Hybrid Atomic Orbitals

These materials were adapted from Prof. George Bodner, Purdue University (http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch8/hybrid.html#geom; excerpted 08/25/2011). This work is licensed under a Creative Commons Attribution-NonCommercial-ShareAlike 3.0 Unported License.
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Hybrid Atomic Orbitals

It is difficult to explain the shapes of even the simplest molecules with atomic orbitals. A solution to this problem was proposed by Linus Pauling, who argued that the valence orbitals on an atom could be combined to form hybrid atomic orbitals.

The geometry of a BeF$_2$ molecule can be explained, for example, by mixing the 2s orbital on the beryllium atom with one of the 2p orbitals to form a set of sp hybrid orbitals that point in opposite directions, as shown in the figure below. One of the valence electrons on the beryllium atom is then placed in each of these orbitals, and these orbitals are allowed to overlap with half-filled 2p orbitals on a pair of fluorine atoms to form a linear BeF$_2$ molecule.

Pauling also showed that the geometry of molecules such as BF$_3$ and the CO$_3^{2-}$ ion could be explained by mixing a 2s orbital with both a 2p$_x$ and a 2p$_y$ orbital on the central atom to form three sp$^2$ hybrid orbitals that point toward the corners of an equilateral triangle. When he mixed a 2s orbital with all three 2p orbitals (2p$_x$, 2p$_y$ and 2p$_z$), Pauling obtained a set of four sp$^3$ orbitals that are oriented toward the corners of a tetrahedron. These sp$^3$ hybrid orbitals are ideal for explaining the geometries of tetrahedral molecules such as CH$_4$ or the SO$_4^{2-}$ ion.

The hybrid atomic orbital model can be extended to molecules whose shapes are based on trigonal bipyramidal or octahedral distributions of electrons by including valence-shell d orbitals. Pauling showed that when the 3d$_{x^2}$ orbital is mixed with the 3s, 3p$_x$, 3p$_y$ and 3p$_z$ orbitals on an atom, the resulting sp$^3$d hybrid orbitals point toward the corners of a trigonal bipyramid. When both the 3d$_{x^2}$ and 3d$_{y^2}$ orbitals are mixed with the 3s, 3p$_x$, 3p$_y$ and 3p$_z$ orbitals, the result is a set of six sp$^3$d$_2$ hybrid orbitals that point toward the corners of an octahedron.

**GEOMETRIES OF HYBRID ORBITALS**

The geometries of the five different sets of hybrid atomic orbitals (sp, sp$^2$, sp$^3$, sp$^3$d and sp$^3$d$_2$) are shown in the figure below.
The Relationship Between the Distribution of Electrons in an Atom and the Hybridization of That Atom

The relationship between hybridization and the distribution of electrons in the valence shell of an atom is summarized below.

<table>
<thead>
<tr>
<th>Number of Places Where Electrons are Found</th>
<th>M o l e c u l a r Geometry</th>
<th>Hybridization</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>linear</td>
<td>sp</td>
<td>BeF₂, CO₂</td>
</tr>
<tr>
<td>3</td>
<td>trigonal planar</td>
<td>p²</td>
<td>BF₃, CO₃²⁻</td>
</tr>
<tr>
<td>4</td>
<td>tetrahedral</td>
<td>sp³</td>
<td>CH₄, SO₄²⁻</td>
</tr>
<tr>
<td>5</td>
<td>trigonal bipyramidal</td>
<td>sp³d</td>
<td>PF₅</td>
</tr>
<tr>
<td>6</td>
<td>octahedral</td>
<td>sp³d²</td>
<td>SF₆</td>
</tr>
</tbody>
</table>

**Molecules with Double and Triple Bonds**

The hybrid atomic orbital model can also be used to explain the formation of double and triple bonds.
Example: Let's consider the bonding in formaldehyde (H₂CO), for example, which has the following Lewis structure.

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

There are three places where electrons can be found in the valence shell of both the carbon and oxygen atoms in this molecule. As a result, the VSEPR theory predicts that the valence electrons on these atoms will be oriented toward the corners of an equilateral triangle. Let's assume, for the sake of argument, that the formaldehyde molecule lies in the XY plane of a coordinate system. We can create a set of sp² hybrid orbitals on the carbon and oxygen atoms that lie in this plane by mixing the 2s, 2pₓ and 2pᵧ orbitals on each atom.

There are four valence electrons on a neutral carbon atom. One of these electrons is placed in each of the three sp² hybrid orbitals. The fourth electron is placed in the 2pₓ orbital that wasn't used during hybridization.

There are six valence electrons on a neutral oxygen atom. A pair of these electrons is placed in each of two of the sp² hybrid orbitals. One electron is then placed in the sp² hybrid orbital that points toward the carbon atom, and another is placed in the unhybridized 2pₓ orbital.

The C-H bonds are formed when the electrons in two of the sp² hybrid orbitals on carbon interact with a 1s electron on a hydrogen atom, as shown in the figure below. A C-O bond is formed when the electron in the other sp² hybrid orbital on carbon interacts with the unpaired electron in the sp² hybrid orbital on the oxygen atom. These bonds are called sigma (s) bonds because they look like an orbital when viewed along the bond.

The electron in the 2pₓ orbital on the carbon atom then interacts with the electron in the 2pₓ orbital on the oxygen atom to form a second covalent bond between these atoms. This is called a pi (p) bond because its looks like a p orbital when viewed along the bond.

Double bonds occur most often in compounds that contain C, N, O, P, or S atoms. There are two reasons for this. First, double bonds by their very nature are covalent bonds. They are therefore most likely to be found among the elements that form covalent compounds. Second, the
interaction between $p_z$ orbitals to form a p bond requires that the atoms come relatively close together, so these bonds tend to be the strongest for atoms that are relatively small.