Skills to Develop

- Describe the formation of covalent bonds in terms of atomic orbital overlap
- Define and give examples of $\sigma$ and $\pi$ bonds
- Explain the concept of atomic orbital hybridization
- Determine the hybrid orbitals associated with various molecular geometries

As we know, a scientific theory is a strongly supported explanation for observed natural laws or large bodies of experimental data. For a theory to be accepted, it must explain experimental data and be able to predict behavior. For example, VSEPR theory has gained widespread acceptance because it predicts three-dimensional molecular shapes that are consistent with experimental data collected for thousands of different molecules. However, VSEPR theory does not provide an explanation of chemical bonding.

There are successful theories that describe the electronic structure of atoms. We can use quantum mechanics to predict the specific regions around an atom where electrons are likely to be located: A spherical shape for an $s$ orbital, a dumbbell shape for a $p$ orbital, and so forth. However, these predictions only describe the orbitals around free atoms. When atoms bond to form molecules, atomic orbitals are not sufficient to describe the regions where electrons will be located in the molecule. A more complete understanding of electron distributions requires a model that can account for the electronic structure of molecules. One popular theory holds that a covalent bond forms when a pair of electrons is shared by two atoms and is simultaneously attracted by the nuclei of both atoms. In the following sections, we will discuss how such
bonds are described by valence bond theory and hybridization.

Valence bond theory describes a covalent bond as the overlap of half-filled atomic orbitals (each containing a single electron) that yield a pair of electrons shared between the two bonded atoms. We say that orbitals on two different atoms overlap when a portion of one orbital and a portion of a second orbital occupy the same region of space. According to valence bond theory, a covalent bond results when two conditions are met:

1. an orbital on one atom overlaps an orbital on a second atom and
2. the single electrons in each orbital combine to form an electron pair.

The mutual attraction between this negatively charged electron pair and the two atoms’ positively charged nuclei serves to physically link the two atoms through a force we define as a covalent bond. The strength of a covalent bond depends on the extent of overlap of the orbitals involved. Orbitals that overlap extensively form bonds that are stronger than those that have less overlap.

The energy of the system depends on how much the orbitals overlap. Figure \(\PageIndex{1}\) illustrates how the sum of the energies of two hydrogen atoms (the colored curve) changes as they approach each other. When the atoms are far apart there is no overlap, and by convention we set the sum of the energies at zero. As the atoms move together, their orbitals begin to overlap. Each electron begins to feel the attraction of the nucleus in the other atom. In addition, the electrons begin to repel each other, as do the nuclei. While the atoms are still widely separated, the attractions are slightly stronger than the repulsions, and the energy of the system decreases. (A bond begins to form.) As the atoms move closer together, the overlap increases, so the attraction of the nuclei for the electrons continues to increase (as do the repulsions among electrons and between the nuclei). At some specific distance between the atoms, which varies depending on the atoms involved, the energy reaches its lowest (most stable) value. This optimum distance between the two bonded nuclei is the bond distance between the two atoms. The bond is stable because at this point, the attractive and repulsive forces combine to create the lowest possible energy configuration. If the distance between the nuclei were to decrease further, the repulsions between nuclei and the repulsions as electrons are confined in closer proximity to each other would become stronger than the attractive forces. The energy of the system would then rise (making the system destabilized), as shown at the far left of Figure \(\PageIndex{1}\).
The interaction of two hydrogen atoms changes as a function of distance. The energy of the system changes as the atoms interact. The lowest (most stable) energy occurs at a distance of 74 pm, which is the bond length observed for the $H_2$ molecule.

The bond energy is the difference between the energy minimum (which occurs at the bond distance) and the energy of the two separated atoms. This is the quantity of energy released when the bond is formed. Conversely, the same amount of energy is required to break the bond. For the $\text{H}_2$ molecule shown in Figure 1, at the bond distance of 74 pm the system is $(7.24 \times 10^{-19})$ J lower in energy than the two separated hydrogen atoms. This may seem like a small number. However, we know from our earlier description of thermochemistry that bond energies are often discussed on a per-mole basis. For example, it requires $(7.24 \times 10^{-19})$ J to break one H–H bond, but it takes $(4.36 \times 10^5)$ J to break 1 mole of H–H bonds. A comparison of some bond lengths and energies is shown in Table 1. We can find many of these bonds in a variety of molecules, and this table provides average values. For example, breaking the first C–H bond in CH4 requires 439.3 kJ/mol, while breaking the first C–H bond in $\text{H–CH}_2\text{C}_6\text{H}_5$ (a common paint thinner) requires 375.5 kJ/mol.

### Table: Representative Bond Energies and Lengths

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (pm)</th>
<th>Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H–H</td>
<td>74</td>
<td>436</td>
</tr>
<tr>
<td>H–C</td>
<td>106.8</td>
<td>413</td>
</tr>
<tr>
<td>H–N</td>
<td>101.5</td>
<td>391</td>
</tr>
<tr>
<td>H–O</td>
<td>97.5</td>
<td>467</td>
</tr>
<tr>
<td>C–C</td>
<td>150.6</td>
<td>347</td>
</tr>
<tr>
<td>C=O</td>
<td>119.7</td>
<td>745</td>
</tr>
<tr>
<td>C–N</td>
<td>142.1</td>
<td>305</td>
</tr>
<tr>
<td>C≡O</td>
<td>113.7</td>
<td>1072</td>
</tr>
<tr>
<td>C≡C</td>
<td>133.5</td>
<td>614</td>
</tr>
<tr>
<td>C≡N</td>
<td>116.1</td>
<td>891</td>
</tr>
</tbody>
</table>

In addition to the distance between two orbitals, the orientation of orbitals also affects their overlap (other than for two $s$ orbitals, which are spherically symmetric). Greater overlap is possible when orbitals are oriented such that they overlap on a direct line between the two nuclei. Figure 2 illustrates this for two $p$ orbitals from different atoms; the overlap is greater when the orbitals overlap end to end rather than at an angle.
Figure \(\PageIndex{2}\): (a) The overlap of two \(p\) orbitals is greatest when the orbitals are directed end to end. (b) Any other arrangement results in less overlap. The dots indicate the locations of the nuclei.

The overlap of two \(s\) orbitals (as in \(H_2\)), the overlap of an \(s\) orbital and a \(p\) orbital (as in \(HCl\)), and the end-to-end overlap of two \(p\) orbitals (as in \(Cl_2\)) all produce sigma bonds (\(\sigma\) bonds), as illustrated in Figure \(\PageIndex{3}\)). A \(\sigma\) bond is a covalent bond in which the electron density is concentrated in the region along the internuclear axis; that is, a line between the nuclei would pass through the center of the overlap region. Single bonds in Lewis structures are described as \(\sigma\) bonds in valence bond theory.

Figure \(\PageIndex{3}\): Sigma (\(\sigma\)) bonds form from the overlap of the following: (a) two \(s\) orbitals, (b) an \(s\) orbital and a \(p\) orbital, and (c) two \(p\) orbitals. The dots indicate the locations of the nuclei.

A \(\pi\) bond (\(\pi\) bond) is a type of covalent bond that results from the side-by-side overlap of two \(p\) orbitals, as illustrated in Figure \(\PageIndex{4}\)). In a \(\pi\) bond, the regions of orbital overlap lie on opposite sides of the internuclear axis. Along the axis itself, there is a node, that is, a plane with no probability of finding an electron.

Figure \(\PageIndex{4}\): Pi (\(\pi\)) bonds form from the side-by-side overlap of two \(p\) orbitals. The dots indicate the location of the nuclei.

While all single bonds are \(\sigma\) bonds, multiple bonds consist of both \(\sigma\) and \(\pi\) bonds. As the Lewis structures suggest, \(O_2\) contains a double bond, and \(N_2\) contains a triple bond. The double bond consists of one \(\sigma\) bond and one \(\pi\) bond, and the triple bond consists of one \(\sigma\) bond and two \(\pi\) bonds. Between any two atoms, the first bond formed will always be a \(\sigma\) bond, but there can only be one \(\sigma\) bond in any one location. In any multiple bond, there will be one \(\sigma\) bond, and the remaining one or two bonds will be \(\pi\) bonds. These bonds are described in more detail later in this chapter.

\[
\begin{align*}
\text{H—Cl} & : & \text{O=O} & : & \text{N≡N} \\
\text{One } \sigma\text{ bond} & & \text{One } \sigma\text{ bond} & & \text{One } \sigma\text{ bond} \\
\text{No } \pi\text{ bonds} & & \text{One } \pi\text{ bond} & & \text{Two } \pi\text{ bonds}
\end{align*}
\]
As seen in Table \(\PageIndex{1}\), an average carbon-carbon single bond is 347 kJ/mol, while in a carbon-carbon double bond, the \(\pi\) bond increases the bond strength by 267 kJ/mol. Adding an additional \(\pi\) bond causes a further increase of 225 kJ/mol. We can see a similar pattern when we compare other \(\sigma\) and \(\pi\) bonds. Thus, each individual \(\pi\) bond is generally weaker than a corresponding \(\sigma\) bond between the same two atoms. In a \(\sigma\) bond, there is a greater degree of orbital overlap than in a \(\pi\) bond.

Example \(\PageIndex{1}\): Counting \(\sigma\) and \(\pi\) Bonds

Butadiene, \(\text{C}_4\text{H}_6\), is used to make synthetic rubber. Identify the number of \(\sigma\) and \(\pi\) bonds contained in this molecule.

\[
\text{Butadiene}
\]

**Solution**

There are six \(\sigma\) C–H bonds and one \(\sigma\) C–C bond, for a total of seven from the single bonds. There are two double bonds that each have a \(\pi\) bond in addition to the \(\sigma\) bond. This gives a total nine \(\sigma\) and two \(\pi\) bonds overall.

Exercise \(\PageIndex{1}\)

Identify each illustration as depicting a \(\sigma\) or \(\pi\) bond:

a. side-by-side overlap of a 4\(p\) and a 2\(p\) orbital
b. end-to-end overlap of a 4\(p\) and 4\(p\) orbital
c. end-to-end overlap of a 4\(p\) and a 2\(p\) orbital

**Answer**

(a) is a \(\pi\) bond with a node along the axis connecting the nuclei while (b) and (c) are \(\sigma\) bonds that overlap along the axis.

Thinking in terms of overlapping atomic orbitals is one way for us to explain how chemical bonds form in diatomic molecules. However, to understand how molecules with more than two atoms form stable bonds, we require a more detailed model. As an example, let us consider the water molecule, in which we have one oxygen atom bonding to two hydrogen atoms. Oxygen has the electron configuration 1\(s^22s^22p^4\), with two unpaired electrons (one in each of the two 2\(p\) orbitals). Valence bond theory would predict that the two O–H bonds form from the overlap of these two 2\(p\) orbitals with the 1\(s\) orbitals of the hydrogen atoms. If this were the case, the bond angle would be 90°, as shown in Figure
because $p$ orbitals are perpendicular to each other. Experimental evidence shows that the bond angle is 104.5°, not 90°. The prediction of the valence bond theory model does not match the real-world observations of a water molecule; a different model is needed.

![Figure 5: The hypothetical overlap of two of the 2p orbitals on an oxygen atom (red) with the 1s orbitals of two hydrogen atoms (blue) would produce a bond angle of 90°. This is not consistent with experimental evidence.]

Quantum-mechanical calculations suggest why the observed bond angles in H$_2$O differ from those predicted by the overlap of the 1s orbital of the hydrogen atoms with the 2p orbitals of the oxygen atom. The mathematical expression known as the wave function, $\psi$, contains information about each orbital and the wavelike properties of electrons in an isolated atom. When atoms are bound together in a molecule, the wave functions combine to produce new mathematical descriptions that have different shapes. This process of combining the wave functions for atomic orbitals is called hybridization and is mathematically accomplished by the linear combination of atomic orbitals, LCAO, (a technique that we will encounter again later). The new orbitals that result are called hybrid orbitals. The valence orbitals in an isolated oxygen atom are a 2s orbital and three 2p orbitals. The valence orbitals in an oxygen atom in a water molecule differ; they consist of four equivalent hybrid orbitals that point approximately toward the corners of a tetrahedron (Figure 6). Consequently, the overlap of the O and H orbitals should result in a tetrahedral bond angle (109.5°). The observed angle of 104.5° is experimental evidence for which quantum-mechanical calculations give a useful explanation: Valence bond theory must include a hybridization component to give accurate predictions.

![Figure 6: (a) A water molecule has four regions of electron density, so VSEPR theory predicts a tetrahedral arrangement of hybrid orbitals. (b) Two of the hybrid orbitals on oxygen contain lone pairs, and the other two overlap with the 1s orbitals of hydrogen atoms to form the O–H bonds in H$_2$O. This description is more consistent with]
The following ideas are important in understanding hybridization:

1. Hybrid orbitals do not exist in isolated atoms. They are formed only in covalently bonded atoms.
2. Hybrid orbitals have shapes and orientations that are very different from those of the atomic orbitals in isolated atoms.
3. A set of hybrid orbitals is generated by combining atomic orbitals. The number of hybrid orbitals in a set is equal to the number of atomic orbitals that were combined to produce the set.
4. All orbitals in a set of hybrid orbitals are equivalent in shape and energy.
5. The type of hybrid orbitals formed in a bonded atom depends on its electron-pair geometry as predicted by the VSEPR theory.
6. Hybrid orbitals overlap to form $\sigma$ bonds. Unhybridized orbitals overlap to form $\pi$ bonds.

In the following sections, we shall discuss the common types of hybrid orbitals.

**sp Hybridization**

The beryllium atom in a gaseous $\text{BeCl}_2$ molecule is an example of a central atom with no lone pairs of electrons in a linear arrangement of three atoms. There are two regions of valence electron density in the $\text{BeCl}_2$ molecule that correspond to the two covalent $\text{Be–Cl}$ bonds. To accommodate these two electron domains, two of the Be atom’s four valence orbitals will mix to yield two hybrid orbitals. This hybridization process involves mixing of the valence $s$ orbital with one of the valence $p$ orbitals to yield two equivalent $sp$ hybrid orbitals that are oriented in a linear geometry (Figure \(\PageIndex{7}\)). In this figure, the set of $sp$ orbitals appears similar in shape to the original $p$ orbital, but there is an important difference. The number of atomic orbitals combined always equals the number of hybrid orbitals formed. The $p$ orbital is one orbital that can hold up to two electrons. The $sp$ set is two equivalent orbitals that point 180° from each other. The two electrons that were originally in the $s$ orbital are now distributed to the two $sp$ orbitals, which are half filled. In gaseous $\text{BeCl}_2$, these half-filled hybrid orbitals will overlap with orbitals from the chlorine atoms to form two identical $\sigma$ bonds.

![Hybridization of an s orbital (blue) and a p orbital (red) of the same atom produces two sp hybrid orbitals (yellow). Each hybrid orbital is oriented primarily in just one direction. Note that each sp orbital contains one lobe that is significantly larger than the other. The set of two sp orbitals are oriented at 180°, which is consistent with the geometry for two domains.](image-url)
We illustrate the electronic differences in an isolated Be atom and in the bonded Be atom in the orbital energy-level diagram in Figure \(\PageIndex{8}\). These diagrams represent each orbital by a horizontal line (indicating its energy) and each electron by an arrow. Energy increases toward the top of the diagram. We use one upward arrow to indicate one electron in an orbital and two arrows (up and down) to indicate two electrons of opposite spin.

**Figure \(\PageIndex{8}\):** This orbital energy-level diagram shows the sp hybridized orbitals on Be in the linear BeCl\(_2\) molecule. Each of the two sp hybrid orbitals holds one electron and is thus half filled and available for bonding via overlap with a Cl 3p orbital.

When atomic orbitals hybridize, the valence electrons occupy the newly created orbitals. The Be atom had two valence electrons, so each of the sp orbitals gets one of these electrons. Each of these electrons pairs up with the unpaired electron on a chlorine atom when a hybrid orbital and a chlorine orbital overlap during the formation of the Be–Cl bonds. Any central atom surrounded by just two regions of valence electron density in a molecule will exhibit sp hybridization. Other examples include the mercury atom in the linear HgCl\(_2\) molecule, the zinc atom in Zn(CH\(_3\))\(_2\), which contains a linear C–Zn–C arrangement, and the carbon atoms in HCCH and CO\(_2\).

**sp\(^2\) Hybridization**

The valence orbitals of a central atom surrounded by three regions of electron density consist of a set of three \(sp^2\) hybrid orbitals and one unhybridized p orbital. This arrangement results from \(sp^2\) hybridization, the mixing of one s orbital and two p orbitals to produce three identical hybrid orbitals oriented in a trigonal planar geometry (Figure \(\PageIndex{9}\)).

**Figure \(\PageIndex{9}\):** The hybridization of an s orbital (blue) and two p orbitals (red) produces three equivalent \(sp^2\) hybridized orbitals (yellow) oriented at 120° with respect to each other. The remaining unhybridized p orbital is not
Although quantum mechanics yields the “plump” orbital lobes as depicted in Figure \(\PageIndex{5}\), sometimes for clarity these orbitals are drawn thinner and without the minor lobes, as in Figure \(\PageIndex{10}\), to avoid obscuring other features of a given illustration. We will use these “thinner” representations whenever the true view is too crowded to easily visualize.

![Image](image1)

*Figure \(\PageIndex{10}\): This alternate way of drawing the trigonal planar \(sp^2\) hybrid orbitals is sometimes used in more crowded figures.*

The observed structure of the borane molecule, BH\(_3\), suggests \(sp^2\) hybridization for boron in this compound. The molecule is trigonal planar, and the boron atom is involved in three bonds to hydrogen atoms (Figure \(\PageIndex{11}\)).

![Image](image2)

*Figure \(\PageIndex{11}\): BH\(_3\) is an electron-deficient molecule with a trigonal planar structure.*

We can illustrate the comparison of orbitals and electron distribution in an isolated boron atom and in the bonded atom in BH\(_3\) as shown in the orbital energy level diagram in Figure \(\PageIndex{12}\). We redistribute the three valence electrons of the boron atom in the three \(sp^2\) hybrid orbitals, and each boron electron pairs with a hydrogen electron when B–H bonds form.
**Figure (\cite{PageIndex{12}}):** In an isolated B atom, there are one 2s and three 2p valence orbitals. When boron is in a molecule with three regions of electron density, three of the orbitals hybridize and create a set of three sp\(^2\) orbitals and one unhybridized 2p orbital. The three half-filled hybrid orbitals each overlap with an orbital from a hydrogen atom to form three \(\sigma\) bonds in BH\(_3\).

Any central atom surrounded by three regions of electron density will exhibit sp\(^2\) hybridization. This includes molecules with a lone pair on the central atom, such as CINO (Figure (\cite{PageIndex{13}})), or molecules with two single bonds and a double bond connected to the central atom, as in formaldehyde, CH\(_2\)O, and ethene, H\(_2\)CCH\(_2\).

**Figure (\cite{PageIndex{13}}):** The central atom(s) in each of the structures shown contain three regions of electron density and are sp\(^2\) hybridized. As we know from the discussion of VSEPR theory, a region of electron density contains all of the electrons that point in one direction. A lone pair, an unpaired electron, a single bond, or a multiple bond would each count as one region of electron density.

**sp\(^3\) Hybridization**

The valence orbitals of an atom surrounded by a tetrahedral arrangement of bonding pairs and lone pairs consist of a set of four sp\(^3\) hybrid orbitals. The hybrids result from the mixing of one s orbital and all three p orbitals that produces four identical sp\(^3\) hybrid orbitals (Figure (\cite{PageIndex{14}})). Each of these hybrid orbitals points toward a different corner of a tetrahedron.

**Figure (\cite{PageIndex{14}}):** The hybridization of an s orbital (blue) and three p orbitals (red) produces four equivalent
A molecule of methane, CH₄, consists of a carbon atom surrounded by four hydrogen atoms at the corners of a tetrahedron. The carbon atom in methane exhibits sp³ hybridization. We illustrate the orbitals and electron distribution in an isolated carbon atom and in the bonded atom in CH₄ in Figure \(\PageIndex{15}\). The four valence electrons of the carbon atom are distributed equally in the hybrid orbitals, and each carbon electron pairs with a hydrogen electron when the C–H bonds form.

![Orbitals in an isolated C atom and in the sp³ hybridized C atom in CH₄](image)

**Figure \(\PageIndex{15}\):** The four valence atomic orbitals from an isolated carbon atom all hybridize when the carbon bonds in a molecule like CH₄ with four regions of electron density. This creates four equivalent sp³ hybridized orbitals. Overlap of each of the hybrid orbitals with a hydrogen orbital creates a C–H σ bond.

In a methane molecule, the 1s orbital of each of the four hydrogen atoms overlaps with one of the four sp³ orbitals of the carbon atom to form a sigma (σ) bond. This results in the formation of four strong, equivalent covalent bonds between the carbon atom and each of the hydrogen atoms to produce the methane molecule, CH₄.

The structure of ethane, C₂H₆, is similar to that of methane in that each carbon in ethane has four neighboring atoms arranged at the corners of a tetrahedron—three hydrogen atoms and one carbon atom (Figure \(\PageIndex{10}\)). However, in ethane an sp³ orbital of one carbon atom overlaps end to end with an sp³ orbital of a second carbon atom to form a σ bond between the two carbon atoms. Each of the remaining sp³ hybrid orbitals overlaps with an s orbital of a hydrogen atom to form carbon–hydrogen σ bonds. The structure and overall outline of the bonding orbitals of ethane are shown in Figure \(\PageIndex{16}\). The orientation of the two CH₃ groups is not fixed relative to each other. Experimental evidence shows that rotation around σ bonds occurs easily.

![Orbitals in the ethane molecule, C₂H₆](image)

**Figure \(\PageIndex{16}\):** (a) In the ethane molecule, C₂H₆, each carbon has four sp³ orbitals. (b) These four orbitals overlap to form seven σ bonds.

An sp³ hybrid orbital can also hold a lone pair of electrons. For example, the nitrogen atom in ammonia is surrounded by three bonding pairs and a lone pair of electrons directed to the four corners of a tetrahedron. The nitrogen atom is sp³ hybridized with one hybrid orbital occupied by the lone pair.
The molecular structure of water is consistent with a tetrahedral arrangement of two lone pairs and two bonding pairs of electrons. Thus we say that the oxygen atom is $sp^3$ hybridized, with two of the hybrid orbitals occupied by lone pairs and two by bonding pairs. Since lone pairs occupy more space than bonding pairs, structures that contain lone pairs have bond angles slightly distorted from the ideal. Perfect tetrahedra have angles of 109.5°, but the observed angles in ammonia (107.3°) and water (104.5°) are slightly smaller. Other examples of $sp^3$ hybridization include CCl$_4$, PCl$_3$, and NCl$_3$.

Assignment of Hybrid Orbitals to Central Atoms

The hybridization of an atom is determined based on the number of regions of electron density that surround it. The geometrical arrangements characteristic of the various sets of hybrid orbitals are shown in Figure \(\PageIndex{16}\). These arrangements are identical to those of the electron-pair geometries predicted by VSEPR theory. VSEPR theory predicts the shapes of molecules, and hybrid orbital theory provides an explanation for how those shapes are formed. To find the hybridization of a central atom, we can use the following guidelines:

1. Determine the Lewis structure of the molecule.
2. Determine the number of regions of electron density around an atom using VSEPR theory, in which single bonds, multiple bonds, radicals, and lone pairs each count as one region.
3. Assign the set of hybridized orbitals from Figure \(\PageIndex{17}\) that corresponds to this geometry.

<table>
<thead>
<tr>
<th>Regions of Electron Density</th>
<th>Arrangement</th>
<th>Hybridization</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>linear</td>
<td>$sp$</td>
</tr>
<tr>
<td>3</td>
<td>trigonal planar</td>
<td>$sp^2$</td>
</tr>
<tr>
<td>4</td>
<td>tetrahedral</td>
<td>$sp^3$</td>
</tr>
<tr>
<td>5</td>
<td>trigonal bipyramidal</td>
<td>$sp^3d$</td>
</tr>
<tr>
<td>6</td>
<td>octahedral</td>
<td>$sp^4$</td>
</tr>
</tbody>
</table>

*Figure \(\PageIndex{17}\):* The shapes of hybridized orbital sets are consistent with the electron-pair geometries. For example, an atom surrounded by three regions of electron density is $sp^2$ hybridized, and the three $sp^2$ orbitals are arranged in a trigonal planar fashion.
It is important to remember that hybridization was devised to rationalize experimentally observed molecular geometries, not the other way around.

The model works well for molecules containing small central atoms, in which the valence electron pairs are close together in space. However, for larger central atoms, the valence-shell electron pairs are farther from the nucleus, and there are fewer repulsions. Their compounds exhibit structures that are often not consistent with VSEPR theory, and hybridized orbitals are not necessary to explain the observed data.

For example, we have discussed the H–O–H bond angle in H₂O, 104.5°, which is more consistent with sp³ hybrid orbitals (109.5°) on the central atom than with 2p orbitals (90°). Sulfur is in the same group as oxygen, and H₂S has a similar Lewis structure. However, it has a much smaller bond angle (92.1°), which indicates much less hybridization on sulfur than oxygen. Continuing down the group, tellurium is even larger than sulfur, and for H₂Te, the observed bond angle (90°) is consistent with overlap of the 5p orbitals, without invoking hybridization. We invoke hybridization where it is necessary to explain the observed structures.

Example (PageIndex{2})): Assigning Hybridization

Ammonium sulfate is important as a fertilizer. What is the hybridization of the sulfur atom in the sulfate ion, \(\text{SO}_4^{2-}\)?

Solution

The Lewis structure of sulfate shows there are four regions of electron density.

The hybridization is sp³, since the carbon has a tetrahedral geometry (Figure (PageIndex{17})).
Example \(\PageIndex{3}\): Assigning Hybridization

Urea, \(\text{NH}_2\text{C}(\text{O})\text{NH}_2\), is sometimes used as a source of nitrogen in fertilizers. What is the hybridization of each nitrogen and carbon atom in urea?

**Solution**

The Lewis structure of urea is

\[
\begin{array}{c}
\text{H} \quad \text{N} \quad \text{C} \quad \text{N} \quad \text{H} \\
\text{H} \\
\end{array}
\]

The nitrogen atoms are surrounded by four regions of electron density, which arrange themselves in a tetrahedral electron-pair geometry. The hybridization in a tetrahedral arrangement is \(sp^3\) (Figure \(\PageIndex{17}\)). This is the hybridization of the nitrogen atoms in urea.

The carbon atom is surrounded by three regions of electron density, positioned in a trigonal planar arrangement. The hybridization in a trigonal planar electron pair geometry is \(sp^2\) (Figure \(\PageIndex{17}\)), which is the hybridization of the carbon atom in urea.

**Exercise \(\PageIndex{2}\)**

Acetic acid, \(\text{H}_3\text{C}(\text{O})\text{OH}\), is the molecule that gives vinegar its odor and sour taste. What is the hybridization of the two carbon atoms in acetic acid?

\[
\begin{array}{c}
\text{O} \\
\text{H} \quad \text{C} \quad \text{O} \\
\text{H} \quad \text{C} \\
\text{H} \quad \text{H} \\
\end{array}
\]

**Answer**

\(\text{H}_3\text{C}, \, sp^3; \, \text{C}(\text{O})\text{OH}, \, sp^2\)
Valence bond theory describes bonding as a consequence of the overlap of two separate atomic orbitals on different atoms that creates a region with one pair of electrons shared between the two atoms. When the orbitals overlap along an axis containing the nuclei, they form a σ bond. When they overlap in a fashion that creates a node along this axis, they form a π bond.

We can use hybrid orbitals, which are mathematical combinations of some or all of the valence atomic orbitals, to describe the electron density around covalently bonded atoms. These hybrid orbitals either form sigma (σ) bonds directed toward other atoms of the molecule or contain lone pairs of electrons. We can determine the type of hybridization around a central atom from the geometry of the regions of electron density about it. Two such regions imply sp hybridization; three, sp² hybridization; four, sp³ hybridization. Pi (π) bonds are formed from unhybridized atomic orbitals (p or d orbitals).

Footnotes

1. Note that orbitals may sometimes be drawn in an elongated “balloon” shape rather than in a more realistic “plump” shape in order to make the geometry easier to visualize.
Glossary

**hybrid orbital**
orbital created by combining atomic orbitals on a central atom

**hybridization**
model that describes the changes in the atomic orbitals of an atom when it forms a covalent compound

**overlap**
coexistence of orbitals from two different atoms sharing the same region of space, leading to the formation of a covalent bond

**node**
plane separating different lobes of orbitals, where the probability of finding an electron is zero

**π bond (π bond)**
covalent bond formed by side-by-side overlap of atomic orbitals; the electron density is found on opposite sides of the internuclear axis

**σ bond (σ bond)**
covalent bond formed by overlap of atomic orbitals along the internuclear axis

**valence bond theory**
description of bonding that involves atomic orbitals overlapping to form σ or π bonds, within which pairs of electrons are shared

**sp hybrid orbital**
one of a set of two orbitals with a linear arrangement that results from combining one s and one p orbital

**sp$^2$ hybrid orbital**
one of a set of three orbitals with a trigonal planar arrangement that results from combining one s and two p orbitals

**sp$^3$ hybrid orbital**
one of a set of four orbitals with a tetrahedral arrangement that results from combining one s and three p orbitals

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