Skills to Develop

- Describe the valence bond (VB) approach to chemical bonding.
- Demonstrate hybridization of atomic orbitals for VB.
- Correlate the molecular shape to the hybrid atomic orbitals of some central atoms.
- Combine the concepts of hybrid orbitals, valence bond theory, VSEPR, resonance structures, and octet rule to describe the shapes and structures of some common molecules.

Valence Bond Theory and Hybrid Atomic Orbitals

This picture is an image of a Centaur from Sphinx Stargate. The Centaur is a race of monsters in Greek mythology, a hybrid animal having the head, arms and torso of a man united to the body and legs of a horse. Mixing a number of atomic orbitals to form the same number of hybrid orbitals to explain chemical bonding and shapes and molecular structures is a rather recent myth.

The most significant development in the first half of the 20th century is the human's ability to understand the structure of atoms and molecules. Computation has made mathematical concepts visible to the extent that we now can see the atomic and molecular orbitals. On the other hand, using everyday encountered materials or toys can also generate beautiful illustrations of hybrid atomic orbitals.

The valence bond (VB) approach is different from the molecular orbital (MO) theory. Despite their differences, most of their results are the same, and they are interesting.

The Valence Bond (VB) Theory

The valence-bond approach considers the overlap of the atomic orbitals (AO) of the participating atoms to form a chemical bond. Due to the overlapping, electrons are localized in the bond region.

The overlapping AOs can be of different types; for example, a sigma bond may be formed by the overlapping of the following AOs.

<table>
<thead>
<tr>
<th>Chemical bonds formed due to overlap of atomic orbitals</th>
</tr>
</thead>
<tbody>
<tr>
<td>s-s</td>
</tr>
<tr>
<td>{\text{H-H}}</td>
</tr>
</tbody>
</table>

However, the atomic orbitals for bonding may not be "pure" atomic orbitals directly from the solution of the Schrodinger Equation. Often, the bonding atomic orbitals have a character of several possible types of orbitals. The methods to get an
AO with the proper character for the bonding is called **hybridization**. The resulting atomic orbitals are called **hybridized atomic orbitals** or simply **hybrid orbitals**.

We shall look at the shapes of some hybrid orbitals first, because these shapes determine the shapes of the molecules.

### Hybridization of Atomic Orbitals

The solution to the Schrodinger Equation provides the wave functions for the following atomic orbitals:

\[ 1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f, \text{etc.} \]

For atoms containing two or more electrons, the energy levels are shifted with respect to those of the \(\ce{H}\) atom. An atomic orbital is really the energy state of an electron bound to an atomic nucleus. The energy state changes when one atom is bonded to another atom.

Quantum mechanical approaches by combining the wave functions to give new wave functions are called **hybridization** of atomic orbitals. Hybridization has a sound mathematical foundation, but it is a little too complicated to show the details here. Leaving out the jargon, we can say that an imaginary mixing process converts a set of atomic orbitals to a new set of **hybrid atomic orbitals** or **hybrid orbitals**.

At this level, we consider the following hybrid orbitals:

\[ sp, \quad sp^2, \quad sp^3, \quad sp^3d, \quad sp^3d^2 \]

### The sp Hybrid Atomic Orbitals

The **sp hybrid atomic orbitals** are possible states of electrons in an atom, especially when it is bonded to others. These electron states have half \(2s\) and half \(2p\) characters. From a mathematical viewpoint, there are two ways to combine the \(2s\) and \(2p\) atomic orbitals:

\[ sp_1 = 2s + 2p \]
\[ sp_2 = 2s - 2p \]

These energy states (\(sp_1\) and \(sp_2\)) have a region of high electron probability each, and the two atomic orbitals are located opposite to each other, centered on the atom. The sp hybrid orbitals are represented by this photograph.

\[ \ce{H}: \underset{\Large{1s}}{\overset{\Large{1s}}{sp_1}}: \ce{Be}: \underset{\Large{1s}}{\overset{\Large{1s}}{sp_2}}: \ce{H} \]
For example, the molecule $\text{H-Be-H}$ is formed due to the overlapping of two 1s orbitals of 2 $\text{H}$ atoms and the two sp hybridized orbitals of $\text{Be}$. Thus, the $\text{H-Be-H}$ molecule is linear. The diagram here shows the overlapping of AOs in the molecule $\text{H-Be-H}$.

The ground state electronic configuration of $\text{Be}$ is $1s^22s^22p^2$, and one may think of the electronic configuration "before" bonding as $1s^2sp^2$. The two electrons in the sp hybrid orbitals have the same energy.

You may say that the concept of hybridizing AOs for the bonding is just a story made up to explain the molecular shape of $\text{Cl-Be-Cl}$. You are right! The story is lovely and interesting, though.

In general, when two and only two atoms bond to a third atom and the third atom makes use of the sp hybridized orbitals, the three atoms are on a straight line. For example, sp hybrid orbitals are used in the central atoms in the molecules shown on the right.

**The sp$^2$ Hybrid Orbitals**

The energy states of the valence electrons in atoms of the second period are in the 2s and 2p orbitals. If we mix two of the 2p orbitals with a 2s orbital, we end up with three sp$^2$ hybridized orbitals. These three orbitals lie on a plane, and they point to the vertices of an equilateral triangle as shown here.

When the central atom makes use of sp$^2$ hybridized orbitals, the compound so formed has a trigonal shape. $\text{BF}_3$ is such a molecule:

Molecules with sp$^2$ hybrid orbitals

F . . -2
Not all three \(sp^2\) hybridized orbitals have to be used in bonding. One of the orbitals may be occupied by a pair or a single electron. If we do not count the unshared electrons, these molecules are bent, rather than linear. The three molecules shown together with the \(\text{BF}_3\) molecule are such molecules.

Carbon atoms also make use of the \(sp^2\) hybrid orbitals in the compound \(\text{H}_2\text{C=CH}_2\). In this molecule, the remaining \(p\) orbital from each of the carbons overlaps to form the additional \(\pi\) bond.

Planar molecules with \(sp^2\) hybrid orbitals

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

Other ions such as \(\text{CO}_3^{2-}\), and \(\text{NO}_3^{-}\), can also be explained in the same way.

The \(sp^3\) Hybrid Orbitals

Mixing one \(s\) and all three \(p\) atomic orbitals produces a set of four equivalent \(sp^3\) hybrid atomic orbitals. The four \(sp^3\) hybrid orbitals point towards the vertices of a tetrahedron, as shown here in this photograph.

When \(sp^3\) hybrid orbitals are used for the central atom in the formation of a molecule, the molecule is said to have the shape of a tetrahedron.

The typical molecule is \(\text{CH}_4\), in which the 1\(s\) orbital of a \(\text{H}\) atom overlaps with one of the \(sp^3\) hybrid orbitals to form a \(\text{C-H}\) bond. Four \(\text{H}\) atoms form four such bonds, and they are all equivalent. The \(\text{CH}_4\) molecule is the most cited molecule to have a tetrahedral shape. Other molecules and ions having tetrahedral shapes include \(\text{SiO}_4^{4-}\) and \(\text{SO}_4^{2-}\).

As are the cases with \(sp^2\) hybrid orbitals, one or two of the \(sp^3\) hybrid orbitals may be occupied by non-bonding electrons. Water and ammonia are such molecules.
The \(\text{C}\), \(\text{N}\) and \(\text{O}\) atoms in \(\text{CH}_4\), \(\text{NH}_3\), and \(\text{OH}_2\) (or \(\text{H}_2\text{O}\)) molecules use the \(sp^3\) hybrid orbitals; however, a lone pair occupies one of the orbitals in \(\text{NH}_3\), and two lone pairs occupy two of the \(sp^3\) hybrid orbitals in \(\text{OH}_2\). The lone pairs must be considered in the VSEPR model, and we can represent a lone pair by \(\text{E}\), and two lone pairs by \(\text{E}_2\). Thus, we have \(\text{NH}_3\text{E}\) and \(\text{OH}_2\text{E}_2\) respectively.

The VSEPR number is equal to the number of bonds plus the number of lone pair electrons. It does not matter what the order of the bond is; any bonded pair is considered on bond. Thus, the VSEPR number is 4 for all of these: \(\text{CH}_4\), \(\text{NH}_3\), and \(\text{OH}_2\).

According the the VSEPR theory, the lone electron pairs require more space, and the \(\text{H-O-H}\) angle is 105 degrees, less than the ideal tetrahedral angle of 109.5 degrees.

The \(dsp^3\) Hybrid Orbitals

The five \(dsp^3\) hybrid orbitals resulted when one 3\(d\), one 3\(s\), and three 3\(p\) atomic orbitals are mixed. When an atom makes use of five \(dsp^3\) hybrid orbitals to bond to five other atoms, the geometry of the molecule is often a trigonal bipyramidal. For example, the molecule \(\text{PCl}_4\) displayed here forms such a structure. In this diagram, the \(\text{Cl}\) atom takes up an axial position of the trigonal bipyramid. There are structures in which the \(\text{Cl}\) atom may take up the equatorial position. The change in arrangement is accomplished by simply changing the bond angles. This link discusses this type of configuration change of this molecule.

Some of the \(dsp^3\) hybrid orbitals may be occupied by electron pairs. The shapes of these molecules are interesting. In \(\text{TeCl}_4\), only one of the hybrid \(dsp^3\) orbitals is occupied by a lone pair. This structure may be represented by \(\text{TeCl}_4\text{E}\), where \(\text{E}\) represents a lone pair of electrons. Two lone pairs occupy two such orbitals in the molecule \(\text{BrF}_3\), or \(\text{BrF}_3\text{E}_2\). These structures are given in a VSEPR table of 5 and 6 coordinations.
The compound \(\text{SF}_4\) is another \(\text{AX}_4\text{E}\) type, and many interhalogen compounds like \(\text{ClF}_3\) and \(\text{IF}_3\) are \(\text{AX}_3\text{E}_2\) type. The ion \(\text{I}_3^-\) is of the type \(\text{AX}_2\text{E}_3\).

**The \(d^2sp^3\) Hybrid Orbitals**

The six \(d^2sp^3\) hybrid orbitals result when two \(3d\), one \(3s\), and three \(3p\) atomic orbitals are mixed. When an atom makes use of six \(d^2sp^3\) hybrid orbitals to bond to six other atoms, the molecule takes the shape of an octahedron, in terms of molecular geometry. The gas compound \(\text{SF}_6\) is a typical such structure. This link provides other shapes as well.

There are also cases that some of the \(d^2sp^3\) hybrid orbitals are occupied by lone pair electrons leading to the structures of the following types:

\[\begin{align*}
\text{AX}_6, & \quad \text{AX}_5\text{E}, \quad \text{AX}_4\text{E}_2, \quad \text{AX}_3\text{E}_3, \\
\text{AX}_2\text{E}_4, & \quad \text{IOF}_5, \quad \text{IF}_5\text{E}, \quad \text{XeF}_4\text{E}_2
\end{align*}\]

No known compounds of \(\text{AX}_3\text{E}_3\) and \(\text{AX}_2\text{E}_4\) are known or recognized, because they are predicted to have a T shape and linear shape respectively when the lone pairs of electrons are ignored.

**Molecular Shapes of Compounds**

While the hybridized orbitals were introduced in the foregoing discussion, the Valence-shell Electron-pair Repulsion (VSEPR) Model was included to suggest the shapes of various molecules. Specifically, the VSEPR model counts unshared electron pairs and the bonded atoms as the **VSEPR number**. A single-, double- and triple-bond is considered as 1. After having considered the hybridized orbitals and the VSEPR model, we can not take a systematic approach to
rationalize the shapes of many molecules based on the number of valence electrons.

A summary in the form of a table is given here to account for the concepts of hybrid orbitals, valence bond theory, VSEPR, resonance structures, and octet rule. In this table, the geometric shapes of the molecules are described by linear, trigonal planar, tetrahedral, trigonal bipyramidal, and octahedral. The hybrid orbitals use are $sp$, $sp^2$, $sp^3$, $dsp^3$, and $d^2sp^3$.

The VSEPR number is the same for all molecules of each group. Instead of using $\text{NH}_3E$ and $\text{OH}_2E_2$, we use $\text{textrm{::NH}_3}$, $\text{textrm{::OH}_2}$ to emphasize the unshared (or lone) electron pairs.

| A summary of hybrid orbitals, valence bond theory, VSEPR, resonance structures, and octet rule. |
|------------------|------------------|------------------|------------------|------------------|
| Linear           | Trigonal planar  | Tetrahedral      | Trigonal bipyramidal | Octahedral       |
| $sp$             | $sp^2$           | $sp^3$           | $dsp^3$           | $d^2sp^3$        |
| $\text{BeH}_2$  | $\text{BeF}_2$  | $\text{CO}_2$   | $\text{CH}_3\text{CN}$ | $\text{BeH}_2$  |
| $\text{CO}_2$   | $\text{NH}_3$   | $\text{HCN}$    | $\text{H}_2\text{CN}$ | $\text{BeH}_2$  |
| $\text{NH}_3$   | $\text{HCN}$    | $\text{H}_2\text{CN}$ | $\text{BeH}_2$  | $\text{BeF}_2$  |
| $\text{BeF}_2$  | $\text{BeF}_2$  | $\text{BeF}_2$  | $\text{BeF}_2$  | $\text{BeF}_2$  |
| $\text{HCN}$    | $\text{HCN}$    | $\text{HCN}$    | $\text{HCN}$    | $\text{HCN}$    |
| $\text{H}_2\text{CN}$ | $\text{H}_2\text{CN}$ | $\text{H}_2\text{CN}$ | $\text{H}_2\text{CN}$ | $\text{H}_2\text{CN}$ |
| $\text{N}_2\text{O}_2$ | $\text{N}_2\text{O}_2$ | $\text{N}_2\text{O}_2$ | $\text{N}_2\text{O}_2$ | $\text{N}_2\text{O}_2$ |
| $\text{SiO}_4$  | $\text{SiO}_4$  | $\text{SiO}_4$  | $\text{SiO}_4$  | $\text{SiO}_4$  |
| $\text{PO}_4$   | $\text{PO}_4$   | $\text{PO}_4$   | $\text{PO}_4$   | $\text{PO}_4$   |
| $\text{SO}_4$   | $\text{SO}_4$   | $\text{SO}_4$   | $\text{SO}_4$   | $\text{SO}_4$   |
| $\text{ClO}_4$  | $\text{ClO}_4$  | $\text{ClO}_4$  | $\text{ClO}_4$  | $\text{ClO}_4$  |

• a lone odd electron : a lone electron pair

This table correlates a lot of interesting chemical concepts in order to understand the molecular structures of these compounds or ions. There are some intriguing chemical relationships among the molecules in each column for you to ponder.

Only $\text{Be}$ and $\text{C}$ atoms are involved in linear molecules. In gas phase, $\text{BeH}_2$ and $\text{BeF}_2$ are stable, and these molecules do not satisfy the octet rule. The element $\text{C}$ makes use of $sp$ hybridized orbitals and it has the ability to form double and triple bonds in these linear molecules.

Carbon compounds are present in trigonal planar and tetrahedral molecules, using different hybrid orbitals. The extra electron in nitrogen for its compounds in these groups appears as a lone unpaired electron or lone electron pairs. More electrons in $\text{O}$ and $\text{S}$ lead to compounds with lone electron pairs. The five-atom anions are tetrahedral, and many resonance structures can be written for them.
Trigonal bipyramidal and octahedral molecules have 5 and 6 VSEPR pairs. When the central atoms contain more than 5 or 6 electrons, the extra electrons form lone pairs. The number of lone pairs can easily be derived using Lewis dot structures for the valence electrons.

In describing the shapes of these molecules, we often ignore the lone pairs. Thus, \(\text{NO}_2\), \(\text{N}_3^-\), \(\text{OO}_2\) (O3), and \(\text{SO}_2\) are bent molecules whereas \(\text{NH}_3\), \(\text{PF}_3\), and \(\text{SOF}_2\) are pyramidal. You already know that \(\text{OH}_2\) (water) and \(\text{SF}_2\) are bent molecules.

The lone electron pair takes up the equatorial location in \(\text{SF}_4\), which has the same structure as \(\text{TeF}_4\) described earlier. If you lay a model of this molecule on the side, it looks like a butterfly. By the same reason, \(\text{ClF}_3\) and \(\text{BrF}_3\) have a T shape, and \(\text{XeF}_2\), \(\text{I}_3^-\), and \(\text{ICl}_2^-\) are linear.

Similarly, \(\text{BrF}_5\) and \(\text{IF}_5\) are square pyramidal whereas \(\text{XeF}_4\) is square planar.

**The Center Atom**

A nice student asked a brilliant question:

**Which atom in the formula is usually the center atom?**

Usually, the atom in the center is more electropositive than the terminal atoms. However, the \(\text{H}\) and halogen atoms are usually at the terminal positions because they form only one bond.

Take a look at the chemical formulas in the table, and see if the above statement is true.

However, the application of VSEPR theory can be expanded to complicated molecules such as

![Chemical structure](image)

By applying the VSEPR theory, one deduces the following results:

- \(\text{H-C-C}\) bond angle = 109°
- \(\text{H-C=C}\) bond angle = 120°, geometry around \(\text{C}\) trigonal planar
- \(\text{C=C=C}\) bond angle = 180°, in other words linear
- \(\text{H-N-C}\) bond angle = 109°, tetrahedral around \(\text{N}\)
- \(\text{C-O-H}\) bond angle = 105 or 109°, 2 lone electron pairs around \(\text{O}\)
Confidence Building Questions

1. In terms of valence bond theory, how is a chemical bond formed?

   **Hint:** A chemical bond is due to the overlap of atomic orbitals.

   **Discussion -**
   Molecular orbital theory considers the energy states of the molecule.

2. When one s and two p atomic orbitals are used to generate hybrid orbitals, how many hybrid orbitals will be generated?

   **Hint:** Using three atomic orbitals generates three hybrid orbitals.

   **Discussion -**
   Number of orbitals does not change in hybridization of atomic orbitals.

3. In the structures of \(\text{SO}_2\) and \(\text{NO}_2\), what are the values of the bond angles?

   **Hint:** The bond angles are expected to be less than 120 degrees.

   **Discussion -**
   Since the lone electron pair in \(\text{SO}_2\) and lone electron in \(\text{NO}_2\) take up more space, we expect the structure to distort leaving a smaller angle than 120 between the bonds.

4. What is the geometrical shape of the molecule \(\text{CH}_4\), methane?

   **Hint:** Methane molecules are tetrahedral.

   **Discussion -**
   The 4 \(\text{H}\) atoms form a tetrahedron, and methane has a tetrahedral shape.

5. What do you expect the bond angles to be in the \(\text{NH}_4^+\) ion?

   **Hint:** All bond angles are 109.5 degrees, the ideal value for a symmetric tetrahedral structure.

   **Discussion -**
   The structure of this ion is very similar to that of \(\text{CH}_4\).

6. What hybrid orbitals does the \(\text{C}\) atom use in the compound \(\text{H-C≡C-H}\), in which the molecule is linear?

   **Hint:** The sp hybrid orbitals are used by the \(\text{C}\) atom.

   **Discussion -**
   Sigma (s) bonds are due to sp hybrid orbitals, and 2 p orbitals are used for pi (p) bonds. The two sigma bonds for each \(\text{C}\) are due to overlap of sp hybrid orbitals of each \(\text{C}\) atom.

7. What hybrid orbitals does \(\text{C}\) use in the molecule:

   \[
   \begin{array}{c}
   \text{H} \\
   \text{O=C<}
   \end{array}
   \]
This is a trigonal planar molecule. It is called formaldehyde, a solvent for preserving biological samples. The compound has an unpleasant smell.

Hint: The $\text{(C)}$ atom uses $sp^2$ hybrid orbitals.

**Skill** -
The $\text{(C)}$ atom has 3 sigma ($s$) bonds by using three $sp^2$ hybrid orbitals and a pi ($p$) bond, due to one $2p$ orbital.

8. **What is the shape of the molecule $\text{(SF}_6\text{)}$?**

Hint: Its shape is octahedral.

**Discussion** -
Since the $\text{(S)}$ atom uses $d^2sp^3$ hybrid orbitals, you expect the shape to be octahedral. The $\text{(F)}$ atoms form an octahedron around the sulfur.

9. **Phosphorus often forms a five coordinated compound $\text{(PX}_5\text{)}$. What hybrid orbitals does $\text{(P)}$ use in these compounds?**

Hint: The $\text{(P)}$ atom uses $dsp^3$ hybrid orbitals.

**Discussion** -
A total of 5 atomic orbitals are used in the hybridization: one $3d$, one $3s$ and three $3p$ orbitals. The $dsp^3$ hybrid orbitals of $\text{(P)}$ give rise to a trigonal bipyramidal coordination around the $\text{(P)}$ atom.

The energy of $d$ orbitals in $\text{(N)}$ is not compatible with $2s$ and $2p$ orbitals for hybridization. Thus, you seldom encounter a compound with formula $\text{(NX}_5\text{)}$ with $\text{(N)}$ as the central atom.

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