Learning Objectives

• To describe the hybridization in the bonding of simple compounds via valence bond theory.

The localized valence bonding theory uses a process called hybridization, in which atomic orbitals that are similar in energy, but not equivalent are combined mathematically to produce sets of equivalent orbitals that are properly oriented to form bonds. These new combinations are called hybrid atomic orbitals because they are produced by combining (hybridizing) two or more atomic orbitals from the same atom.

Hybridization of \( s \) and \( p \) Orbitals

In BeH\(_2\), we can generate two equivalent orbitals by combining the 2\( s \) orbital of beryllium and any one of the three degenerate 2\( p \) orbitals. By taking the sum and the difference of Be 2\( s \) and 2\( p_z \) atomic orbitals, for example, we produce two new orbitals with major and minor lobes oriented along the \( z \)-axes, as shown in Figure \( \PageIndex{0} \).

\begin{align*}
\text{sp} &= \frac{1}{\sqrt{2}} (2s + 2p_z) \label{11.3.1a} \\
\text{sp} &= \frac{1}{\sqrt{2}} (2s - 2p_z) \label{11.3.1b}
\end{align*}

Figure \( \PageIndex{0} \): The position of the atomic nucleus with respect to an sp hybrid orbital. The nucleus is actually located slightly inside the minor lobe, not at the node separating the major and minor lobes.

Because the difference \( A - B \) can also be written as \( A + (\neg B) \), in Figure \( \PageIndex{1} \) and subsequent figures we have reversed the phase(s) of the orbital being subtracted, which is the same as multiplying it by \( \neg 1 \) and adding. This gives us Equation 11.3.1, where the value \( \frac{1}{\sqrt{2}} \) is needed mathematically to indicate that the 2\( s \) and 2\( p \) orbitals contribute equally to each hybrid orbital.

\begin{align*}
\text{sp} &= \frac{1}{\sqrt{2}} (2s + 2p_z) \label{11.3.1a} \\
\text{sp} &= \frac{1}{\sqrt{2}} (2s - 2p_z) \label{11.3.1b}
\end{align*}

Figure \( \PageIndex{1} \): The Formation of sp Hybrid Orbitals. Taking the sum and difference of an \( ns \) and an \( np \) atomic orbital where \( n = 2 \) gives two equivalent sp hybrid orbitals oriented at 180° to each other.
The nucleus resides just inside the minor lobe of each orbital. In this case, the new orbitals are called *sp hybrids* because they are formed from one *s* and one *p* orbital. The two new orbitals are equivalent in energy, and their energy is between the energy values associated with pure *s* and *p* orbitals, as illustrated in this diagram:

![Energy Level Diagram](image)

Figure \(\PageIndex{2}\), each *sp* orbital on Be has the correct orientation for the major lobes to overlap with the 1s atomic orbital of an H atom. The formation of two energetically equivalent Be–H bonds produces a linear \((\text{BeH}_2)\) molecule. Thus valence bond theory does what neither the Lewis electron structure nor the VSEPR model is able to do; it explains why the bonds in \((\text{BeH}_2)\) are equivalent in energy and why \((\text{BeH}_2)\) has a linear geometry.

Because both promotion and hybridization require an input of energy, the formation of a set of singly occupied hybrid atomic orbitals is energetically uphill. The overall process of forming a compound with hybrid orbitals will be energetically favorable only if the amount of energy released by the formation of covalent bonds is greater than the amount of energy used to form the hybrid orbitals (Figure \(\PageIndex{3}\)). As we will see, some compounds are highly unstable or do not exist because the amount of energy required to form hybrid orbitals is greater than the amount of energy that would be released by the formation of additional bonds.
Figure 3: A Hypothetical Stepwise Process for the Formation of BeH$_2$ from a Gaseous Be Atom and Two Gaseous H Atoms. The promotion of an electron from the 2s orbital of beryllium to one of the 2p orbitals is energetically uphill. The overall process of forming a BeH$_2$ molecule from a Be atom and two H atoms will therefore be energetically favorable only if the amount of energy released by the formation of the two Be–H bonds is greater than the amount of energy required for promotion and hybridization.

The concept of hybridization also explains why boron, with a 2s$^2$2p$^1$ valence electron configuration, forms three bonds with fluorine to produce BF$_3$, as predicted by the Lewis and VSEPR approaches. With only a single unpaired electron in its ground state, boron should form only a single covalent bond. By the promotion of one of its 2s electrons to an unoccupied 2p orbital, however, followed by the hybridization of the three singly occupied orbitals (the 2s and two 2p orbitals), boron acquires a set of three equivalent hybrid orbitals with one electron each, as shown here:

Figure 4). Because the hybrid atomic orbitals are formed from one s and two p orbitals, boron is said to be $sp^2$ hybridized (pronounced “s-p-two” or “s-p-squared”). The singly occupied $sp^2$ hybrid atomic orbitals can overlap with the singly occupied orbitals on each of the three F atoms to form a trigonal planar structure with three energetically equivalent B–F bonds.
Figure \(\PageIndex{4}\): Formation of \(sp^2\) Hybrid Orbitals. Combining one \(ns\) and two \(np\) atomic orbitals gives three equivalent \(sp^2\) hybrid orbitals in a trigonal planar arrangement; that is, oriented at 120° to one another.

Looking at the \(2s^22p^2\) valence electron configuration of carbon, we might expect carbon to use its two unpaired \(2p\) electrons to form compounds with only two covalent bonds. We know, however, that carbon typically forms compounds with four covalent bonds. We can explain this apparent discrepancy by the hybridization of the \(2s\) orbital and the three \(2p\) orbitals on carbon to give a set of four degenerate \(sp^3\) ("s-p-three" or "s-p-cubed") hybrid orbitals, each with a single electron:

The large lobes of the hybridized orbitals are oriented toward the vertices of a tetrahedron, with 109.5° angles between them (Figure \(\PageIndex{5}\)). Like all the hybridized orbitals discussed earlier, the \(sp^3\) hybrid atomic orbitals are predicted to be equal in energy.

Figure \(\PageIndex{5}\): Formation of \(sp^3\) Hybrid Orbitals. Combining one \(ns\) and three \(np\) atomic orbitals results in four \(sp^3\) hybrid orbitals oriented at 109.5° to one another in a tetrahedral arrangement.

In addition to explaining why some elements form more bonds than would be expected based on their valence electron configurations, and why the bonds formed are equal in energy, valence bond theory explains why these compounds are so stable: the amount of energy released increases with the number of bonds formed. In the case of carbon, for example, much more energy is released in the formation of four bonds than two, so compounds of carbon with four bonds tend to be more stable than those with only two. Carbon does form compounds with only two covalent bonds (such as \(CH_2\) or \(CF_2\)), but these species are highly reactive, unstable intermediates that form in only certain chemical reactions.

Valence bond theory explains the number of bonds formed in a compound and the relative bond strengths.

The bonding in molecules such as \(NH_3\) or \(H_2O\), which have lone pairs on the central atom, can also be described in terms of hybrid atomic orbitals. In \(NH_3\), for example, \(N\), with a \(2s^22p^3\) valence electron configuration, can hybridize its \(2s\) and \(2p\) orbitals to produce four \(sp^3\) hybrid orbitals. Placing five valence electrons in the four hybrid orbitals, we obtain three that are singly occupied and one with a pair of electrons:
The three singly occupied \(sp^3\) lobes can form bonds with three H atoms, while the fourth orbital accommodates the lone pair of electrons. Similarly, \(H_2O\) has an \(sp^3\) hybridized oxygen atom that uses two singly occupied \(sp^3\) lobes to bond to two H atoms, and two to accommodate the two lone pairs predicted by the VSEPR model. Such descriptions explain the approximately tetrahedral distribution of electron pairs on the central atom in \(NH_3\) and \(H_2O\). Unfortunately, however, recent experimental evidence indicates that in \(CH_4\) and \(NH_3\), the hybridized orbitals are not entirely equivalent in energy, making this bonding model an active area of research.

Example \(\PageIndex{1}\)

Use the VSEPR model to predict the number of electron pairs and molecular geometry in each compound and then describe the hybridization and bonding of all atoms except hydrogen.

\[
a. \ H_2S \\
b. \ CHCl_3
\]

**Given:** two chemical compounds

**Asked for:** number of electron pairs and molecular geometry, hybridization, and bonding

**Strategy:**

A. Using the VSEPR approach to determine the number of electron pairs and the molecular geometry of the molecule.

B. From the valence electron configuration of the central atom, predict the number and type of hybrid orbitals that can be produced. Fill these hybrid orbitals with the total number of valence electrons around the central atom and describe the hybridization.

**Solution:**

1. A \(H_2S\) has four electron pairs around the sulfur atom with two bonded atoms, so the VSEPR model predicts a molecular geometry that is bent, or V shaped. B Sulfur has a \(3s^23p^4\) valence electron configuration with six electrons, but by hybridizing its \(3s\) and \(3p\) orbitals, it can produce four \(sp^3\) hybrids. If the six valence electrons are placed in these orbitals, two have electron pairs and two are singly occupied. The two \(sp^3\) hybrid orbitals that are singly occupied are used to form S–H bonds, whereas the other two have lone pairs of electrons. Together, the four \(sp^3\) hybrid orbitals produce an approximately tetrahedral arrangement of electron pairs, which agrees with the molecular geometry predicted by the VSEPR model.

2. A The \(CHCl_3\) molecule has four valence electrons around the central atom. In the VSEPR model, the carbon atom has four electron pairs, and the molecular geometry is tetrahedral. B Carbon has a \(2s^22p^2\) valence electron configuration. By hybridizing its \(2s\) and \(2p\) orbitals, it can form four \(sp^3\) hybridized orbitals that are equal in energy. Eight electrons around the central atom (four from C, one from H, and one from each of the three Cl atoms) fill three \(sp^3\) hybrid orbitals to form C–Cl bonds, and one forms a C–H bond. Similarly, the Cl atoms, with seven electrons each in their \(3s\) and \(3p\) valence subshells, can be viewed as \(sp^3\) hybridized. Each Cl atom uses a singly occupied \(sp^3\) hybrid orbital to form a C–Cl bond and three hybrid orbitals to accommodate lone pairs.

Exercise \(\PageIndex{1}\)
Use the VSEPR model to predict the number of electron pairs and molecular geometry in each compound and then describe the hybridization and bonding of all atoms except hydrogen.

a. the BF$_4^-$ ion
b. hydrazine (H$_2$N–NH$_2$)

**Answer**

a. B is sp$^3$ hybridized; F is also sp$^3$ hybridized so it can accommodate one B–F bond and three lone pairs. The molecular geometry is tetrahedral.

b. Each N atom is sp$^3$ hybridized and uses one sp$^3$ hybrid orbital to form the N–N bond, two to form N–H bonds, and one to accommodate a lone pair. The molecular geometry about each N is trigonal pyramidal.

The number of hybrid orbitals used by the central atom is the same as the number of electron pairs around the central atom.

**Hybridization Using d Orbitals**

Hybridization is not restricted to the ns and np atomic orbitals. The bonding in compounds with central atoms in the period 3 and below can also be described using hybrid atomic orbitals. In these cases, the central atom can use its valence (n − 1)d orbitals as well as its ns and np orbitals to form hybrid atomic orbitals, which allows it to accommodate five or more bonded atoms (as in PF$_5$ and SF$_6$). Using the ns orbital, all three np orbitals, and one (n − 1)d orbital gives a set of five sp$^3$d hybrid orbitals that point toward the vertices of a trigonal bipyramid (part (a) in Figure \(\PageIndex{6}\)). In this case, the five hybrid orbitals are not all equivalent: three form a triangular array oriented at 120° angles, and the other two are oriented at 90° to the first three and at 180° to each other.

Similarly, the combination of the ns orbital, all three np orbitals, and two nd orbitals gives a set of six equivalent sp$^3$d$^2$ hybrid orbitals oriented toward the vertices of an octahedron (part (b) in Figure \(\PageIndex{6}\)). In the VSEPR model, PF$_5$ and SF$_6$ are predicted to be trigonal bipyramidal and octahedral, respectively, which agrees with a valence bond description in which sp$^3$d or sp$^3$d$^2$ hybrid orbitals are used for bonding.
Figure \(\PageIndex{6}\): Hybrid Orbitals Involving \(d\) Orbitals. The formation of a set of (a) five \(sp^3d\) hybrid orbitals and (b) six \(sp^3d^2\) hybrid orbitals from \(ns\), \(np\), and \(nd\) atomic orbitals where \(n = 4\).

Example \(\PageIndex{2}\)

What is the hybridization of the central atom in each species? Describe the bonding in each species.

a. \(\text{XeF}_4\)
b. \(\text{SO}_4^{2-}\)
c. \(\text{SF}_4\)

Given: three chemical species
Asked for: hybridization of the central atom

Strategy:

A. Determine the geometry of the molecule using the strategy in Example 1. From the valence electron configuration of the central atom and the number of electron pairs, determine the hybridization.

B. Place the total number of electrons around the central atom in the hybrid orbitals and describe the bonding.

Solution:

a. A Using the VSEPR model, we find that Xe in XeF₄ forms four bonds and has two lone pairs, so its structure is square planar and it has six electron pairs. The six electron pairs form an octahedral arrangement, so the Xe must be \(sp^3d^2\) hybridized. B With 12 electrons around Xe, four of the six \(sp^3d^2\) hybrid orbitals form Xe–F bonds, and two are occupied by lone pairs of electrons.

b. A The S in the SO₄²⁻ ion has four electron pairs and has four bonded atoms, so the structure is tetrahedral. The sulfur must be \(sp^3\) hybridized to generate four S–O bonds. B Filling the \(sp^3\) hybrid orbitals with eight electrons from four bonds produces four filled \(sp^3\) hybrid orbitals.

c. A The S atom in SF₄ contains five electron pairs and four bonded atoms. The molecule has a seesaw structure with one lone pair:

   \[\begin{array}{c}
   \text{F} \\
   \text{S} \\
   \text{F} \\
   \text{F} \\
   \end{array}\]

   To accommodate five electron pairs, the sulfur atom must be \(sp^3d\) hybridized. B Filling these orbitals with 10 electrons gives four \(sp^3d\) hybrid orbitals forming S–F bonds and one with a lone pair of electrons.

Exercise \(\PageIndex{2}\)

What is the hybridization of the central atom in each species? Describe the bonding.

a. PCl₄⁺

b. BrF₃

c. SiF₆²⁻

Answer

a. \(sp^3\) with four P–Cl bonds

b. \(sp^3d\) with three Br–F bonds and two lone pairs

c. \(sp^3d^2\) with six Si–F bonds

Hybridization using \(d\) orbitals allows chemists to explain the structures and properties of many molecules and ions. Like most such models, however, it is not universally accepted. Nonetheless, it does explain a fundamental difference between the chemistry of the elements in the period 2 (C, N, and O) and those in period 3 and below (such as Si, P, and S).
Period 2 elements do not form compounds in which the central atom is covalently bonded to five or more atoms, although such compounds are common for the heavier elements. Thus whereas carbon and silicon both form tetrafluorides (CF₄ and SiF₄), only SiF₄ reacts with F⁻ to give a stable hexafluoro dianion, SiF₆²⁻. Because there are no 2d atomic orbitals, the formation of octahedral CF₆²⁻ would require hybrid orbitals created from 2s, 2p, and 3d atomic orbitals. The 3d orbitals of carbon are so high in energy that the amount of energy needed to form a set of sp³d² hybrid orbitals cannot be equaled by the energy released in the formation of two additional C–F bonds. These additional bonds are expected to be weak because the carbon atom (and other atoms in period 2) is so small that it cannot accommodate five or six F atoms at normal C–F bond lengths due to repulsions between electrons on adjacent fluorine atoms. Perhaps not surprisingly, then, species such as CF₆²⁻ have never been prepared.

Example \(\PageIndex{3}\): \(\text{OF}_4\)

What is the hybridization of the oxygen atom in OF₄? Is OF₄ likely to exist?

**Given:** chemical compound

**Asked for:** hybridization and stability

**Strategy:**

A. Predict the geometry of OF₄ using the VSEPR model.
B. From the number of electron pairs around O in OF₄, predict the hybridization of O. Compare the number of hybrid orbitals with the number of electron pairs to decide whether the molecule is likely to exist.

**Solution:**

A. The VSEPR model predicts that OF₄ will have five electron pairs, resulting in a trigonal bipyramidal geometry with four bonding pairs and one lone pair. B. To accommodate five electron pairs, the O atom would have to be sp³d hybridized. The only d orbital available for forming a set of sp³d hybrid orbitals is a 3d orbital, which is much higher in energy than the 2s and 2p valence orbitals of oxygen. As a result, the OF₄ molecule is unlikely to exist. In fact, it has not been detected.

Exercise \(\PageIndex{3}\)

What is the hybridization of the boron atom in \(\text{BF}_6^{3−}\)? Is this ion likely to exist?

**Answer** sp³d² hybridization; no

**Summary**

- Hybridization increases the overlap of bonding orbitals and explains the molecular geometries of many species whose geometry cannot be explained using a VSEPR approach.

The *localized bonding* model (called *valence bond theory*) assumes that covalent bonds are formed when atomic orbitals overlap and that the strength of a covalent bond is proportional to the amount of overlap. It also assumes that
atoms use combinations of atomic orbitals (hybrids) to maximize the overlap with adjacent atoms. The formation of hybrid atomic orbitals can be viewed as occurring via promotion of an electron from a filled \( ns^2 \) subshell to an empty \( np \) or \((n - 1)d\) valence orbital, followed by hybridization, the combination of the orbitals to give a new set of (usually) equivalent orbitals that are oriented properly to form bonds. The combination of an \( ns \) and an \( np \) orbital gives rise to two equivalent sp hybrids oriented at 180°, whereas the combination of an \( ns \) and two or three \( np \) orbitals produces three equivalent \( sp^2 \) hybrids or four equivalent \( sp^3 \) hybrids, respectively. The bonding in molecules with more than an octet of electrons around a central atom can be explained by invoking the participation of one or two \((n - 1)d\) orbitals to give sets of five \( sp^3d \) or six \( sp^3d^2 \) hybrid orbitals, capable of forming five or six bonds, respectively. The spatial orientation of the hybrid atomic orbitals is consistent with the geometries predicted using the VSEPR model.