

Valence Bond Theory

Theory

Atom

Orbitals

Bonding

Valence Bond Theory

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. Dipole moments can be used to determine partial separations of charges between atoms. 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, sp^2 hybridization; four, sp^3 hybridization; five, sp^3d hybridization; and six, sp^3d^2 hybridization. Pi (π) bonds are formed from unhybridized atomic orbitals (p or d orbitals). Multiple bonds consist of a σ bond located along the axis between two atoms and one or two π bonds. The σ bonds are usually formed by the overlap of hybridized atomic orbitals, while the π bonds are formed by the side-by-side overlap of unhybridized orbitals. Resonance occurs when there are multiple unhybridized orbitals with the appropriate alignment to overlap, so the placement of π bonds can vary.

21.1 Valence Bond Theory

Learning Objectives

By the end of this section, you will be able to:

- Describe the formation of covalent bonds in terms of atomic orbital overlap
- Define and give examples of σ and π bonds

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.

Atomic Orbital Overlap

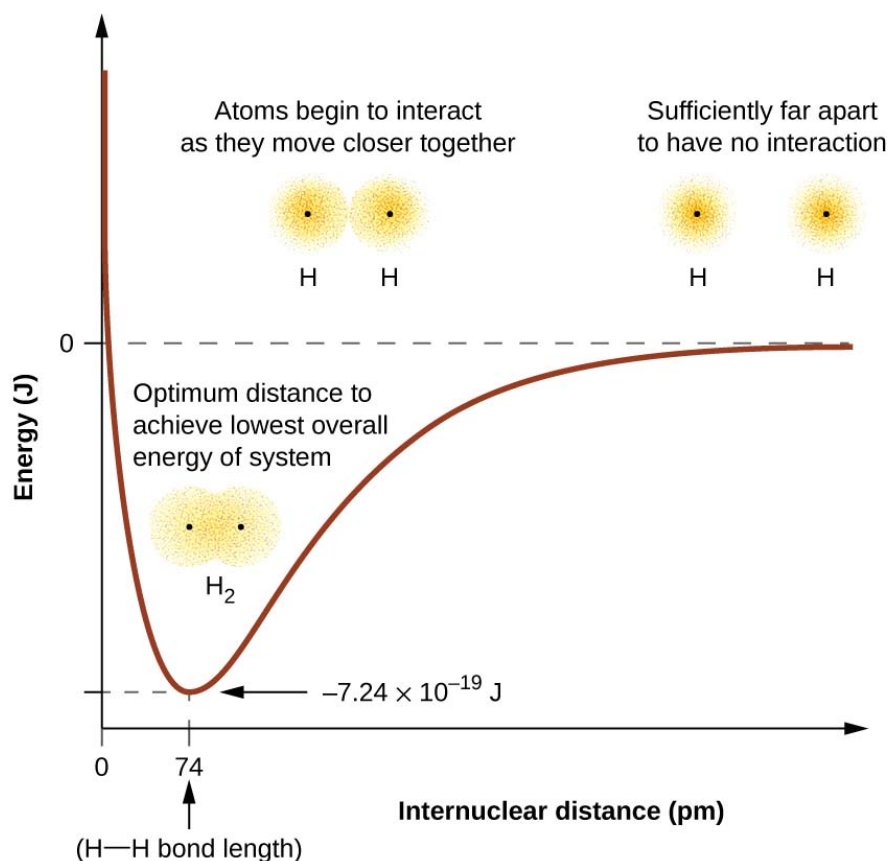
There are successful theories that describe the electronic structure of atoms. We can use quantum mechanics to predict the specific regions around an atom where electrons are likely to be located: A spherical shape for an s orbital, a dumbbell shape for a p orbital, and so forth. However, these predictions 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 21.1](#) 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 21.1](#).

Figure 21.1

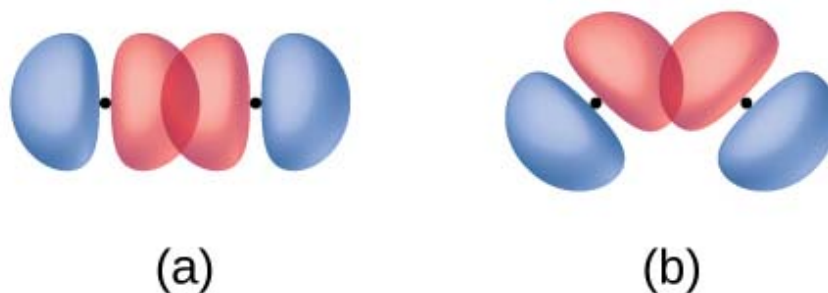
(a) The interaction of two hydrogen atoms changes as a function of distance. (b) The energy of the system changes as the atoms interact. The lowest (most stable) energy occurs at a distance of 74 pm, which is the bond length observed for the H_2 molecule.



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 21.2](#) 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 21.2

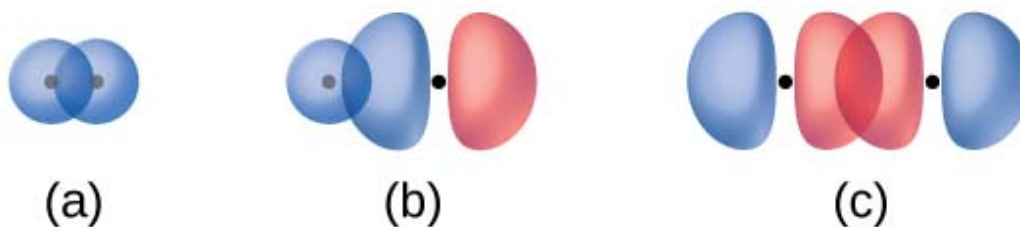
(a) The overlap of two *p* orbitals is greatest when the orbitals are directed end to end. (b) Any other arrangement results in less overlap. The dots indicate the locations of the nuclei.



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 (σ bonds), as illustrated in [Figure 21.3](#). A σ 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 σ bonds in valence bond theory.

Figure 21.3

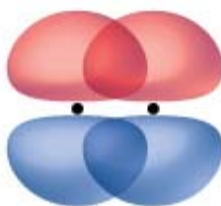
Sigma (σ) bonds form from the overlap of the following: (a) two s orbitals, (b) an s orbital and a p orbital, and (c) two p orbitals. The dots indicate the locations of the nuclei.



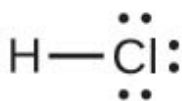
A pi bond (π bond) is a type of covalent bond that results from the side-by-side overlap of two p orbitals, as illustrated in [Figure 21.4](#). In a π bond, the regions of orbital overlap lie on opposite sides of the internuclear axis. Along the axis itself, there is a node, that is, a plane with no probability of finding an electron.

Figure 21.4

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



One σ bond
No π bonds



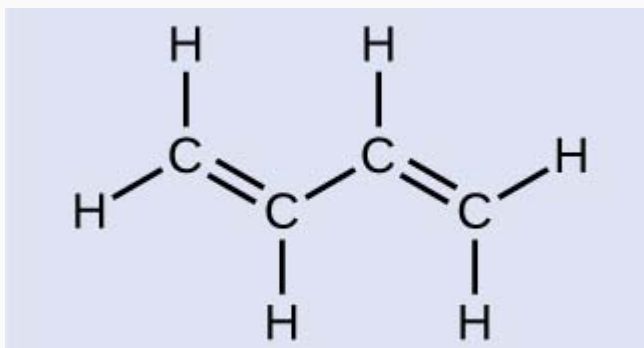
One σ bond
One π bond



One σ bond
Two π bonds

Example 21.1

Counting σ and π Bonds



Butadiene, C_4H_6 , is used to make synthetic rubber. Identify the number of σ and π bonds contained in this molecule.

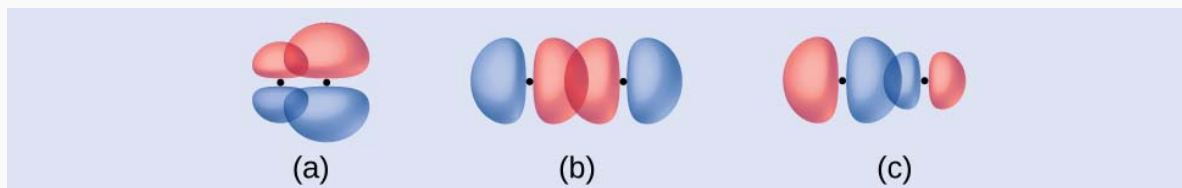
Solution

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

Check Your Learning

Identify each illustration as depicting a σ or π bond:

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



Answer

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

Dipole Moments and Ionic Character

Now that we have seen the importance of understanding the connection between the location of electrons in atoms and the properties of elements, we can expand our understanding of the connection between atoms. This will be an introduction to more advanced aspects of the chemical bond, which is the very heart of chemistry itself. With the sole exception of the noble gases, atoms by themselves do not possess the most stable possible electron configuration.

That is where the concept of chemical bonding comes into its own: atoms can attain a stable configuration by exchanging electrons with another atom, resulting in the formation of ions.

Ions, in turn, can associate by charge – simple Coulombic attraction – resulting in the formation of compounds we call ionic compounds. We will look at the ionic nature of bonds first, from a simple positive-negative attraction standpoint. Just as important is that some atoms bond by sharing rather than exchanging electrons; the sharing of electrons gives rise to the covalent bond. To add just one more dimension, some chemical species are neither completely ionic nor completely covalent; these species possess a permanent dipole, and are classified as polar.

In your introductory physics course, you will likely discuss the concept of Coulombic interactions in much more rigorous detail than we will do here. We are interested primarily in the differences in properties between species that arise from their relative covalent, ionic, or polar nature – not in a rigorous model of those properties. We are concerned with the connection between potential energy and force and the relative separation (or lack of separation) between charges. We begin by defining the electric or Coulomb force as the product of the charges divided by the square of the distance between those charges:

$$F = \frac{Q_1 Q_2}{d^2}$$

Here, Q is taken to be the fundamental constant of electron charge: one electron has a charge of

$$1.60218 \times 10^{-19} \text{ C}$$

. (We will work exclusively in the SI system, so distances will be measured in meters (m)).

And as you may recall, energy is force times distance, so

$$E = \frac{Q_1 Q_2}{d}$$

To illustrate the trend in attractive force, we will consider first the attractive force between two ions of single charge separated by a distance of $2d$:

$$F = \frac{(1)(-1)}{(2d)^2} = -\frac{1}{4d^2}$$

And then the attractive force between two ions of double charge separated by a distance d :

$$F = \frac{(2)(-2)}{(d)^2} = -\frac{4}{d^2}$$

The force of attraction increases with the charge and decreases with increased distance. If all matter were composed of ions that would be the end of the story, but it clearly is not. There are molecules for which the charge – either positive or negative – is permanently concentrated more on one atom than the other. Notice we say atom, because these compounds are not composed of ions but rather of atoms sharing electrons through covalent bonds.

Bond Dipole Moments

The concept of a bond dipole moment allows us to examine the partial separation of charge between atoms. It is a simple model when applied to diatomic molecules, which will be more than sufficient for our purposes. The dipole moment of a bond is defined as the charge times the distance – charge once again being measured in multiples of the charge on an electron, or coulombs. The distance will always be in meters. Because we are considering very small charges and distances, and because it is the relative separation of charge rather than the actual value for it that we are interested in, we will introduce a new unit called the Debye, named after the physical chemist Peter Debye:

$$1 \text{ Debye (D)} = 3.336 \times 10^{-30} \text{ C}\cdot\text{m} \qquad \mu = Q \times d$$

The usefulness of the Debye unit will be shown by example:

For HCl, the bond dipole moment is known to be 1.08 D

For HI, the bond dipole moment is known to be 0.44 D

Comparing the two, we can see that HI is less polar than HCl, which is what we would expect based on electronegativity values.

We have now made a transition between the concept of an ionic compound and a partially ionic one. Of course, the partially ionic compound must also by definition be partially covalent.

Partial Ionic Character

The concept of the bond dipole moment helps bridge the concepts of ionic and covalent bonding. Because there is a separation of charge that is less complete than it is in an ionic bond, we can refer to polar bonds as being partially ionic in nature. In contrast to sodium chloride, hydrogen chloride shows partial charges (indicated with a delta notation) on the hydrogen and chlorine. As you would expect from the electronegativity values, hydrogen carries a partial positive charge, while chlorine carries a partial negative charge. Where do these charges come from?

It is easy to come up with the partial charges by comparing the actual dipole moments (which can be obtained experimentally, using spectroscopy) with the dipole expected in the limiting case (that is, if we were to consider the molecule ionic). The actual dipole moment is 1.03 D.

Example 21.2

Finding the Partial Ionic Character

What are the partial charges of an HCl molecule, whose bond length is 0.127 nm?

Solution

The bond dipole moment is

$$(1.60218 \times 10^{-19} \text{ C})(0.127 \times 10^{-9} \text{ m})$$

or

$$2.03 \times 10^{-29} \text{ C}\cdot\text{m}$$

. Converted to D, this is

$$(2.03 \times 10^{-29} \text{ C}\cdot\text{m})\left(\frac{1 \text{ Debye}}{3.336 \times 10^{-30} \text{ C}\cdot\text{m}}\right)$$

or 6.09 D. Were HCl completely ionic, this would be its molecular dipole moment. To get the partial ionic character, we divide the experimentally measured bond moment by this limiting value:

$$\% \text{ ionic character} = \frac{\mu_{\text{exp}}}{\mu_{\text{lim}}} \times 100\% = \frac{(1.03 \text{ D})}{(6.09 \text{ D})} \times 100\% = 17\%$$

. This means the bond is about 17% ionic – or, put another way, the positive charge in H is +0.17 and the partial negative charge on chlorine, –0.17.

Check Your Learning

Repeat the calculation for HI, which has a dipole moment of 0.42 D and a bond length of 0.161 nm.

Answer: Calculated 7.73, percent 5.43

What does the result suggest about the relative polarity of the HI bond vs. that of the HCl bond? Does the calculated dipole and percent ionic character reconcile with the difference in electronegativity between Cl and I?

The electron configuration of an atom or ion is key to understanding the chemical behavior of an element. The atoms that make up the element combine in various ways, ranging from the mostly ionic (NaCl) to the partially ionic (HCl) to what we will call purely covalent. At the most fundamental level, all chemical bonds involve electrons, and a significant percentage of chemical and physical properties can be explained by considering the location and separation of charge in a species. By understanding the structure of matter at the atomic level, we can begin to build an understanding of the behavior of matter at both the microscopic and macroscopic levels.

An understanding of dipoles and partial ionic character is fundamental to understanding the interactions between particles, which we will examine in the chapter on liquids and solids. These intermolecular forces become important in the liquid and solid states of matter.

Link to Supplemental Exercises

[Supplemental exercises](#) are available if you would like more practice with these concepts.

21.2 Hybrid Atomic Orbitals

Learning Objectives

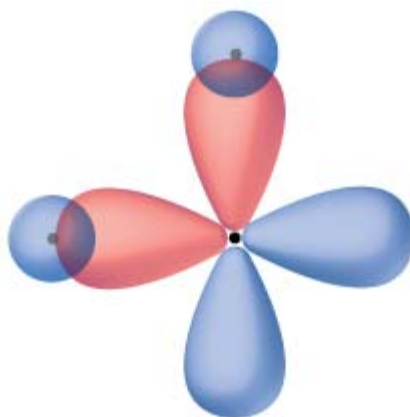
By the end of this section, you will be able to:

- Explain the concept of atomic orbital hybridization
- Determine the hybrid orbitals associated with various molecular geometries

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 $1s^2 2s^2 2p^4$, with two unpaired electrons (one in each of the two $2p$ orbitals). Valence bond theory would predict that the two O–H bonds form from the overlap of these two $2p$ orbitals with the $1s$ orbitals of the hydrogen atoms. If this were the case, the bond angle would be 90° , as shown in [Figure 21.5](#), 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 21.5

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.¹

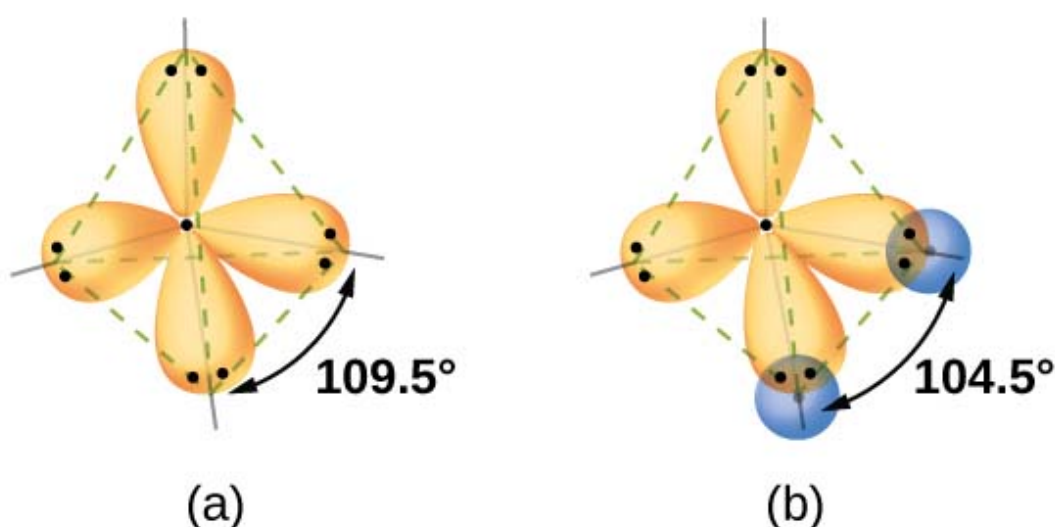


Quantum-mechanical calculations suggest why the observed bond angles in H_2O differ from those predicted by the overlap of the $1s$ orbital of the hydrogen atoms with the $2p$ orbitals of the oxygen atom. The mathematical expression known as the wave function, ψ , contains information about each orbital 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 21.6). 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 21.6

(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_2O . This description is more consistent with the experimental structure.



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 σ bonds. Unhybridized orbitals overlap to form π bonds.

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

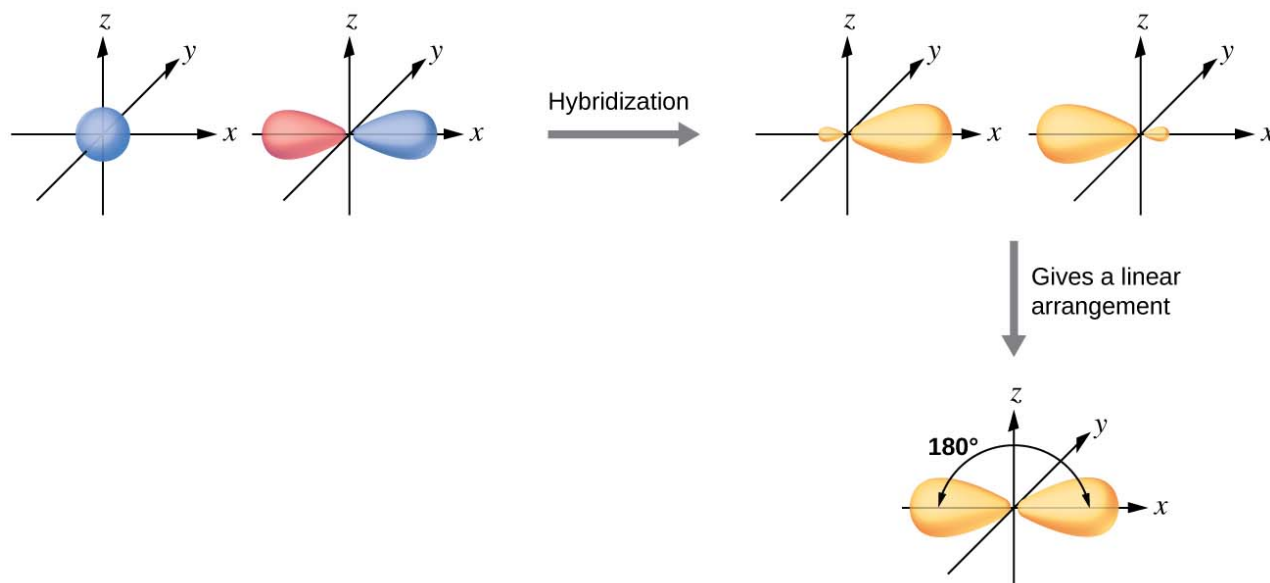
sp Hybridization

The beryllium atom in a gaseous $BeCl_2$ 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 $BeCl_2$ molecule that correspond to the two covalent 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

21.7). 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 BeCl_2 , these half-filled hybrid orbitals will overlap with orbitals from the chlorine atoms to form two identical σ bonds.

Figure 21.7

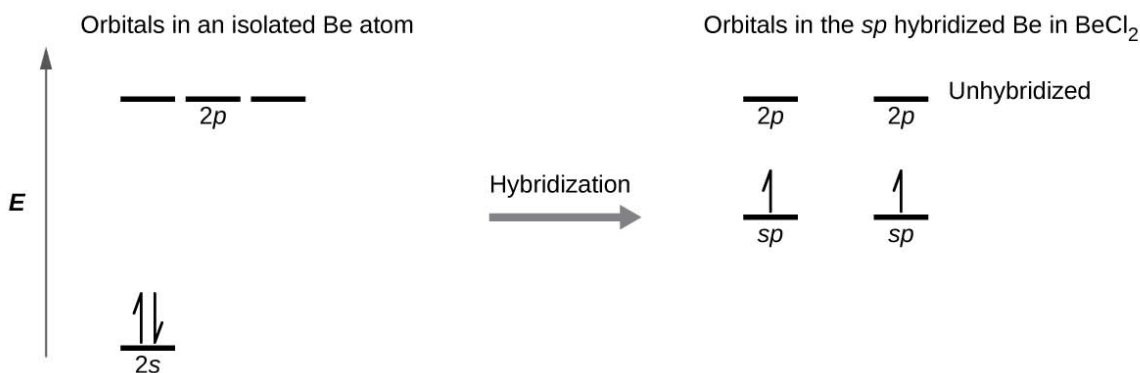
Hybridization of an s orbital (blue) and a p orbital (red) of the same atom produces two sp hybrid orbitals (yellow). Each hybrid orbital is oriented primarily in just one direction. Note that each sp orbital contains one lobe that is significantly larger than the other. The set of two sp orbitals are oriented at 180° , which is consistent with the geometry for two domains.



We illustrate the electronic differences in an isolated Be atom and in the bonded Be atom in the orbital energy-level diagram in [Figure 21.8](#). 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 21.8

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 $\text{Zn}(\text{CH}_3)_2$, which contains a linear C–Zn–C arrangement, and the carbon atoms in HCCH and CO_2 .

Link to Learning

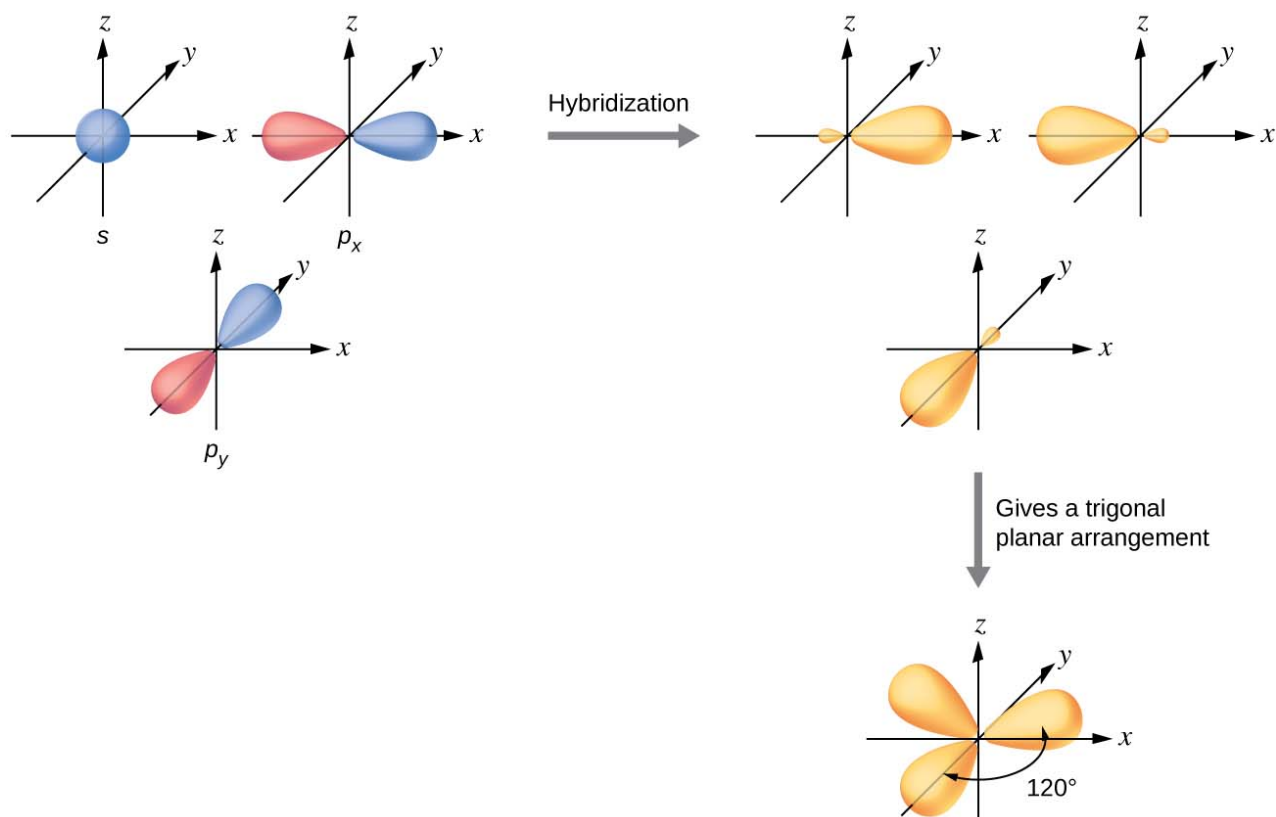
Learn to [visualize hybrid orbitals](#) in three dimensions from the University of Wisconsin-Oshkosh.

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 21.9](#)).

Figure 21.9

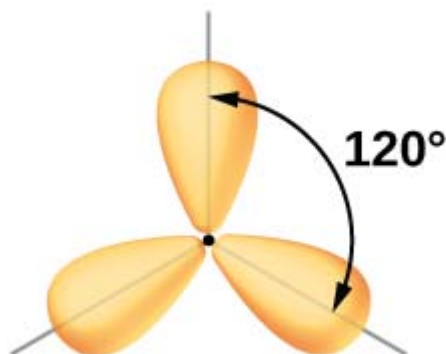
The hybridization of an s orbital (blue) and two p orbitals (red) produces three equivalent sp^2 hybridized orbitals (yellow) oriented at 120° with respect to each other. The remaining unhybridized p orbital is not shown here, but is located along the z axis.



Although quantum mechanics yields the “plump” orbital lobes as depicted in [Figure 21.9](#), sometimes for clarity these orbitals are drawn thinner and without the minor lobes, as in [Figure 21.10](#), 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.

Figure 21.10

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 21.11](#)). 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 21.12](#). 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 21.11

BH_3 is an electron-deficient molecule with a trigonal planar structure.

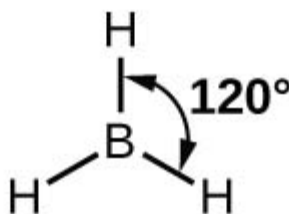
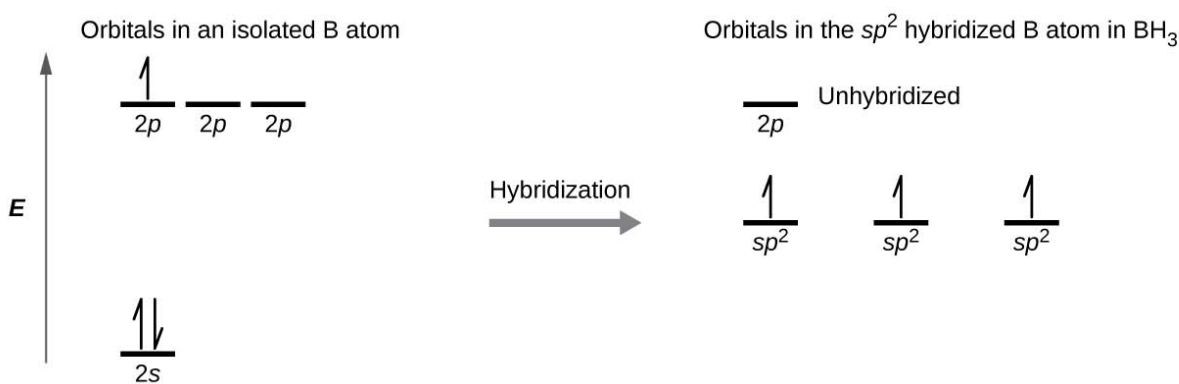


Figure 12.12

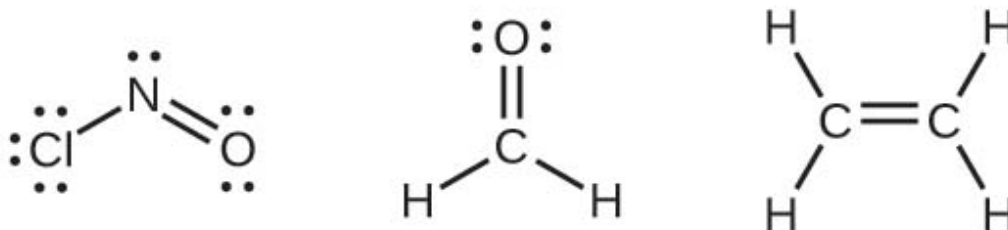
In an isolated B atom, there are one 2s and three 2p valence orbitals. When boron is in a molecule with three regions of electron density, three of the orbitals hybridize and create a set of three sp^2 orbitals and one unhybridized 2p orbital. The three half-filled hybrid orbitals each overlap with an orbital from a hydrogen atom to form three σ 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 ClNO (Figure 21.13), or molecules with two single bonds and a double bond connected to the central atom, as in formaldehyde, CH_2O , and ethene, H_2CCH_2 .

Figure 21.13

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.

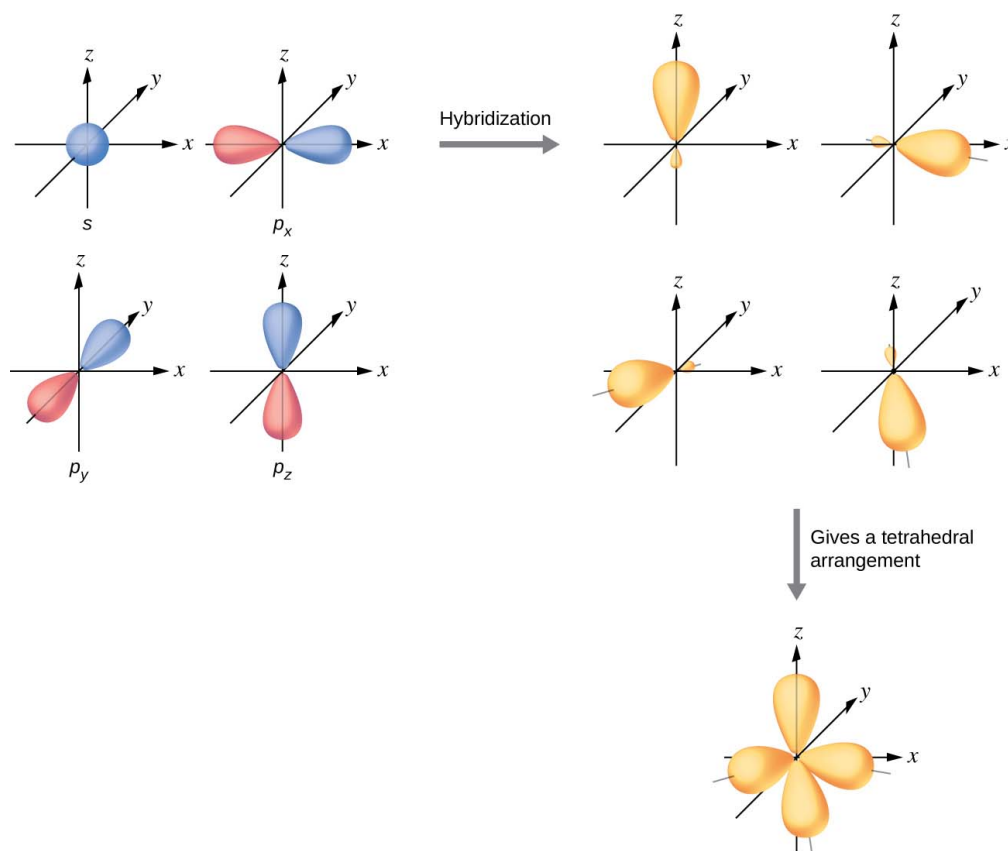


sp^3 Hybridization

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 21.14). Each of these hybrid orbitals points toward a different corner of a tetrahedron.

Figure 21.14

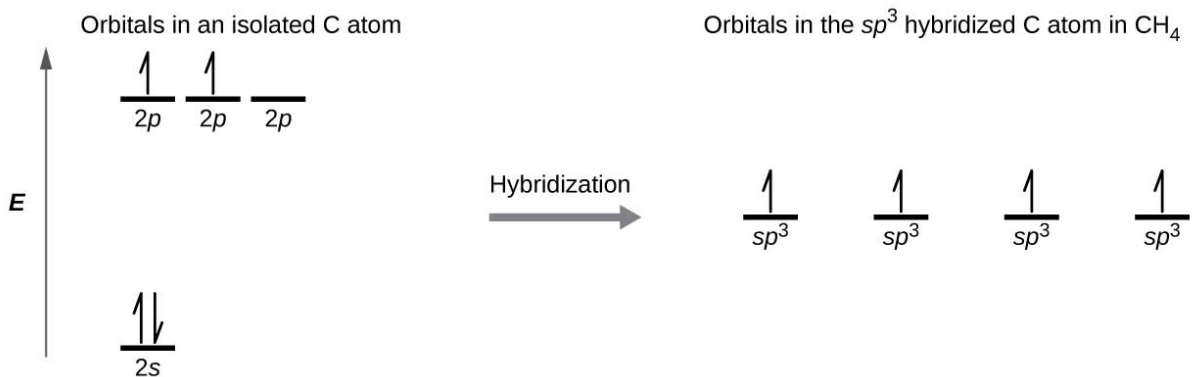
The hybridization of an s orbital (blue) and three p orbitals (red) produces four equivalent sp^3 hybridized orbitals (yellow) oriented at 109.5° with respect to each other.



A molecule of methane, CH_4 , consists of a carbon atom surrounded by four hydrogen atoms at the corners of a tetrahedron. The carbon atom in methane exhibits sp^3 hybridization. We illustrate the orbitals and electron distribution in an isolated carbon atom and in the bonded atom in CH_4 in [Figure 21.15](#). 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.

Figure 21.15

The four valence atomic orbitals from an isolated carbon atom all hybridize when the carbon bonds in a molecule like CH_4 with four regions of electron density. This creates four equivalent sp^3 hybridized orbitals. Overlap of each of the hybrid orbitals with a hydrogen orbital creates a C–H σ bond.

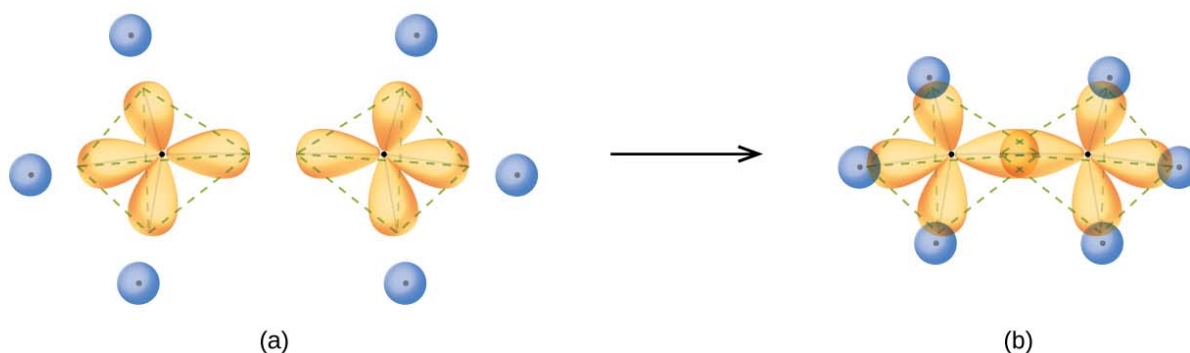


In a methane molecule, the $1s$ orbital of each of the four hydrogen atoms overlaps with one of the four sp^3 orbitals of the carbon atom to form a sigma (σ) bond. This results in the formation of four strong, equivalent covalent bonds between the carbon atom and each of the hydrogen atoms to produce the methane molecule, CH_4 .

The structure of ethane, C_2H_6 , 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 21.16). However, in ethane an sp^3 orbital of one carbon atom overlaps end to end with an sp^3 orbital of a second carbon atom to form a σ bond between the two carbon atoms. Each of the remaining sp^3 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 21.16. The orientation of the two CH_3 groups is not fixed relative to each other. Experimental evidence shows that rotation around σ bonds occurs easily.

Figure 21.16

(a) In the ethane molecule, C_2H_6 , each carbon has four sp^3 orbitals. (b) These four orbitals overlap to form seven σ bonds.



An sp^3 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 sp^3 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 .

sp^3d and sp^3d^2 Hybridization

To describe the five bonding orbitals in a trigonal bipyramidal arrangement, we must use five of the valence shell atomic orbitals (the s orbital, the three p orbitals, and one of the d orbitals), which gives five sp^3d hybrid orbitals. With an octahedral arrangement of six hybrid orbitals, we must use six valence shell atomic orbitals (the s orbital, the three p orbitals, and two of the d orbitals in its valence shell), which gives six sp^3d^2 hybrid orbitals. These hybridizations are only possible for atoms that have d orbitals in their valence subshells (that is, not those in the first or second period).

In a molecule of phosphorus pentachloride, PCl_5 , there are five P–Cl bonds (thus five pairs of valence electrons around the phosphorus atom) directed toward the corners of a trigonal bipyramid. We use the $3s$ orbital, the three $3p$ orbitals, and one of the $3d$ orbitals to form the set of five sp^3d hybrid orbitals (Figure 21.18) that are involved in the P–Cl bonds. Other atoms that exhibit sp^3d hybridization include the sulfur atom in SF_4 and the chlorine atoms in ClF_3 and in



(The electrons on fluorine atoms are omitted for clarity.)

Figure 21.17

The three compounds pictured exhibit sp^3d hybridization in the central atom and a trigonal bipyramidal form. SF_4 and ClF_4^+ have one lone pair of electrons on the central atom, and ClF_3 has two lone pairs giving it the T-shape shown.

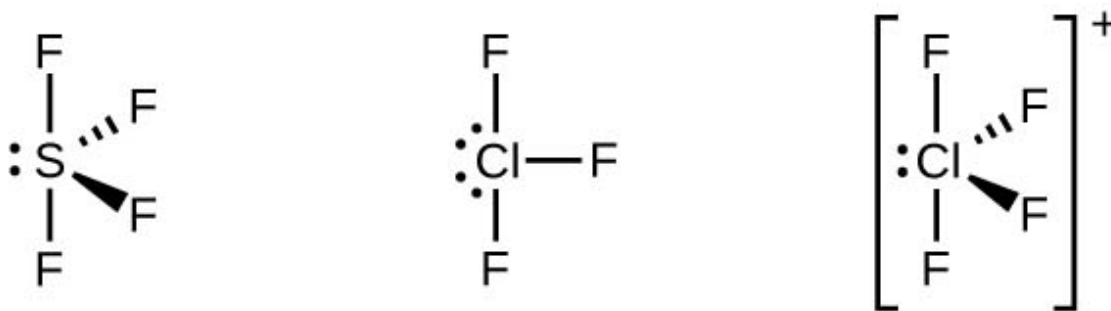
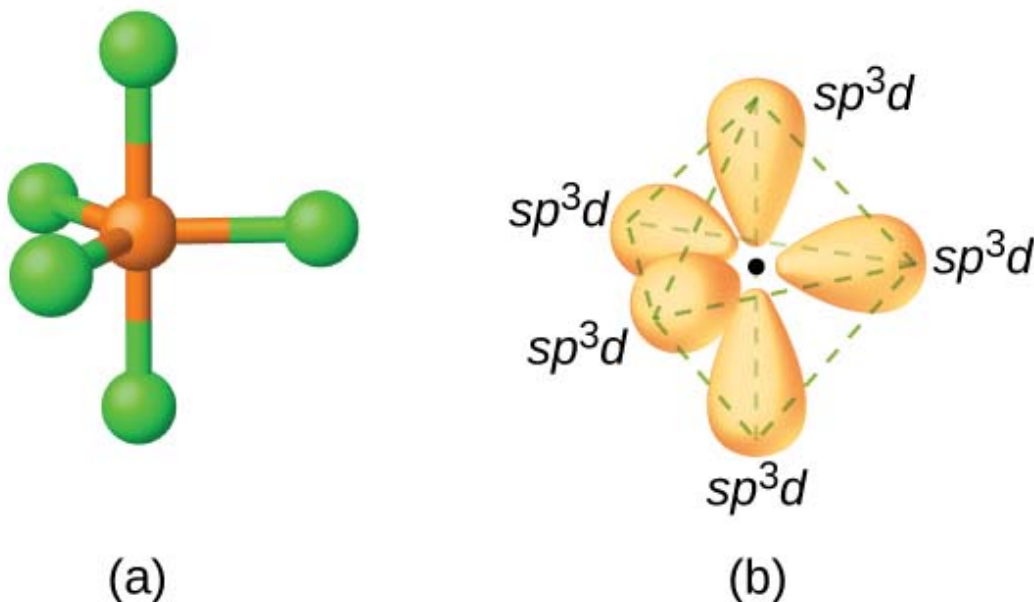


Figure 21.18

(a) The five regions of electron density around phosphorus in PCl_5 require five hybrid sp^3d orbitals. (b) These orbitals combine to form a trigonal bipyramidal structure with each large lobe of the hybrid orbital pointing at a vertex. As before, there are also small lobes pointing in the opposite direction for each orbital (not shown for clarity).



The sulfur atom in sulfur hexafluoride, SF_6 , exhibits sp^3d^2 hybridization. A molecule of sulfur hexafluoride has six bonding pairs of electrons connecting six fluorine atoms to a single sulfur atom. There are no lone pairs of electrons on the central atom. To bond six fluorine atoms, the $3s$ orbital, the three $3p$ orbitals, and two of the $3d$ orbitals form six equivalent sp^3d^2 hybrid orbitals, each directed toward a different corner of an octahedron. Other atoms that exhibit sp^3d^2 hybridization include the phosphorus atom in



the iodine atom in the interhalogens

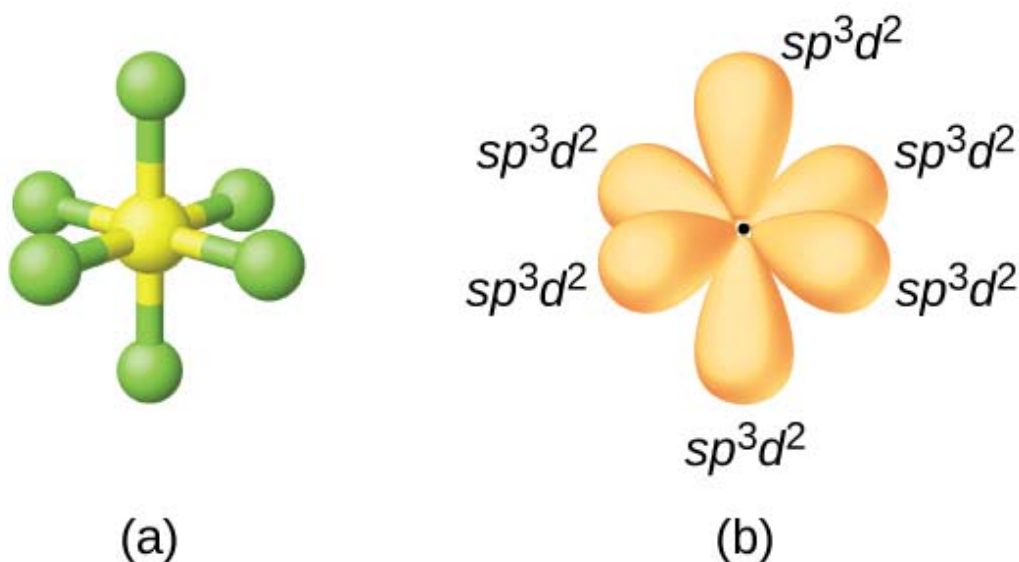




and the xenon atom in XeF_4 .

Figure 21.19

(a) Sulfur hexafluoride, SF_6 , has an octahedral structure that requires sp^3d^2 hybridization. (b) The six sp^3d^2 orbitals form an octahedral structure around sulfur. Again, the minor lobe of each orbital is not shown for clarity.



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 21.20](#). 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:

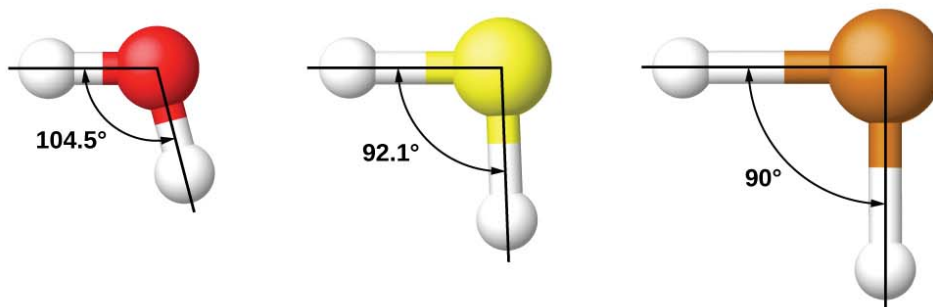
1. Determine the Lewis structure of the molecule.
2. Determine the number of regions of electron density around an atom using VSEPR theory, in which single bonds, multiple bonds, radicals, and lone pairs each count as one region.
3. Assign the set of hybridized orbitals from [Figure 21.20](#) that corresponds to this geometry.

Figure 21.20

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.

Regions of Electron Density	Arrangement		Hybridization	
2		linear	sp	
3		trigonal planar	sp^2	
4		tetrahedral	sp^3	
5		trigonal bipyramidal	sp^3d	
6		octahedral	sp^3d^2	

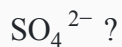
It is important to remember that hybridization was devised to rationalize experimentally observed molecular geometries. The model works well for molecules containing small central atoms, in which the valence electron pairs are close together in space. However, for larger central atoms, the valence-shell 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 H_2O , 104.5° , which is more consistent with sp^3 hybrid orbitals (109.5°) on the central atom than with $2p$ orbitals (90°). Sulfur is in the same group as oxygen, and H_2S 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 H_2Te , 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 21.3

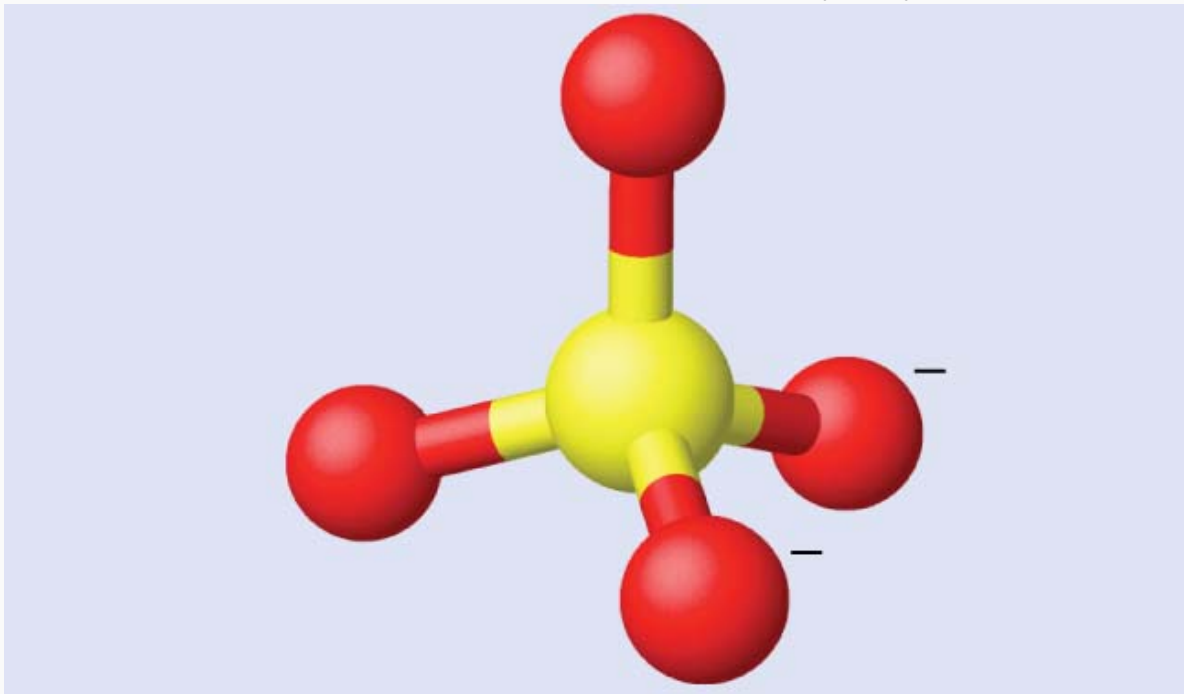
Assigning Hybridization

Ammonium sulfate is important as a fertilizer. What is the hybridization of the sulfur atom in the sulfate ion,



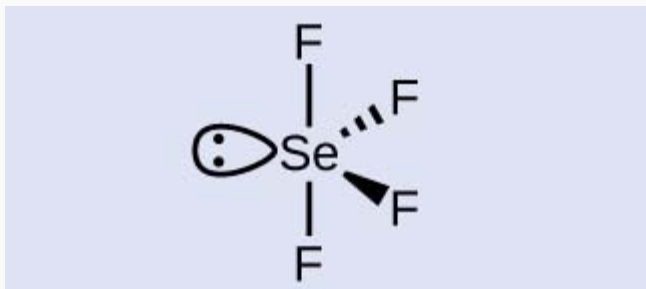
Solution

The Lewis structure of sulfate shows there are four regions of electron density. The hybridization is sp^3 .



Check Your Learning

What is the hybridization of the selenium atom in SeF_4 ?



Answer

The selenium atom is sp^3d hybridized.

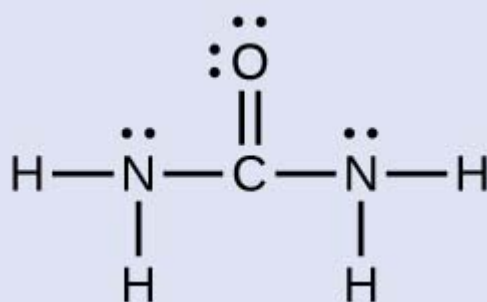
Example 21.4

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 the carbon atom in urea?

Solution

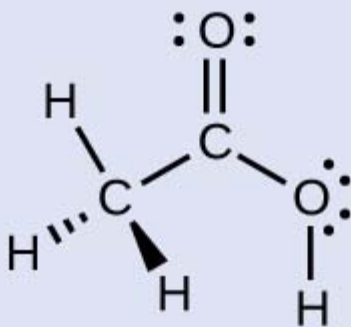
The Lewis structure of urea is



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 21.20), which is the hybridization of the carbon atom in urea.

Check Your Learning

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



Answer

H_3C , sp^3 ; $\text{C}(\text{O})\text{OH}$, sp^2

Link to Supplemental Exercises

[Supplemental exercises](#) are available if you would like more practice with these concepts.

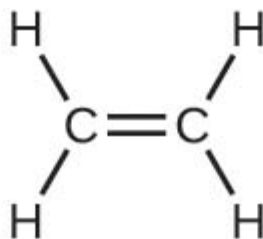
21.3 Multiple Bonds

Learning Objectives

By the end of this section, you will be able to:

- Describe multiple covalent bonding in terms of atomic orbital overlap
- Relate the concept of resonance to π -bonding and electron delocalization

The hybrid orbital model appears to account well for the geometry of molecules involving single covalent bonds. Is it also capable of describing molecules containing double and triple bonds? We have already discussed that multiple bonds consist of σ and π bonds. Next we can consider how we visualize these components and how they relate to hybrid orbitals. The Lewis structure of ethene, C_2H_4 , shows us that each carbon atom is surrounded by one other carbon atom and two hydrogen atoms.



The three bonding regions form a trigonal planar electron-pair geometry. Thus we expect the σ bonds from each carbon atom are formed using a set of sp^2 hybrid orbitals that result from hybridization of two of the $2p$ orbitals and the $2s$ orbital ([Figure 21.21](#)). These orbitals form the C–H single bonds and the σ bond in the



double bond ([Figure 21.22](#)). The π bond in the



double bond results from the overlap of the third (remaining) $2p$ orbital on each carbon atom that is not involved in hybridization. This unhybridized p orbital (lobes shown in red and blue in [Figure 21.22](#)) is perpendicular to the plane of the sp^2 hybrid orbitals. Thus the unhybridized $2p$ orbitals overlap in a side-by-side fashion, above and below the internuclear axis ([Figure 21.22](#)) and form a π bond.

Figure 21.21

In ethene, each carbon atom is sp^2 hybridized, and the sp^2 orbitals and the p orbital are singly occupied. The hybrid orbitals overlap to form σ bonds, while the p orbitals on each carbon atom overlap to form a π bond.

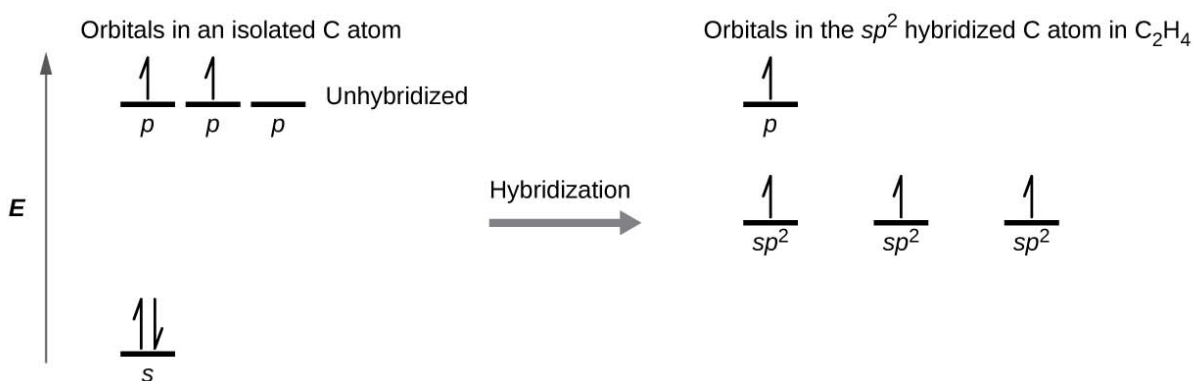
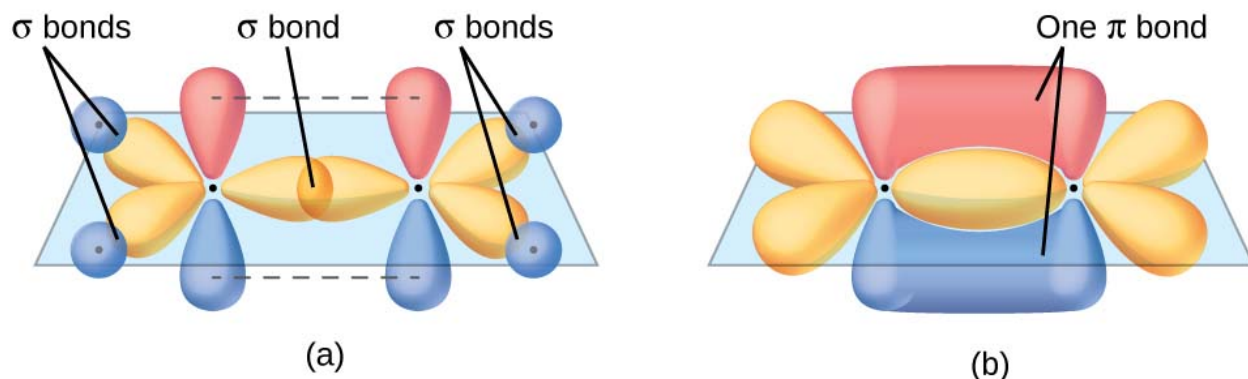


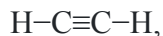
Figure 21.22

In the ethene molecule, C_2H_4 , there are (a) five σ bonds. One C–C σ bond results from overlap of sp^2 hybrid orbitals on the carbon atom with one sp^2 hybrid orbital on the other carbon atom. Four C–H bonds result from the overlap between the C atoms' sp^2 orbitals with s orbitals on the hydrogen atoms. (b) The π bond is formed by the side-by-side overlap of the two unhybridized p orbitals in the two carbon atoms. The two lobes of the π bond are above and below the plane of the σ system.



In an ethene molecule, the four hydrogen atoms and the two carbon atoms are all in the same plane. If the two planes of sp^2 hybrid orbitals tilted relative to each other, the p orbitals would not be oriented to overlap efficiently to create the π bond. The planar configuration for the ethene molecule occurs because it is the most stable bonding arrangement. This is a significant difference between σ and π bonds; rotation around single (σ) bonds occurs easily because the end-to-end orbital overlap does not depend on the relative orientation of the orbitals on each atom in the bond. In other words, rotation around the internuclear axis does not change the extent to which the σ bonding orbitals overlap because the bonding electron density is symmetric about the axis. Rotation about the internuclear axis is much more difficult for multiple bonds; however, this would drastically alter the off-axis overlap of the π bonding orbitals, essentially breaking the π bond.

In molecules with sp hybrid orbitals, two unhybridized p orbitals remain on the atom ([Figure 21.23](#)). We find this situation in acetylene,



which is a linear molecule. The sp hybrid orbitals of the two carbon atoms overlap end to end to form a σ bond between the carbon atoms ([Figure 21.24](#)). The remaining sp orbitals form σ bonds with hydrogen atoms. The two unhybridized p orbitals per carbon are positioned such that they overlap side by side and, hence, form two π bonds. The two carbon atoms of acetylene are thus bound together by one σ bond and two π bonds, giving a triple bond.

Figure 21.23

Diagram of the two linear sp hybrid orbitals of a carbon atom, which lie in a straight line, and the two unhybridized p orbitals at perpendicular angles.

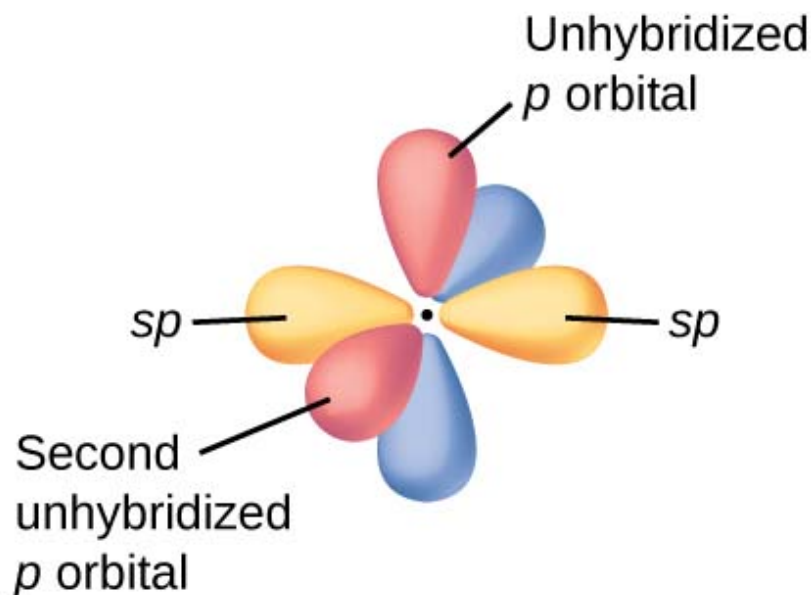
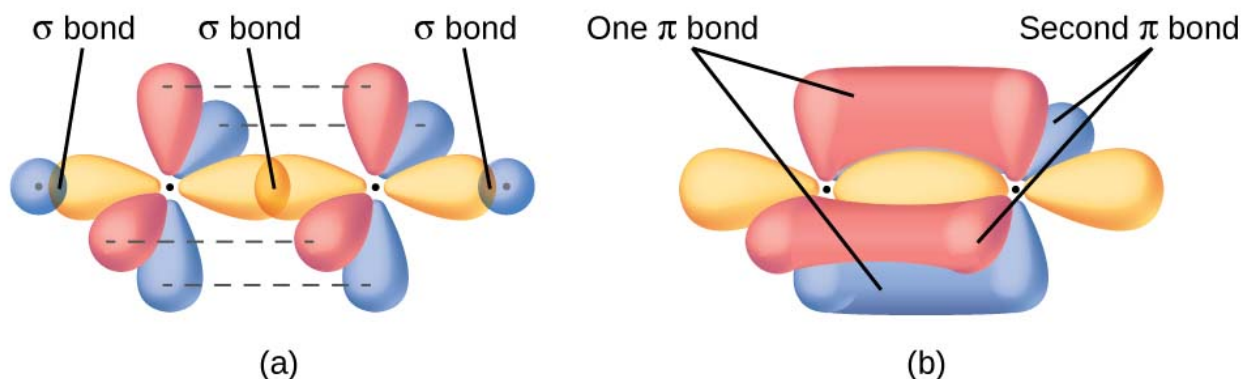


Figure 21.24

(a) In the acetylene molecule, C_2H_2 , there are two $C-H$ σ bonds and a $C\equiv C$ triple bond involving one $C-C$ σ bond and two $C-C$ π bonds. The dashed lines, each connecting two lobes, indicate the side-by-side overlap of the four unhybridized p orbitals. (b) This shows the overall outline of the bonds in C_2H_2 . The two lobes of each of the π bonds are positioned across from each other around the line of the $C-C$ σ bond.



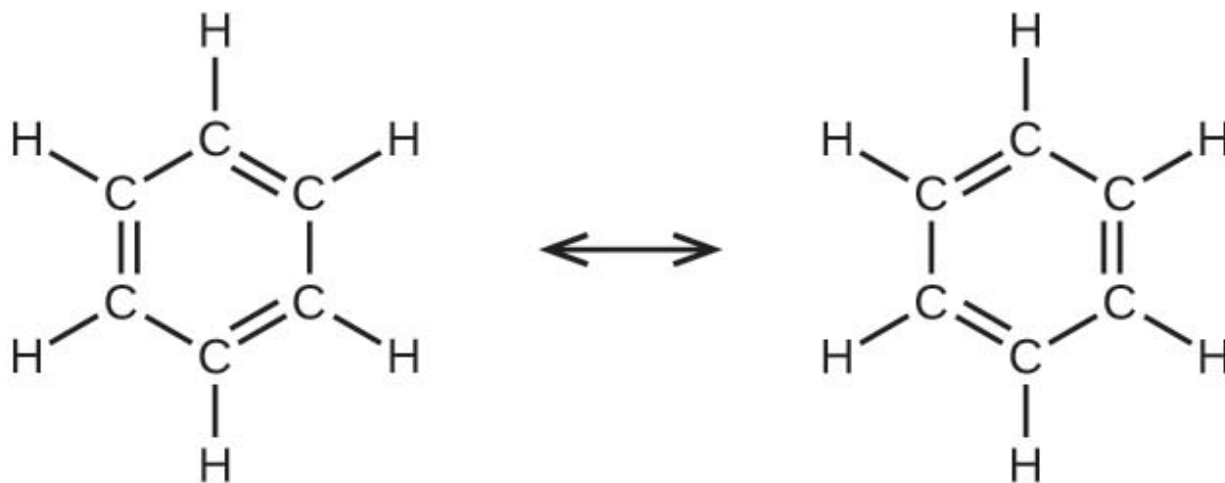
Hybridization involves only σ bonds, lone pairs of electrons, and single unpaired electrons (radicals). Structures that account for these features describe the correct hybridization of the atoms. However, many structures also include resonance forms. Remember that resonance forms occur when various arrangements of π bonds are possible. Since the arrangement of π bonds involves only the unhybridized orbitals, resonance does not influence the assignment of hybridization.

For example, molecule benzene has two resonance forms ([Figure 21.25](#)). We can use either of these forms to determine that each of the carbon atoms is bonded to three other atoms with no lone pairs, so the correct hybridization is sp^2 . The electrons in the unhybridized p orbitals form π bonds. Neither resonance structure completely describes the electrons in the π bonds. They are not located in one position or the other, but in reality are delocalized throughout the

ring. Valence bond theory does not easily address delocalization. Bonding in molecules with resonance forms is better described by molecular orbital theory. (See the next module.)

Figure 21.25

Each carbon atom in benzene, C_6H_6 , is sp^2 hybridized, independently of which resonance form is considered. The electrons in the π bonds are not located in one set of p orbitals or the other, but rather delocalized throughout the molecule.



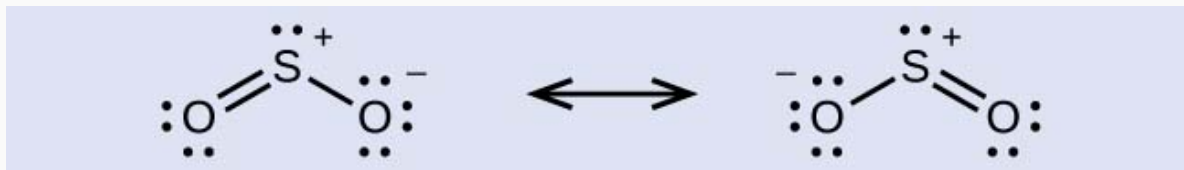
Example 21.5

Assignment of Hybridization Involving Resonance

Some acid rain results from the reaction of sulfur dioxide with atmospheric water vapor, followed by the formation of sulfuric acid. Sulfur dioxide, SO_2 , is a major component of volcanic gases as well as a product of the combustion of sulfur-containing coal. What is the hybridization of the S atom in SO_2 ?

Solution

The resonance structures of SO_2 are



The sulfur atom is surrounded by two bonds and one lone pair of electrons in either resonance structure. Therefore, the electron-pair geometry is trigonal planar, and the hybridization of the sulfur atom is sp^2 .

Check Your Learning

Another acid in acid rain is nitric acid, HNO_3 , which is produced by the reaction of nitrogen dioxide, NO_2 , with atmospheric water vapor. What is the hybridization of the nitrogen atom in NO_2 ? (Note: the lone electron on nitrogen occupies a hybridized orbital just as a lone pair would.)

Answer

sp^2

Link to Supplemental Exercises

[Supplemental exercises](#) are available if you would like more practice with these concepts.

Footnote

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.

Files

[Open in Google Drive](#)

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