In Chapter 8 we used Lewis structures to account for the formulas of covalent compounds. Lewis structures, however, do not indicate the shapes of molecules; they simply show the number and types of bonds. For example, the Lewis structure of $\text{CCl}_4$ tells us only that four Cl atoms are bonded to a central C atom:

The Lewis structure is drawn with the atoms all in the same plane, however, the actual arrangement is the Cl atoms at the corners of a tetrahedron, a geometric object with four corners and four faces, each an equilateral triangle.

Thus, the shape and size of $\text{CCl}_4$ are completely described by stating that the molecule is tetrahedral with bonds of length 1.78 Å.

The shape of a molecule is determined by its bond angles, the angles made by the lines joining the nuclei of the atoms in the molecule.

The bond angles of a molecule, together with the bond lengths, define the shape and size of the molecule. In the Figure, you should be able to see that the Cl-C-Cl bond angles in $\text{CCl}_4$ all have the same value of 109.5°, the angle size characteristic of a tetrahedron. In addition, all four Cl-C bonds are the same length (1.78 Å).
We begin our discussion of molecular shapes with molecules (and ions) that, like $\text{CCl}_4$, have a single central atom bonded to two or more atoms of the same type. Such molecules have the general formula $\text{AB}_n$ in which the central atom A is bonded to n B atoms. Both $\text{CO}_2$ and $\text{H}_2\text{O}$ are $\text{AB}_2$ molecules, for example, whereas $\text{SO}_3$ and $\text{NH}_3$ are $\text{AB}_3$ molecules, and so on.

The number of shapes possible for $\text{AB}_n$ molecules depends on the value of n. An $\text{AB}_2$ molecule must be either linear or bent. For $\text{AB}_3$ molecules, the two most common shapes place the B atoms at the corners of an equilateral triangle.

If the A atom lies in the same plane as the B atoms, the shape is trigonal planar.

If the A atom lies above the plane of the B atoms, the shape is trigonal pyramidal (a pyramid with an equilateral triangle as its base).

The $\text{NF}_3$ molecule is pyramidal because the three atoms bonded to nitrogen lie at the base of a trigonal pyramid.

In addition to the shapes we have already seen, there are five or six atoms surrounding a central atom. The trigonal bipyramid can be thought of as two face-to-face trigonal pyramids; the octahedron is like two face-to-face square pyramids.

Some $\text{AB}_3$ molecules, such as $\text{ClF}_3$, are T-shaped. The atoms lie in one plane, but the angles between them vary as shown. (bond angle = 180°)

Notice the difference between $\text{NF}_3$ and $\text{CCl}_4$. The $\text{CCl}_4$ molecule is tetrahedral because the four atoms bonded to the carbon are disposed at the four apexes (heads) of a tetrahedron around the central atom.
Some molecules have shapes other than those shown earlier, but we can usually derive the shape of those molecules from the previous figure. Neither trigonal pyramidal nor bent is shown in previous Figure, for instance, but removing atoms from the tetrahedral shape results in new shapes.

In addition to tetrahedral, other common shapes for $\text{AB}_4$ and $\text{AB}_5$ molecules are square-planar and square pyramid. In $\text{AB}_4$, all five atoms lie in the same plane, with the B atoms at the corners of a square and the A atom at the center of the square.

In $\text{AB}_5$, four B atoms lie in the same plane with A, the B atoms are located at the corners of a square and a fifth B atom lies at the top corner of the pyramid.
Why do so many $AB_n$ molecules have shapes related to those shown in previous Figure? Can we predict these shapes?

When $A$ is a representative element (one from the $s$ block or $p$ block of the periodic table), we can answer these questions by using the valence-shell electron-pair repulsion (VSEPR) model. Although the name is rather imposing, the model is quite simple.

THE VSEPR MODEL

Imagine tying two identical balloons together at their ends. The two balloons naturally orient themselves to point away from each other; that is, they try to "get out of each other's way" as much as possible. If we add a third balloon, the balloons orient themselves toward the vertices of an equilateral triangle, and if we add a fourth balloon, they adopt a tetrahedral shape. We see that an optimum geometry exists for each number of balloons.

In some ways, the electrons in molecules behave like these balloons. We have seen that a single covalent bond is formed between two atoms when a pair of electrons occupies the space between the atoms. A bonding pair of electrons thus defines a region in which the electrons are most likely to be found. We will refer to such a region as an electron domain.

Likewise, a nonbonding pair (or lone pair) of electrons defines an electron domain that is located principally on one atom. For example, the Lewis structure of $\text{NH}_3$ has four electron domains around the central nitrogen atom (three bonding pairs, represented as usual by short lines, and one nonbonding pair, represented by dots):

\[
\text{H} \equiv \text{N} \equiv \text{H} \quad \text{H}
\]

Two balloons linear orientation

Three balloons trigonal-planar orientation

Four balloons tetrahedral orientation

In some ways, the electrons in molecules behave like these balloons. We have seen that a single covalent bond is formed between two atoms when a pair of electrons occupies the space between the atoms. A bonding pair of electrons thus defines a region in which the electrons are most likely to be found. We will refer to such a region as an electron domain.

Likewise, a nonbonding pair (or lone pair) of electrons defines an electron domain that is located principally on one atom. For example, the Lewis structure of $\text{NH}_3$ has four electron domains around the central nitrogen atom (three bonding pairs, represented as usual by short lines, and one nonbonding pair, represented by dots):
The VSEPR model is based on the idea that electron domains are negatively charged and, therefore, repel one another.

Electron domains try to stay out of one another’s way. The best arrangement of a given number of electron domains is the one that minimizes the repulsions among them.

Like the balloons, two electron domains orient linearly, three domains orient in a trigonal-planar fashion, and four orient tetrahedrally.

The arrangement of electron domains around the central atom of an $AB_n$ molecule or ion is called its electron-domain geometry. In contrast, the molecular geometry is the arrangement of only the atoms in a molecule or ion, any nonbonding pairs in the molecule are not part of the description of the molecular geometry.

In determining the shape of any molecule, we first draw the Lewis structure, then use the VSEPR model to predict the electron-domain geometry. From knowing how many of the domains are due to nonbonding pairs, we can then predict the molecular geometry. When all the electron domains in a molecule arise from bonds, the molecular geometry is identical to the electron-domain geometry.

When, however, one or more domains involve nonbonding pairs of electrons, we must remember to ignore those domains when talking about molecular shape.
We can generalize the steps we follow in using the VSEPR model to predict the shapes of molecules or ions:

1. **Draw the Lewis structure of the molecule or ion, and count the number of electron domains around the central atom.** Each nonbonding electron pair, each single bond, each double bond, and each triple bond counts as one electron domain.

2. **Determine the electron-domain geometry by arranging the electron domains about the central atom so that the repulsions among them are minimized (this results in one of the basic geometries).**

3. **Use the arrangement of the bonded atoms to determine the molecular geometry.**

The Figure below shows how these steps are applied to predict the geometry of the NH₃ molecule. The three bonds and one nonbonding pair in the Lewis structure tell us we have four electron domains.

We know from Table that the repulsions among four electron domains are minimized when the domains point toward the vertices of a tetrahedron, so the electron-domain geometry of NH₃ is tetrahedral.

We know from the Lewis structure that one electron domain holds a nonbonding pair of electrons, which occupies one of the four vertices of the tetrahedron. The bonding arrangement is therefore three atoms bonded to a central atom, with the central atom not in the same plane as the three others.

Hence, the molecular geometry of NH₃ is trigonal pyramidal.

Notice that the tetrahedral arrangement of the four electron domains leads us to predict the trigonal-pyramidal molecular geometry.

Because the trigonal-pyramidal molecular geometry is based on a tetrahedral electron-domain geometry, the ideal bond angles are 109.5°. Bond angles deviate from ideal values when the surrounding atoms and electron domains are not identical.
As one more example, let’s determine the shape of the CO$_2$ molecule. Its Lewis structure reveals two electron domains (each one a double bond) around the central carbon:

\[ \text{O} \equiv \text{C} \equiv \text{O} \]

Two electron domains around the central C atom orient in a linear electron-domain geometry. Because neither domain is a nonbonding pair of electrons, the molecular geometry is also linear, and the bond angle is 180°.

A summary of the possible molecular geometries when an AB$_n$ molecule has four or fewer electron domains around A is shown below. These geometries are important because they include all the shapes usually seen in molecules or ions that obey the octet rule.

---

**Use the VSEPR model to predict the molecular geometry of (a) O$_3$, (b) SnCl$_3$.**

Because of resonance, the bonds between the central O atom and the outer O atoms are of equal length. In both resonance structures the central O atom is bonded to the two outer O atoms and has one nonbonding pair.

Thus, there are three electron domains around the central O atoms. (Remember that a double bond counts as a single electron domain). The arrangement of three electron domains is trigonal planar. Two of the domains are from bonds, and one is due to a nonbonding pair. So, the molecule has a bent shape with an ideal bond angle of 120°.
(b) Molecular geometry of SnCl$_3^-$

The Lewis structure shows that the central Sn atom is bonded to the three Cl atoms and has one nonbonding pair; thus, we have four electron domains, meaning tetrahedral electron-domain geometry with one vertex occupied by a nonbonding pair of electrons.

Tetrahedral electron-domain geometry with three bonding and one nonbonding domains means the molecular geometry is trigonal pyramidal.

Predict the electron-domain and molecular geometries for (a) SeCl$_2^-$, (b) CO$_3^{2-}$.

Drawing Lewis structure for SeCl$_2^-$ gives:

a. 4 electron domains around Se suggests a tetrahedral electron domain geometry. Since there are two lone e pairs a bent molecular geometry is obtained.

Drawing Lewis structure for CO$_3^{2-}$ gives:

b. The Lewis structure for CO$_3^{2-}$ gives three electron domains, with no nonbonding electrons on the central C atom. This results in a trigonal planar electron domain and molecular geometry.
Effect of Nonbonding Electrons and Multiple Bonds on Bond Angles

We can refine the VSEPR model to explain slight distortions from the ideal geometries. For example, consider methane (CH$_4$), ammonia (NH$_3$), and water (H$_2$O). All three have a tetrahedral electron-domain geometry, but their bond angles differ slightly:

Notice that the bond angles decrease as the number of nonbonding electron pairs increases. A bonding pair of electrons is attracted by both nuclei of the bonded atoms, but a nonbonding pair is attracted primarily by only one nucleus. Because a nonbonding pair experiences less nuclear attraction, its electron domain is spread out more in space than is the electron domain for a bonding pair.

Nonbonding electron pairs therefore take up more space than bonding pairs. As a result, electron domains for nonbonding electron pairs exert greater repulsive forces on adjacent electron domains and tend to compress bond angles.

Because three electron domains surround the central atom, we might expect a trigonal-planar geometry with 120° bond angles. The double bond, however, seems to act much like a nonbonding pair of electrons, reducing the Cl-C-Cl bond angle to 111.4°.

In general, electron domains for multiple bonds exert a greater repulsive force on adjacent electron domains than do electron domains for single bonds.

Because multiple bonds contain a higher electronic-charge density than single bonds, multiple bonds also represent enlarged electron domains. Consider the Lewis structure of phosgene:
One resonance structure of the nitrate ion is:

\[
\begin{align*}
\text{NO}_3^- & \quad \text{Nitrate Ion} \\
\end{align*}
\]

The bond angles are $120^\circ$. Is this observation consistent with the preceding discussion of the effect of multiple bonds on bond angles?

No, because electron domains for multiple bonds exert a greater repulsive force on adjacent electron domains than do electron domains for single bonds, thus the N-O-N angle should be less than $120^\circ$ while the two O-N-O should be greater than $120^\circ$.

It should be noted that the bond angle, however, is $120^\circ$ since resonance makes all bonds between N and O the same.
Molecules with Expanded Valence Shells

Atoms from period 3 and beyond may be surrounded by more than four electron pairs. Molecules with five or six electron domains around the central atom have molecular geometries based on either a trigonal-bipyramidal (five domains) or octahedral (six domains) electron-domain geometry.

The most stable electron-domain geometry for five electron domains is the trigonal bipyramid (two trigonal pyramids sharing a base).
Suppose a molecule has five electron domains, and there are one or more nonbonding pairs. Will the domains from the nonbonding pairs occupy axial or equatorial positions?

To answer this question, we must determine which location minimizes repulsion between domains. Repulsion between two domains is much greater when they are situated $90^\circ$ from each other than when they are at $120^\circ$. An equatorial domain is $90^\circ$ from only two other domains (the axial domains), but an axial domain is $90^\circ$ from three other domains (the equatorial domains). Hence, an equatorial domain experiences less repulsion than an axial domain. Because the domains from nonbonding pairs exert larger repulsions than those from bonding pairs, nonbonding domains always occupy the equatorial positions in a trigonal bipyramid.

The most stable electron-domain geometry for six electron domains is the octahedron. An octahedron is a polyhedron with six vertices and eight faces, each an equilateral triangle. An atom with six electron domains around it can be visualized as being at the center of the octahedron with the electron domains pointing toward the six vertices. All bond angles are $90^\circ$, and all six vertices are equivalent. Therefore, if an atom has five bonding electron domains and one nonbonding domain, we can put the nonbonding domain at any of the six vertices of the octahedron. The result is always a square-pyramidal molecular geometry.

When there are two nonbonding electron domains, however, their repulsions are minimized by pointing them toward opposite sides of the octahedron, producing a square-planar molecular geometry.
Use the VSEPR model to predict the molecular geometry of SF$_4$.

First draw the Lewis structure for SF$_4$ and find the number of electron domains around the central atom:

The sulfur has five electron domains around it: four from the bonds and one from the nonbonding pair. Each domain points toward a vertex (highest point) of a trigonal bipyramid. The domain from the nonbonding pair will point toward an equatorial position. The four bonds point toward the remaining four positions, resulting in a molecular geometry that is described as seesaw-shape.
Use the VSEPR model to predict the molecular geometry of IF₅.
First, draw Lewis structure:
The iodine has six electron domains around it, one of which is nonbonding. The electron-domain geometry is therefore octahedral, with one position occupied by the nonbonding pair, and the molecular geometry is square pyramidal:

Predict the electron-domain and molecular geometries of BrF₃.
Lewis structure of BrF₃ shows that there are 5 electron domains, three bonds and two pairs of electrons, which makes it a trigonal bipyramid. This results in a T-shaped geometry.
Predict the electron-domain and molecular geometries of \( \text{ICl}_4^- \).

Lewis structure of \( \text{ICl}_4^- \) shows that there are 6 electron domains, four bonds and two pairs of electrons, which makes it an octahedral. This results in a square planar geometry.
Shapes of Larger Molecules

Although the molecules and ions we have considered contain only a single central atom, the VSEPR model can be extended to more complex molecules. For the acetic acid molecule (CH$_3$COOH), for example, we can use the VSEPR model to predict the geometry about each atom: The left C has four electron domains (all bonding), and so the electron-domain and molecular geometries around that atom are both tetrahedral. The central C has three electron domains (counting the double bond as one domain), making both the electron-domain and the molecular geometries trigonal planar.

Eye drops for dry eyes usually contain a water-soluble polymer called poly(vinyl alcohol), which is based on the monomeric organic molecule, vinyl alcohol:

Predict the approximate values for the H-O-C and O-C-C bond angles in vinyl alcohol.
Predict the H-C-H and C-C-C bond angles in propyne, CH$_3$CCH.

The O atoms have four electron domains, which is a tetrahedral, however two of the domains are nonbonding pairs and thus the geometry H-O-C is bent. Each carbon has three electron domains resulting in trigonal planar geometry for each carbon. The bond angle in H-O-C is less than $109.5^\circ$ and that for H-C-H is less than $120^\circ$ due to double bond domain, while C=C-H and C=C-O are more than $120^\circ$. 
MOLECULAR SHAPE AND MOLECULAR POLARITY

Recall that bond polarity is a measure of how equally the electrons in a bond are shared between the two atoms of the bond. As the difference in electronegativity between the two atoms increases, so does the bond polarity.

We saw that the dipole moment of a diatomic molecule is a measure of the amount of charge separation in the molecule. For a molecule consisting of more than two atoms, the dipole moment depends on both the polarities of the individual bonds and the geometry of the molecule. For each bond in the molecule, we consider the bond dipole, which is the dipole moment due only to the two atoms in that bond.

The bond dipoles, like the numbers, “cancel” each other. Therefore, the dipole moment of CO₂ is zero, even though the individual bonds are polar. The geometry of the molecule dictates that the overall dipole moment be zero, making CO₂ a nonpolar molecule.

Bond dipoles and dipole moments are vector quantities; that is, they have both a magnitude and a direction. The dipole moment of a polyatomic molecule is the vector sum of its bond dipoles. Both the magnitudes and the directions of the bond dipoles must be considered when summing vectors.

The two bond dipoles in CO₂, although equal in magnitude, are opposite in direction. Adding them is the same as adding two numbers that are equal in magnitude but opposite in sign. However, the compound O=C=S has different bond dipoles and thus a net dipole (in the direction of O, since it is more electronegative.)
Heterodiatomic molecules, like H-Cl, are polar, while homodiatomic and molecules in which the central atom is symmetrically surrounded by identical atoms (BF$_3$ and CCl$_4$) are nonpolar.

H$_2$O is a bent molecule with two polar bonds. Again, the two bonds are identical, and the bond dipoles are equal in magnitude. Because the molecule is bent, however, the bond dipoles do not directly oppose each other and therefore do not cancel. Hence, the H$_2$O molecule has an overall non-zero dipole moment ($\mu = 1.85$ D) and is therefore a polar molecule. The oxygen atom carries a partial negative charge, and the hydrogen atoms each have a partial positive charge.

For AB$_n$ molecules in which all the B atoms are the same, certain symmetrical shapes—linear (like CO$_2$ and BeF$_2$, AB$_2$), trigonal planar (like BF$_3$, AB$_3$), tetrahedral (like CCl$_4$, AB$_4$), and square planar (like XeF$_4$, AB$_4$), trigonal bipyramidal (like PCl$_5$, AB$_5$), and octahedral (like SF$_6$, AB$_6$)—must lead to nonpolar molecules even though the individual bonds might be polar. However, when some B is exchanged with other atoms or nonbonding electron pairs, the molecule may become polar.
Predict whether these molecules are polar or nonpolar: (a) BrCl, (b) SO$_2$, (c) SF$_6$.

a. Br-Cl is a polar molecule since Cl is more electronegative than Br.

b. For SO$_2$, we should draw Lewis structure and determine the geometry. Doing so gives 3 electron domains around S, one of these domains is a lone pair of e’s. Therefore, SO$_2$ has a bent geometry. The dipoles of S-O point differently, thus SO$_2$ is polar.

c. Drawing Lewis structure for SF$_6$ suggests 6 electron domains around S (6 single bonds) indicating a symmetric octahedral geometry, which is nonpolar.

Determine whether the following molecules are polar or nonpolar: (a) NF$_3$, (b) BCl$_3$.

(a) Drawing Lewis structure for NF$_3$ shows 4 electron domains, one of them is a nonbonding electron pair. Therefore, NF$_3$ is polar because polar bonds are arranged in a trigonal-pyramidal geometry.

(b) Drawing Lewis structure for BCl$_3$ shows 3 electron domains, surrounding the B atom (3 single bonds). Therefore, BCl$_3$ is nonpolar because polar bonds are arranged in a trigonal-planar geometry.

The sum of these is zero.

Valence Bond Theory: Orbital Overlap

In Lewis theory, covalent bonding occurs when atoms share electrons because the sharing concentrates electron density between the nuclei.

The mixing of Lewis’s notion of electron-pair bonds and the idea of atomic orbitals leads to a model of chemical bonding, called valence-bond theory.

In valence-bond theory, we visualize the buildup of electron density between two nuclei as occurring when a valence atomic orbital of one atom shares space, or overlaps, with a valence atomic orbital of another atom.

The overlap of orbitals allows two electrons of opposite spin to share the space between the nuclei, forming a covalent bond.
In HCl, for example, chlorine has the electron configuration [Ne]3s\(^2\)3p\(^5\). All the valence orbitals of chlorine are full except one 3p orbital, which contains a single electron. This 3p electron is paired to the single 1s electron of H to form a covalent bond.

Because the other two chlorine 3p orbitals are already filled with a pair of electrons, they do not participate in the bonding to hydrogen. Likewise, we can explain the covalent bond in Cl\(_2\) in terms of the overlap of the singly occupied 3p orbital of one Cl atom with the singly occupied 3p orbital of another.

There is always an optimum distance between the two nuclei in any covalent bond. When H\(_2\) atoms are infinitely far apart, they do not “feel” each other and so the energy approaches zero. As the distance between the atoms decreases, the overlap between their 1s orbitals increases.

Because of the resultant increase in electron density between the nuclei, the potential energy of the system decreases. That is, the strength of the bond increases, as shown by the decrease in the potential energy of the two-atom system.
HYBRID ORBITALS

The VSEPR model, simple as it is, does a surprisingly good job at predicting molecular shape, despite the fact that it has no obvious relationship to the filling and shapes of atomic orbitals.

For example, based on the shapes and orientations of the 2s and 2p orbitals on a carbon atom, it is not obvious why a CH$_4$ molecule rather than a CH$_2$ should form, and why a CH$_4$ molecule has a tetrahedral geometry. How can we interpret the fact that all covalent bonds formed from overlap of atomic orbitals are identical and indistinguishable?

However, as the atoms come closer together than the bond length, the energy increases sharply. This increase, which becomes significant at short internuclear distances, is due mainly to the electrostatic repulsion between the nuclei. The internuclear distance, or bond length, is the distance that corresponds to the minimum of the potential-energy curve.

The potential energy at this minimum corresponds to the bond strength. Thus, the observed bond length is the distance at which the attractive forces between unlike charges (electrons and nuclei) are balanced by the repulsive forces between like charges (electron-electron and nucleus-nucleus).

---

**Element** | **Configuration** | **Orbital Notation**
--- | --- | ---
H | 1s$^1$ | 1
He | 1s$^2$ | 1 1
Li | 1s$^2$2s$^1$ | 1 1
Be | 1s$^2$2s$^2$ | 1 1 1
B | 1s$^2$2s$^2$2p$^1$ | 1 1 1 1
C | 1s$^2$2s$^2$2p$^2$ | 1 1 1 1
N | 1s$^2$2s$^2$2p$^3$ | 1 1 1 1 1
O | 1s$^2$2s$^2$2p$^4$ | 1 1 1 1 1
To begin with, we recall that atomic orbitals are mathematical functions that come from the quantum mechanical model for atomic structure. To explain molecular geometries, we can assume that the atomic orbitals on an atom (usually the central atom) mix to form new orbitals called hybrid orbitals.

The shape of any hybrid orbital is different from the shapes of the original atomic orbitals. The process of mixing atomic orbitals is a mathematical operation called hybridization. The total number of atomic orbitals on an atom remains constant, so the number of hybrid orbitals on an atom equals the number of atomic orbitals that are mixed.

Hybridization of atomic orbitals
- Without modifications the VB theory predicts bond angles of 90° at the central atom of polyatomic molecules such as H₂O, NH₃ and CH₄ which is inconsistent with the experiment.

The orbital diagram for a ground-state Be atom is:

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1s</td>
<td>2s</td>
<td>2p</td>
</tr>
</tbody>
</table>

Because it has no unpaired electrons, the Be atom in its ground state cannot bond with the fluorine atoms. The Be atom could form two bonds, however, by "promoting" one of the 2s electrons to a 2p orbital:

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1s</td>
<td>2s</td>
<td>2p</td>
</tr>
</tbody>
</table>

The Be atom now has two unpaired electrons and can therefore form two polar covalent bonds with F atoms.

sp Hybrid Orbitals
To illustrate the process of hybridization, consider the BeF₂ molecule, which has the Lewis structure:

The VSEPR model correctly predicts that BeF₂ is linear with two identical B-F bonds. How can we use valence-bond theory to describe the bonding? The electron configuration of F (1s²2s²2p³) indicates an unpaired electron in a 2p orbital. This electron can be paired with an unpaired Be electron to form a polar covalent bond. Which orbitals on the Be atom, however, overlap with those on the F atoms to form the B-F bonds?
The two bonds would not be identical, however, because a Be 2s orbital would be used to form one of the bonds and a 2p orbital would be used to form the other. Therefore, although the promotion of an electron allows two bonds to form, we still have not explained the structure of BeF$_2$.

We can solve this dilemma by “mixing” the 2s orbital with one 2p orbital to generate two new orbitals.

Like p orbitals, each new orbital has two lobes. Unlike p orbitals, however, one lobe is much larger than the other. The two new orbitals are identical in shape, but their large lobes point in opposite directions. These two new orbitals are hybrid orbitals. Because we have hybridized one s and one p orbital, we call each hybrid an sp hybrid orbital. According to the valence-bond model, a linear arrangement of electron domains implies sp hybridization.

The remaining two 2p atomic orbitals of Be remain unhybridized and are vacant. Remember also that each fluorine atom has two other valence p atomic orbitals, each containing one nonbonding electron pair.

For the Be atom of BeF$_2$, we write the orbital diagram for the formation of two sp hybrid orbitals as:

The electrons in the sp hybrid orbitals can form bonds with the two fluorine atoms. Because the sp hybrid orbitals are equivalent but point in opposite directions, BeF$_2$ has two identical bonds and a linear geometry.
**sp² and sp³ Hybrid Orbitals**

Whenever we mix a certain number of atomic orbitals, we get the same number of hybrid orbitals. Each hybrid orbital is equivalent to the others but points in a different direction.

Thus, mixing one 2s and one 2p atomic orbital yields two equivalent sp hybrid orbitals that point in opposite directions. Other combinations of atomic orbitals can be hybridized to obtain different geometries. In BF₃, for example, mixing the one 2s and two of the 2p atomic orbitals yields three equivalent sp² (pronounced "s-p-two") hybrid orbitals.

The three sp² hybrid orbitals lie in the same plane, 120° apart from one another. They are used to make three equivalent bonds with the three fluorine atoms, leading to the trigonal-planar molecular geometry of BF₃. Notice that an unfilled 2p atomic orbital remains unhybridized.
An s atomic orbital can also mix with all three p atomic orbitals in the same subshell. For example, the carbon atom in CH₄ forms four equivalent bonds with the four hydrogen atoms. We envision this process as resulting from the mixing of the 2s and all three 2p atomic orbitals of carbon to create four equivalent sp³ (pronounced "s-p-three") hybrid orbitals.

Each sp³ hybrid orbital has a large lobe that points toward one vertex of a tetrahedron. These hybrid orbitals can be used to form two-electron bonds by overlap with the atomic orbitals of an atom, such as H.
The bonding in molecules containing nonbonding pairs of electrons.

In H$_2$O, the electron-domain geometry around the central O atom is approximately tetrahedral. Thus, the four electron pairs can be envisioned as occupying sp$^3$ hybrid orbitals. Two of the hybrid orbitals contain nonbonding pairs of electrons, and the other two form bonds with the hydrogen atoms.

So far our discussion of hybridization has extended only to period 2 elements, specifically carbon, nitrogen, and oxygen. The elements of period 3 and beyond introduce a new consideration because in many of their compounds these elements have more than an octet of electrons in the valence shell.

How do we analyze the bonding in compounds such as PCl$_5$, SF$_6$, or BrF$_5$? The use of only s and p orbitals on the central atom limits us to four hybrid orbitals, yet in these compounds the central atom is involved in bonding to five or six other atoms.
For such elements, the number of hybrid orbitals formed could be increased by including valence-shell d orbitals. For example, to explain the bonding in SF$_6$ we could include two sulfur 3d orbitals in addition to the 3s and three 3p orbitals.

These six atomic orbitals could make six hybrid orbitals, but there are other factors involved in hybridization than simply finding a set of orbitals that point in the right directions; we must also consider orbital energies.

The sulfur 3d orbitals lie substantially higher in energy than the 3s and 3p orbitals. The amount of energy needed to form the six hybrid orbitals is greater than the amount returned by forming bonds with the six fluorine atoms.

Theoretical calculations seem to show that the sulfur 3d orbitals do not participate to a significant degree in the bonding between sulfur and the six fluorine atoms.

The valence-bond model we have developed for period 2 elements works well for compounds of period 3 elements so long as we have no more than an octet of electrons in the valence-shell orbitals. Thus, for example, it is appropriate to discuss the bonding in PF$_3$ or H$_2$Se in terms of hybrid s and p orbitals on the central atom. However, the model turns out not to be appropriate when there is more than an octet of electrons around the central atom.

How then do we account for the bonding in SF$_6$ and other compounds of the main group elements in which the central atom has more than an octet of valence electrons? We will not elaborate on the bonding theory for such molecules, fortunately, the VSEPR model, although it does not explain the bonding in such molecules, can accurately predict their geometries.
Molecular Geometry and Bonding Theories (3)
Lecture 27

Can a NCl₅ molecule exist?
Nitrogen is in the same Group of the Periodic Table as phosphorus, and you might expect it to form a similar range of compounds. In fact, it doesn’t. For example, the compound NCl₃ exists, but there is no such thing as NCl₅.
Nitrogen is 1s²2s²2pₓ¹2pᵧ¹2pᶻ¹. The reason that NCl₅ doesn’t exist is that in order to form five bonds, the nitrogen would have to promote one of its 2s electrons. The problem is that there aren’t any 2d orbitals to promote an electron into - and the energy gap to the next level (the 3s) is far too great.

Hybrid Orbital Summary
Overall, hybrid orbitals provide a convenient model for using valence-bond theory to describe covalent bonds in molecules in which the molecular geometry conforms to the electron-domain geometry predicted by the VSEPR model. When we know the electron-domain geometry we can employ hybridization to describe the atomic orbitals used by the central atom in bonding.

To obtain the bonding description of any atom in a molecule, you proceed as follows:
1. Write the Lewis electron-dot formula for the molecule.
2. From the Lewis formula, use the VSEPR theory to determine the electron domain geometry.
3. From the geometric arrangement of the electron pairs, obtain the hybridization type.
4. Assign valence electrons to the hybrid orbitals of this atom one at a time, pairing only when necessary.
5. Form bonds to this atom by overlapping singly occupied orbitals of other atoms with the singly occupied hybrid orbitals of this atom.
These steps are illustrated by showing how the hybridization at N in NH$_3$ is determined.

1. Draw Lewis structure.
2. Determine electron-domain geometry about central atom.
3. sp$^3$ hybridization.

Indicate the orbital hybridization around the central atom in NH$_2^-$.

To determine the central atom hybrid orbitals, we must know the electron-domain geometry around the atom. Thus, we draw the Lewis structure to determine the number of electron domains around the central atom. The hybridization conforms to the number and geometry of electron domains around the central atom as predicted by the VSEPR model. The Lewis structure is:

Because there are four electron domains around N, the electron-domain geometry is tetrahedral. The hybridization that gives a tetrahedral electron-domain geometry is sp$^3$.

Two of the sp$^3$ hybrid orbitals contain nonbonding pairs of electrons, and the other two are used to make bonds with the hydrogen atoms.
MUTLIPLE BONDS

In the covalent bonds we have considered thus far, the electron density is concentrated along the line connecting the nuclei (the internuclear axis). In other words, the line joining the two nuclei passes through the middle of the overlap region. These bonds are called sigma (σ) bonds.

The overlap of two s orbitals in H₂, the overlap of an s and a p, sp, sp², and sp³, also, the overlap of two p orbitals in Cl₂, and the overlap of a p orbital and an sp, sp², and sp³ are all σ bonds.

Predict the electron-domain geometry and hybridization of the central atom in SO₃²⁻.

Drawing Lewis structure gives 4 electron domains, three bonds and one lone pair on S. VSEPR suggests a tetrahedral orientation, and thus a SP³ hybridization.
To describe multiple bonding, we must consider a second kind of bond, this one the result of overlap between two $p$ orbitals oriented perpendicularly to the internuclear axis. This sideways overlap of $p$ orbitals produces a $\pi$ bond. A $\pi$ bond is one in which the overlap regions lie above and below the internuclear axis.

The sideways orientation of $p$ orbitals in a $\pi$ bond makes for weaker overlap. As a result, $\pi$ bonds are generally weaker than $\sigma$ bonds.
We use eight electrons to form the four C–H bonds. The C–C bond is formed by the overlap of two sp² hybrid orbitals, one on each carbon atom, and requires two more electrons. Thus, ten of the 12 valence electrons in the C₂H₄ molecule are used to form five bonds.

The remaining two valence electrons reside in the unhybridized 2p orbitals, one electron on each carbon. These two orbitals can overlap sideways with each other. The resultant electron density is concentrated above and below the bond axis, which means this is a π bond.

Thus, the double bond in ethylene consists of one σ bond and one π bond. You should note that unhybridized p orbitals on both carbons form the π bond. As pointed out earlier, π bonds are generally weaker than σ bonds.

To see how these ideas are used, consider ethylene (C₂H₄), which has a C=C double bond. The three bond angles about each carbon are all approximately 120°, suggesting that each carbon atom uses sp² hybrid orbitals to form σ bonds with the other carbon and with two hydrogen.

Because carbon has four valence electrons, after sp² hybridization one electron in each carbon remains in the unhybridized 2p orbital, which is directed perpendicular to the plane that contains the three sp² hybrid orbitals.
Although we cannot experimentally observe a bond directly (all we can observe are the positions of the atoms), the structure of ethylene provides strong support for its presence. First, the bond length in ethylene (1.34 Å) is much shorter than in compounds with single bonds (1.54 Å), consistent with the presence of a stronger double bond. Second, all six atoms in \( \text{C}_2\text{H}_4 \) lie in the same plane. The \( p \) orbitals that make up the \( \pi \) bond can achieve a good overlap only when the two \( \text{CH}_2 \) fragments lie in the same plane. If the \( \pi \) bond were absent, there would be no reason for the two \( \text{CH}_2 \) fragments to lie in the same plane.

Because \( \pi \) bonds require that portions of a molecule be planar, they can introduce rigidity into molecules.

The molecule called diazine has the formula \( \text{N}_2\text{H}_4 \) and the Lewis structure: \( \text{H} \rightarrow \text{N} \equiv \text{N} \rightarrow \text{H} \). Do you expect diazine to be a linear molecule (all four atoms on the same line)? If not, do you expect the molecule to be planar (all four atoms in the same plane)?

a. Definitely, diazine is not a linear molecule, since 3 electron domains are present on each \( \text{N} \) atom (each \( \text{N} \) atom is \( \text{sp}^2 \) hybrid) which make the N-N-H bond angle about 120°.

b. For \( \pi \) bonds to form between \( \text{N} \) \( \text{N} \) atoms, overlap requires a planar geometry. Therefore diazine is expected to be planar.

Triple bonds can also be explained using hybrid orbitals. Acetylene (\( \text{C}_2\text{H}_2 \)), for example, is a linear molecule containing a triple bond:

\[
\text{H} - \text{C} \equiv \text{C} - \text{H}
\]

The linear geometry suggests that each carbon atom uses \( \text{sp} \) hybrid orbitals to form \( \sigma \) bonds with the other carbon and one hydrogen. Each carbon atom thus has two unhybridized \( 2p \) orbitals at right angles to each other and to the axis of the \( \text{sp} \) hybrid set. These \( p \) orbitals overlap to form a pair of \( \pi \) bonds. Thus, the triple bond in acetylene consists of one \( \sigma \) bond and \( \pi \) two bonds.
Formaldehyde has the Lewis structure:

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

Describe how the bonds in formaldehyde are formed in terms of overlaps of hybrid and unhybridized orbitals. The C atom has three electron domains around it, which suggests a trigonal-planar geometry with bond angles of about 120°. This geometry implies sp² hybrid orbitals on C. These hybrids are used to make the two C-H and one C-O bonds. There remains an unhybridized 2p orbital on carbon, perpendicular to the plane of the three sp² hybrids.

The O atom also has three electron domains around it, and so we assume it has sp² hybridization as well. One of these hybrid orbitals participates in the σ bond, while the other two hold the two nonbonding electron pairs of the O atom. Like the C atom, therefore, the O atom has an unhybridized 2p orbital that is perpendicular to the plane of the molecule. These two orbitals overlap to form a π bond.

(a) Predict the bond angles around each carbon atom in acetonitrile:

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

(b) Describe the hybridization at each carbon atom, and (c) determine the number of σ and π bonds in the molecule.

a. Bond angle in C-C N is 180°, carbon 2 has sp hybridization and two p orbitals unhybridized. C-C-H and H-C-H bond angle is about 109.5° since C1 has tetrahedral geometry and sp³ hybridization. N has two electron domains and thus a sp hybridization, in addition to unhybridized p orbitals.

b. Acetonitrile has 5 sigma bonds and two π bonds.
Resonance Structures, Delocalization, and Bonding

In the molecules we have discussed thus far in this section, the bonding electrons are localized. By this we mean that the $\sigma$ and $\pi$ electrons are associated totally with the two atoms that form the bond. In many molecules, however, we cannot adequately describe the bonding as being entirely localized. This situation arises particularly in molecules that have two or more resonance structures involving bonds.

One molecule that cannot be described with localized bonds is benzene ($C_6H_6$), which has two resonance structures:

To describe the bonding in benzene using hybrid orbitals, we first choose a hybridization scheme consistent with the geometry of the molecule. Because each carbon is surrounded by three atoms at 120 angles, the appropriate hybrid set is $sp^2$. Six localized $C-H \sigma$ bonds and six localized $C-C \sigma$ bonds are formed from the $sp^2$ hybrid orbitals.

This leaves on each carbon a 2p orbital oriented perpendicular to the plane of the molecule. The situation is very much like that in ethylene except we now have six carbon 2p orbitals arranged in a ring.

Each unhybridized 2p orbital is occupied by one electron, leaving six electrons to be accounted for by $\pi$ bonding.
We could envision using the unhybridized 2p orbitals to form three localized bonds. There are two equivalent ways to make these localized bonds, each corresponding to one resonance structure. However, a representation that reflects both resonance structures has the six electrons "smeared out" among all six carbon atoms.

Notice how this combined representation corresponds to the circle-in-a-hexagon drawing we often use to represent benzene.

This model leads us to predict that all the carbon–carbon bond lengths will be identical, with a bond length between that of a single bond (1.54 Å) and that of a double bond (1.34 Å). This prediction is consistent with the observed carbon–carbon bond length in benzene (1.40 Å).

Because we cannot describe the bonds in benzene as individual bonds between neighboring atoms, we say that the bonds are delocalized among the six carbon atoms.

Delocalization of the electrons in its bonds gives benzene a special stability.

Another important point to remember about delocalized bonds is the constraint they place on the geometry of a molecule. For optimal overlap of the unhybridized p orbitals, all the atoms involved in a delocalized bonding network should lie in the same plane.

This restriction imparts a certain rigidity to the molecule that is absent in molecules containing only σ bonds.

a. Which of the following molecules or ions will exhibit delocalized bonding: SO$_3$, SO$_3^{2-}$, H$_2$CO, NO$_3^-$, O$_3$, NH$_4^+$?

Assume a maximum of octet around central atom

Answer: SO$_3$, NO$_3^-$, and O$_3$
b. Describe the bonding in the nitrate ion, $\text{NO}_3^-$, Does this ion have delocalized bonds?

Drawing Lewis structure and deriving geometry suggests that 3 electron domains are present around N, which results in the following structure:

Therefore, we have 3 s and one p bond. The p bond can be between the nitrogen atom and either O, which means a resonance. In each structure, the electron-domain geometry at nitrogen is trigonal planar, which implies sp$^2$ hybridization of the N atom.

Reliability of Valence Bond Theory

As one can see, Valence Bond Theory can help describe how bonds are formed. However, there are some notable failures when it comes to Valence Bond Theory. One such failure is dioxygen. Valence Bond Theory fails to predict dioxygen’s paramagnetism; it predicts that oxygen is diamagnetic.

A species is paramagnetic if electrons are not spin paired and diamagnetic if the electrons are spin paired. Since Valence Bond theory begins with the basis that atomic orbitals overlap to create bonds and through that reasoning, one can see that electrons are spin paired when bonds overlap, dioxygen is indeed predicted to be diamagnetic if Valence Bond Theory is used.
MOLECULAR ORBITALS

Valence bond theory and hybrid orbitals allow us to move in a straightforward way from Lewis structures to rationalizing the observed geometries of molecules in terms of atomic orbitals. The valence-bond model, however, does not explain all aspects of bonding. Some aspects of bonding are better explained by a more sophisticated model called molecular orbital theory. We have seen that electrons in atoms can be described by wave functions, which we call atomic orbitals. In a similar way, molecular orbital theory describes the electrons in molecules by using specific wave functions called molecular orbitals (MO).

The Hydrogen Molecule

We begin our study of MO theory with the hydrogen molecule, $H_2$. Whenever two atomic orbitals overlap, two molecular orbitals form. Thus, the overlap of the $1s$ orbitals of two hydrogen atoms to form $H_2$ produces two MOs.

One MO is formed by adding the wave functions for the two $1s$ orbitals. We refer to this as constructive combination. The energy of the resulting MO is lower than the energy of the two atomic orbitals from which it was made. It is called the bonding molecular orbital.

Need for Molecular Orbital Theory

Valence bond theory predicts the double bond, but not the paramagnetism of oxygen.

Resonance is another example of the limitations of valence bond theory. Bond lengths and strengths are intermediate between single, double or triple bonds.

Molecular orbital theory is often a better approach to use with molecules that have extended $\pi$ systems.

Molecular orbitals have many of the same characteristics as atomic orbitals. For example, an MO can hold a maximum of two electrons (with opposite spins), it has a definite energy, and we can visualize its electron-density distribution by using a contour representation, as we did with atomic orbitals.

Unlike atomic orbitals, however, MOs are associated with an entire molecule, not with a single atom.
The other MO is formed by combining the two atomic orbitals in a way that causes the electron density to be more or less canceled in the central region where the two overlap. We refer to this as destructive combination.

The energy of the resulting MO, referred to as the antibonding molecular orbital, is higher than the energy of the atomic orbitals.

In the bonding MO electron density is concentrated in the region between the two nuclei. This sausage-shaped MO results from summing the two atomic orbitals so that the atomic orbital wave functions combine in the region between the two nuclei.

Because an electron in the bonding MO is attracted to both nuclei, the electron is more stable (it has lower energy) than it is in the 1s atomic orbital of an isolated hydrogen atom. Further, because this bonding MO concentrates electron density between the nuclei, it holds the atoms together in a covalent bond.

By contrast, the antibonding MO has very little electron density between the nuclei. Instead of combining in the region between the nuclei, the atomic orbital wave functions cancel each other in this region, leaving the greatest electron density on opposite sides of the two nuclei. Thus, this MO excludes electrons from the region in which a bond must be formed. Antibonding orbitals invariably have a nodal plane in the region between the nuclei, where the electron density is zero.
As the MO diagram for $H_2$ shows, each H atom brings one electron to the molecule, so there are two electrons in $H_2$. These two electrons occupy the lower-energy bonding MO ($\sigma_{1s}$), and their spins are paired. Electrons occupying a bonding molecular orbital are called bonding electrons. Because the MO is lower in energy than the $1s$ atomic orbitals, the $H_2$ molecule is more stable than the two separate $H$ atoms.

By analogy with atomic electron configurations, the electron configurations for molecules can be written with superscripts to indicate electron occupancy. The electron configuration for $H_2$, then, is $\sigma_{1s}^2$.

Bond Order

In molecular orbital theory, the stability of a covalent bond is related to its bond order, defined as half the difference between the number of bonding electrons and the number of antibonding electrons:

$$\text{Bond order} = \frac{1}{2} (\text{no. of bonding electrons} - \text{no. of antibonding electrons})$$

A bond order of 1 represents a single bond, a bond order of 2 represents a double bond, and a bond order of 3 represents a triple bond.

Because MO theory also treats molecules containing an odd number of electrons, bond orders of $\frac{1}{2}$, $\frac{3}{2}$, or $\frac{5}{2}$ or are possible.

The energy-level diagram for the hypothetical He$_2$ molecule, which requires four electrons to fill its molecular orbitals, is also shown in the previous figure. Because only two electrons can go in the $\sigma_{1s}$ MO, the other two electrons must go in the $\sigma_{1s}^*$ MO. The electron configuration of He$_2$ is thus $\sigma_{1s}^2 \sigma_{1s}^*$. The energy decrease realized in going from He atomic orbitals to the He bonding MO is offset by the energy increase realized in going from the atomic orbitals to the He antibonding MO. Hence, He$_2$ is an unstable molecule.

Molecular orbital theory correctly predicts that hydrogen forms diatomic molecules but helium does not.
What is the bond order in $\text{H}_2$ and $\text{He}_2$? Which is more stable?

$\text{H}_2$ has two bonding electrons and zero antibonding electrons, it has a bond order of 1.

Bond order in $\text{H}_2 = \frac{1}{2}(2-0) = 1$

Because $\text{He}_2$ has two bonding electrons and two antibonding electrons, it has a bond order of 0. A bond order of 0 means that no bond exists. Therefore $\text{H}_2$ is more stable than $\text{He}_2$.

Suppose one electron in $\text{H}_2$ is excited from the s MO to the s* MO. Would you expect the H atoms to remain bonded, or would the molecule fall apart?

Bond order in $\text{H}_2 = \frac{1}{2}(1-1) = 0$

This means breakdown of the H-H bond.

What is the bond order of the $\text{He}_2^+$ ion? Would you expect this ion to be stable relative to the separated He atom and $\text{He}^+$ ion?

Bond order in $\text{He}_2^+ = \frac{1}{2}(2-1) = \frac{1}{2}$

Because the bond order is greater than 0, we predict the $\text{He}_2^+$ ion to be stable relative to the separated He and $\text{He}^+$.

PERIOD 2 HOMONUCLEAR DIATOMIC MOLECULES

Period 2 atoms have valence 2s and 2p orbitals, and we need to consider how they interact to form MOs. The following rules summarize some of the guiding principles for the formation of MOs and how they are populated by electrons:

1. The number of MOs formed equals the number of atomic orbitals combined.
2. Atomic orbitals combine most effectively with other atomic orbitals of similar energy.
3. The effectiveness with which two atomic orbitals combine is proportional to their overlap. That is, as the overlap increases, the energy of the bonding MO is lowered and the energy of the antibonding MO is raised.
4. Each MO can accommodate, at most, two electrons, with their spins paired.
5. When MOs of the same energy are populated, one electron enters each orbital (with the same spin) before spin pairing occurs (Hund's rule).

Determine the bond order of the $\text{H}_2^-$ ion.

Bond order in $\text{H}_2^- = \frac{1}{2}(2-1) = \frac{1}{2}$
Energy-level diagram for the Be$_2$ molecule

Bond order = ½ (4-4) = 0
Therefore, Be$_2$ does not exist

Energy-level diagram for the Li$_2$ molecule

Bond order = ½ (4-2) = 1
Note that core electrons do not contribute to stability

Molecular Orbitals from 2p Atomic Orbitals

$\pi$ Bonds

$\sigma$ Bonds

$\sigma_{1p}$
Electron Configurations for \( B_2 \) through \( \text{Ne}_2 \)

These have valence 2s and 2p atomic orbitals. The following features of the diagram are notable:

1. The 2s atomic orbitals are substantially lower in energy than the 2p atomic orbitals. Consequently, both MOs formed from the 2s orbitals are lower in energy than the lowest-energy MO derived from the 2p atomic orbitals.

2. The overlap of the two 2p\(_z\) orbitals is greater than that of the two 2p\(_x\) or 2p\(_y\) orbitals. As a result, the \( \sigma_{2p} \) bonding MO is lower in energy than the \( \pi_{2p} \) MOs, and the \( \sigma^*_{2p} \) antibonding MO is higher in energy than the \( \pi^*_{2p} \) MOs.

3. Both the \( \pi_{2p} \) and \( \pi^*_{2p} \) MOs are doubly degenerate; that is, there are two degenerate MOs of each type.
The effect of interactions between 2s and 2p atomic orbitals

The interaction between 2s and 2p orbitals in molecules can lead to the formation of bonding and antibonding orbitals. This is illustrated in the diagram, which shows the energy-level diagrams for different molecules. The diagrams depict the stabilization of bonding orbitals and the destabilization of antibonding orbitals due to the overlap of atomic orbitals.

For instance, in the case of $\text{O}_2$, the overlap of the 2s and 2p orbitals on the oxygen atoms results in the formation of bonding and antibonding orbitals, which are crucial for understanding the electronic structure and stability of the molecule.

The diagrams also highlight the stabilization of bonding orbitals (e.g., $\sigma_2^+$) and the destabilization of antibonding orbitals (e.g., $\pi^*$), which are essential for predicting the chemical behavior of molecules.