ozone** The three unhybridized 2$p_z$ atomic orbitals interact with one another to form three molecular orbitals: one π bonding orbital at lower energy, one π* antibonding orbital at higher energy, and a nonbonding orbital in between. Placing four electrons in this diagram fills the bonding and nonbonding orbitals. With one filled π bonding orbital holding three atoms together, the net π bond order is 1/2 per O–O bond. The combined σ/π bond order is thus 1 1/2 for each O–O bond.

We can now place the remaining four electrons in the three energy levels shown in Figure 5.4.6, thereby filling the π bonding and the nonbonding levels. The result is a single π bond holding three oxygen atoms together, or 1/2 π bonds per O–O. We therefore predict the overall O–O bond order to be 1 1/2 (1/2 π bond plus 1 σ bond), just as predicted using resonance structures. The molecular orbital approach, however, shows that the π nonbonding orbital is localized on the terminal O atoms, which suggests that they are more electron rich than the central O atom. The reactivity of ozone is consistent with the predicted charge localization.

**Note the Pattern**

Resonance structures are a crude way of describing molecular orbitals that extend over more than two atoms.
Example 5.4.2

Describe the bonding in the nitrite ion in terms of a combination of hybrid atomic orbitals and molecular orbitals. Lewis dot structures and the VSEPR model predict that the NO$_2^-$ ion is bent.

**Given:** chemical species and molecular geometry

**Asked for:** bonding description using hybrid atomic orbitals and molecular orbitals

**Strategy:**

A Calculate the number of valence electrons in NO$_2^-$.

B Predict the number and type of molecular orbitals that form during bonding. Use valence electrons to fill these orbitals and then calculate the number of electrons that remain.

C If there are unhybridized orbitals, place the remaining electrons in these orbitals in order of increasing energy. Calculate the bond order and describe the bonding.

**Solution:**

A The lone pair of electrons on nitrogen and a bent structure suggest that the bonding in NO$_2^-$ is similar to the bonding in ozone. This conclusion is supported by the fact that nitrite also contains 18 valence electrons (5 from N and 6 from each O, plus 1 for the −1 charge). The bent structure implies that the nitrogen is $sp^2$ hybridized.

B If we assume that the oxygen atoms are $sp^2$ hybridized as well, then we can use two $sp^2$ hybrid orbitals on each oxygen and one $sp^2$ hybrid orbital on nitrogen to accommodate the five lone pairs of electrons. Two $sp^2$ hybrid orbitals on nitrogen form σ bonds with the remaining $sp^2$ hybrid orbital on each oxygen. The σ bonds and lone pairs account for 14 electrons. We are left with three unhybridized 2$p$ orbitals, one on each atom, perpendicular to the plane of the molecule, and 4 electrons. Just as with ozone, these three 2$p$ orbitals interact to form bonding, nonbonding, and antibonding π molecular orbitals. The bonding molecular orbital is spread over the nitrogen and both oxygen atoms.

C Placing 4 electrons in the energy-level diagram fills both the bonding and nonbonding molecular orbitals and gives a π bond order of 1/2 per N–O bond. The overall N–O bond order is 1 1/2 consistent with a resonance structure.
Exercise

Describe the bonding in the formate ion (HCO$_2^-$), in terms of a combination of hybrid atomic orbitals and molecular orbitals.

**Answer:** Like nitrite, formate is a planar polyatomic ion with 18 valence electrons. The σ bonding framework can be described in terms of $sp^2$ hybridized carbon and oxygen, which account for 14 electrons. The three unhybridized $2p$ orbitals (on C and both O atoms) form three π molecular orbitals, and the remaining 4 electrons occupy both the bonding and nonbonding π molecular orbitals. The overall C–O bond order is therefore 1 1/2

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**Summary**

To describe the bonding in more complex molecules with multiple bonds, we can use an approach that uses hybrid atomic orbitals to describe the σ bonding and molecular orbitals to describe the π bonding. In this approach, unhybridized $np$ orbitals on atoms bonded to one another are allowed to interact to produce bonding, antibonding, or nonbonding combinations. For π bonds between two atoms (as in ethylene or acetylene), the resulting molecular orbitals are virtually identical to the π molecular orbitals in diatomic molecules such as O$_2$ and N$_2$. Applying the same approach to π bonding between three or four atoms requires combining three or four unhybridized $np$ orbitals on adjacent atoms to generate π bonding, antibonding, and nonbonding molecular orbitals extending over all of the atoms. Filling the resulting energy-level diagram with the appropriate number of electrons explains the bonding in molecules or ions that previously required the use of resonance structures in the Lewis electron-pair approach.

**Key Takeaway**

- Polyatomic systems with multiple bonds can be described using hybrid atomic orbitals for σ bonding and molecular orbitals to describe π bonding.

**Conceptual Problems**

1. What information is obtained by using the molecular orbital approach to bonding in O$_3$ that is not obtained using the VSEPR model? Can this information be obtained using a Lewis electron-pair approach?

2. How is resonance explained using the molecular orbital approach?

3. Indicate what information can be obtained by each method:
Lewis Electron Structures  VSEPR Model  Valence Bond Theory  Molecular Orbital Theory

Geometry
Resonance
Orbital Hybridization
Reactivity
Expanded Valences
Bond Order

**Numerical Problems**

1. Using both a hybrid atomic orbital and molecular orbital approaches, describe the bonding in BCl$_3$ and CS$_3^{2-}$.

2. Use both a hybrid atomic orbital and molecular orbital approaches to describe the bonding in CO$_2$ and N$_3^{-}$.

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