Chapter 10

Chemical Bonding II: Molecular Geometry and Hybridization of Atomic Orbitals

This is the second chapter on chemical bonding. Chapter 9 introduced the concepts of ionic and covalent bonding and the use of Lewis structures. This chapter uses the concepts from Chapter 9 to discuss molecular geometries and related concepts. Upon completion of Chapter 10, the student should be able to:

1. Fill in the following chart using the VSEPR model:

<table>
<thead>
<tr>
<th>Category</th>
<th>Molecular Geometry</th>
<th>Angle(s)</th>
<th>Sketch of the Shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>AB6E0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AB5E1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AB4E2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AB3E3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AB2E4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AB5E0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AB4E1</td>
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<tr>
<td>AB3E2</td>
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<tr>
<td>AB2E3</td>
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<td></td>
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</tr>
<tr>
<td>AB1E4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AB0E5</td>
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<td></td>
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</tr>
<tr>
<td>AB2E0</td>
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<td></td>
<td></td>
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<tr>
<td>AB1E1</td>
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<td></td>
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<tr>
<td>AB0E2</td>
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<td>AB3E0</td>
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<tr>
<td>AB2E1</td>
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<td></td>
</tr>
<tr>
<td>AB1E0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2. Identify using the VSEPR model, what category (and thus the corresponding molecular geometry, angle(s) and sketch) a molecular or ion belongs given its formula.

3. Rationalize the observed decrease in angles for AB6E0, AB5E1, and AB4E2 and for AB3E0 and AB2E1.

4. Apply VSEPR model to compounds with more than one central atom.

5. Use the concepts of electronegativity, dipole moments, and VSEPR geometries to identify polar and nonpolar molecules.

6. Use dipole moment concepts to predict properties of cis and trans isomers.

7. Relate how a microwave oven functions and how the type of chemical bonds present effects the amount of energy absorbed.

8. Sketch and justify how potential energy changes versus the interatomic distance for a diatomic molecule.

9. Use Valence Bond theory, hybrid orbitals, and hybridization to explain the geometries predicted by VSEPR model.

10. Identify what type of hybrid orbitals are in common compounds and ions.

11. Apply the concepts of sigma and pi bonds and Valence Bond theory to explain properties of double and triple bonds and the concept of resonance.

12. State what physical property of oxygen gas is not accounted for by Valence Bond theory but is in Molecular Orbital theory.

13. Explain the difference between bonding and anti-bonding orbitals using the concepts of constructive and destructive interference of waves.

14. Show molecular orbital energy diagrams for first and second row diatomic molecules identifying
sigma and pi bonding and anti-bonding molecular orbitals.

15. Write molecular orbital electron configurations for simple diatomics.

16. Relate molecular orbital energy diagrams to bond order, bond length and bond strength.

17. Describe resonance using the Molecular Orbital theory.

18. Suggest the significance of the discoveries of fullerenes and nanotubes.

Section 10.1 Molecular Geometry

In Chapter 9, we used Lewis structures to describe the arrangement of atoms in molecules. Lewis structures also can be used to determine if double or triple bonds are likely in a molecule and if the atoms have lone pairs of electrons. Lewis structures do not, however, give the shape or geometry of the molecule. For example, the correct Lewis structure of water is

\[
\text{H} \quad \text{O} \quad \text{H}
\]

which gives no indication that the HOH angle is 104.5°. It is for this reason that VSEPR is used. When discussing molecular geometries with your students, it may be useful to suggest that what we are doing is looking at molecules through a “special microscope” that will allow us to see the atoms but not be able to see pairs of electrons greatly affect the shape of molecules, we do not include them in our molecular geometry description.

The first step in VSEPR is to have your students understand the geometries associated with \( \text{AB}_x \text{E}_y \) where \( x \) ranges from two through six and \( y \) is zero. These correspond to molecules with no lone pairs of electrons on A. \( \text{AB}_x \text{E}_y \) must be linear because two atoms will describe a line. Your author uses \( \text{BeCl}_2, \text{BF}_3, \text{CH}_4, \text{PCl}_5, \text{SF}_6 \) as examples of \( \text{AB}_2 \text{E}_0, \text{AB}_3 \text{E}_0, \text{AB}_4 \text{E}_0, \text{AB}_5 \text{E}_0 \) and \( \text{AB}_6 \text{E}_0 \), respectively. It should be noted that the angles for the tetrahedral geometry are all 109.5°. The \( \text{AB}_5 \text{E}_0 \), trigonal bipyramid, contains axial and equatorial positions. Even though the \( \text{AB}_6 \text{E}_0 \) octahedral geometry is formed by joining two square pyramids, it is called octahedral and not square bipyramid.

The next step in VSEPR is to expand into those molecules that contain lone pairs of electrons. The key point is to realize that starting geometry is dictated by the sum of \( x \) and \( y \) when the molecule is written in the form \( \text{AB}_x \text{E}_y \). If the sum of \( x \) and \( y \) is six, then the starting geometry is octahedral; if five, trigonal bipyramid; if four, tetrahedral; if three, trigonal planar; and if two, linear. For example, \( \text{SO}_2 \) is \( \text{AB}_2 \text{E}_1 \) so the sum of \( x \) and \( y \) is three; therefore, the starting geometry is a variation on trigonal planar. However, since \( \text{SO}_2 \) has a lone pair of electrons that our "special microscope" cannot see, the geometry will include only the sulfur atom and the two oxygen atoms. Recall that the lone pair of electrons requires a bit more space than bonding pairs, thus the OSO angle will be smaller than 120° (the angle for trigonal planar geometry), perhaps 117° or so. VSEPR thus predicts \( \text{SO}_2 \) to be bent and not linear with an angle of about 117°.

Water has the form \( \text{AB}_2 \text{E}_2 \), and the sum of \( x \) and \( y \) is four. Thus, water will be a variation on the tetrahedral structure that has 109.5° angles. Once again, the lone pairs (two lone pairs this time) require a bit more room so that HOH angle is less than 109.5° (104.5° actual measured angle). Therefore, water is a bent molecule with an angle of less than 109.5°.

In the guidelines for applying the VSEPR model, your author suggests that we treat double and triple bonds around a central atom as though they were single bonds. Students frequently find this confusing. Another method for determining VSEPR geometries is to follow the steps below. You should warn your students that this method does NOT follow the rules set forth by Lewis structures and the octet rule and is a different model that gives correct VSEPR geometries. This procedure is:

1) determine the total number of valence electrons in the molecule

2) connect each terminal atom with a pair of bonding electrons to the central atom
3) place six more electrons around each terminal atom (the exception is hydrogen where the one pair of bonding electrons is sufficient)

4) if, upon placing a total of eight electrons around all the terminal atoms, there are still additional valence electrons left over, they are placed around the central atom (Note that the central atom may or may not follow the octet rule).

It may be useful to use lines to represent pairs of electrons and not dots so that your students realize that this is a different model than Lewis dot.

Let us use TeCl₄ as an example. The procedure would be:

**Step A** Te has six valence electrons, and each Cl has seven valence electrons.
Total number of valence electrons is 6 + 4(7) = 34

**Step B** Te is the central atom and the four chlorine atoms are terminal atoms.

The placement of the Cl's at this point do not give us information on geometry.

**Step C** Each line represents two valence electrons, thus we have accounted for 32 valence electrons.
Therefore, this molecule has the form \(AB_3E_1\). It is a variation on trigonal bipyramid. Recall that the lone pair will be placed in the equatorial position, thus this molecule will have a distorted tetrahedron geometry.

One more example would be \(I_3\)

**Step A** \((3)(7) + 1 = 22\) valence electrons

**Step B**

\[
\begin{array}{c}
\text{I} \\
\text{I} \\
\text{I}
\end{array}
\]

**Step C**

\[
\begin{array}{c}
\text{I} \\
\text{I} \\
\text{I} \\
\text{I}
\end{array}
\]

**Step D** \(22 - 16 = 6\) valence electrons left to be placed on central atom

\[
\begin{array}{c}
\text{I} \\
\text{I} \\
\text{I} \\
\text{I} \\
\text{I}
\end{array}
\]

This molecule is \(AB_3E_3\), so again it is a variation on trigonal bipyramid. We need three pairs of non-bonding electrons (all in the equatorial position) so we then have \(I_3\) as a linear molecule.

**Section 10.2 Dipole Moments**

There are two criteria that must be met for a molecule to have a net dipole moment. The first is that there must be polar covalent bonds in the molecule and the second is that the geometry must be such that the vector sum of the individual dipole moments do not cancel. Molecules with the form \(AB_xE_y\) where \(y\) is zero will be nonpolar because their symmetry will cancel the dipole moments. In addition, \(AB_xE_x\) (square planar) will also be nonpolar. Homonuclear molecules or ions will be nonpolar because they do not contain polar covalent bonds.

**Section 10.3 Valence Bond Theory**

In order to explain the molecular geometries described by VSEPR theory, two quantum mechanical bonding theories have arisen. They are the Valence Bond theory and the Molecular Orbital theory. The Valence Bond theory suggests that the overlap of atomic orbitals results in the formation of chemical bonds. This theory, for example, explains the observed change in potential energy as two hydrogen atoms approach each other. The same concepts can be used to describe bond formation in other molecules. Molecular Orbital theory is described in Section 10.6.
Section 10.4 Hybridization of Atomic Orbitals

There are five hybrid atom orbitals that your author considers. They are sp, sp$^2$, sp$^3$, sp$^3$d, and sp$^3$d$^2$. The reason that hybrid orbitals are needed is to explain such observations as tetrahedral geometry and the fact that all four CH bonds are identical in methane. To determine what type of hybrid orbital a given atom has, one counts the number of lone pairs and the number of connections (single, double or triple bonds are all considered as one connection) associated with the atom being discussed. The sum of the lone pairs and connections gives the number of equal hybridized atomic orbitals or energy boxes that are required. For example, CH$_4$ has four connections and zero lone pairs around the central C atom, thus it needs four equal hybridized atomic orbitals or energy boxes

\[
\begin{array}{c}
\text{sp}^3 \\
\end{array}
\] (one s atomic orbital and three p atomic orbitals resulting in four equal sp$^3$ orbitals)

Because carbon has four valence electrons, one electron from carbon is placed in each sp$^3$ orbital. Each then combines with the electrons from the four hydrogens resulting in the tetrahedral geometry. Using the same method for ammonia, NH$_3$, suggests that nitrogen will require sp$^3$ hybrid orbitals also because the nitrogen has three connections and one lone pair. Since nitrogen has five valence electrons, the sp$^3$ energy boxes will have one lone pair of electrons in them

\[
\begin{array}{c}
\text{sp}^3 \\
\end{array}
\]

which gives rise to the single lone pair of non-bonding electrons and three electrons available to bond with the three hydrogen atoms to form the expected trigonal pyramid geometry of NH$_3$.

Another example is acetylene, C$_2$H$_2$, which uses sp hybrid orbitals on each of the carbons. This is determined by counting two connections around each C atom (the triple bond is one connection) thus two equal energy boxes are required and two p orbitals are left unhybridized. Carbon has four valence electrons thus two electrons enter the sp orbitals and two remain in the unhybridized p orbitals

\[
\begin{array}{c}
\text{py, pz} \\
\end{array}
\]

\[
\begin{array}{c}
\text{sp} \\
\end{array}
\]

The result is one of the sp hybrid orbitals is filled by the electron from the H atom and the other from the adjoining C atom each forming sigma bonds. The two electrons in the p orbitals combine with electrons in similar p orbitals from the other carbon atom to form the two pi bonds. These two pi bonds, along with the sigma bond, results in the carbon-carbon triple bond.

The final example is I$_3^-$ which has two connections and three lone pairs of electrons surrounding the
central atom. This would require five energy boxes or sp\(^3\)d hybrid orbitals with a total of seven valence electrons placed in them.

\[ \begin{array}{cccccc}
\uparrow & \downarrow & \uparrow & \uparrow & \uparrow & \text{sp}\(^3\)d
\end{array} \]

One of the three electrons that is available pairs with the extra electron to give the ion a negative one charge and results in three pairs of non-bonding electrons on the central iodine. The other two electrons are used to bond to each of the terminal iodine atoms.

It should be noted that sp, sp\(^2\), and sp\(^3\) are the only three hybrid orbitals available for second-period elements since 2d orbitals do not exist. Therefore, sp\(^3\)d and sp\(^3\)d\(^2\) are not acceptable for second-period elements.

**Section 10.5 Hybridization in Molecules Containing Double and Triple Bonds**

Single bonds are almost always sigma bonds. Double bonds are usually composed of a sigma bond and one pi bond. Triple bonds are always a sigma bond and two pi bonds. Sigma bonds have the electron density concentrated between the two nuclei while pi bonds have the electron density concentrated above and below the plane of the nuclei. See the previous section of this manual for a discussion on the formation of multiple bonds using hybrid orbitals.

**Section 10.6 Molecular Orbital Theory**

An observation that is not adequately explained by hybrid atomic orbitals is that oxygen molecules are paramagnetic. One method to attempt to explain this observation is the use of Molecular Orbital theory. The premise of this theory is that the wave characteristics of electrons give rise to constructive interference (bonding molecular orbitals) and destructive interference (anti-bonding molecular orbitals). As in Valence Bond theory, Molecular Orbital theory describes the formation of sigma and pi bonds. However, it should be understood that the combination of a bonding orbital with a corresponding anti-bonding orbital results in no net chemical bond formation.

**Section 10.7 Molecular Orbital Configurations**

Many similarities exist between electron configuration for atoms and molecular orbital configurations from Molecular Orbital theory. For example, Hund's rule and the Pauli exclusion principle hold in both cases. In Molecular Orbital theory, bond order is defined as the number of electrons in bonding molecular orbitals minus the number of electrons in anti-bonding molecular orbitals - that quantity times one half. It is, therefore, possible for bond orders to be a fraction. Bond order, in a general sense, corresponds to single, double, and triple bonds for bond orders of 1, 2, and 3, respectively.

The energy box diagrams for homonuclear diatomic molecules of the second-period elements are shown in Table 10.5. It is important to show that oxygen molecules are predicted to be paramagnetic as experimentally observed.

**Section 10.8 Delocalized Molecular Orbital**

Delocalized molecular orbitals refer to the spreading out of molecular orbitals over several atoms within
a molecule. This concept is used to describe resonance in such molecules as benzene and ozone. These
delocalized molecular orbitals do not have the same reactivity as normal double bonds. This can be shown by
the classical reaction of cyclohexene with aqueous KMnO₄ which turns the purple KMnO₄ solution to a
brown precipitate. Toluene, on the other hand, does not react with KMnO₄ because the benzene ring does not
have double bonds as cyclohexene does. A similar reaction is to use the yellow solution composed of Br₂
dissolved in CCl₄, which clears in the presence of a true double bond, but remains yellow when mixed with
toluene. Both of these reactions can be demonstrated to fairly large classes or can be shown easily in a
laboratory setting.