Valence Bond (VB) Theory

• A more sophisticated treatment of bonding is a quantum mechanical description of bonding, in which bonding electrons are viewed as being localized between the nuclei of the bonded atoms.

• The overlap of bonding orbitals is increased through a process called hybridization, which results in the formation of stronger bonds.

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Hybrid Orbitals

For polyatomic molecules we would like to be able to explain:

• The number of bonds formed
• Their geometries

**sp Hybrid Orbitals**

Consider the Lewis structure of gaseous molecules of BeF₂:

\[
\begin{array}{c}
  \bullet F \\
  \bullet \text{Be} \\
  \bullet F
\end{array}
\]

• The VSEPR model predicts this structure will be linear
• What would *valence bond theory* predict about the structure?
The fluorine atom electron configuration:

- $1s^22s^22p^5$

$\begin{array}{c|c|c|c|c|c}
\text{1s} & \text{2s} & \text{2p} \\
\end{array}$

- There is an unpaired electron in a $2p$ orbital
- This unpaired $2p$ electron can be paired with an unpaired electron in the Be atom to form a covalent bond

The Be atom electron configuration:

- $1s^22s^2$

$\begin{array}{c|c|c|c|c|c}
\text{1s} & \text{2s} & \text{2p} \\
\end{array}$

- In the ground state, there are no unpaired electrons (the Be atom is incapable of forming a covalent bond with a fluorine atom
- However, the Be atom could obtain an unpaired electron by promoting an electron from the $2s$ orbital to the $2p$ orbital:

$\begin{array}{c|c|c|c|c|c|c|c}
\text{1s} & \text{2s} & \text{1} & \text{1} & \text{1} & \text{1} & \text{2p} \\
\end{array}$

*This would actually result in two unpaired electrons, one in a $2s$ orbital and another in a $2p$ orbital*

- The Be atom can now form two covalent bonds with fluorine atoms
- We would not expect these bonds to be identical (one is with a $2s$ electron orbital, the other is with a $2p$ electron orbital)

*However, the structure of BeF$_2$ is linear and the bond lengths are identical*

- We can combine wavefunctions for the $2s$ and $2p$ electrons to produce a "hybrid" orbital for both electrons
• This hybrid orbital is an "sp" hybrid orbital

- The orbital diagram for this hybridization would be represented as:

\[
\begin{array}{c|c|c}
1s & 1 & 1 \\
\hline
2s_p & & 2p \\
\end{array}
\]

Be \(2sp\) hybrid orbitals

F \(2p\) orbitals

Bonding orbital overlap

Note:

• The Be \(2sp\) orbitals are identical and oriented 180° from one another (i.e. bond lengths will be identical and the molecule linear)

• The promotion of a Be \(2s\) electron to a \(2p\) orbital to allow \(sp\) hybrid orbital formation requires energy.
  - The elongated \(sp\) hybrid orbitals have one large lobe which can overlap (bond) with another atom more effectively
  - This produces a stronger bond (higher bond energy) which offsets the energy required to promote the \(2s\) electron

\(sp^2\) and \(sp^3\) Hybrid Orbitals

Whenever orbitals are mixed (hybridized):
- The number of hybrid orbitals produced is equal to the sum of the orbitals being hybridized
- Each hybrid orbital is identical except that they are oriented in different directions

BF$_3$

Boron electron configuration:

- The three $sp^2$ hybrid orbitals have a trigonal planar arrangement to minimize electron repulsion

CH$_4$

- An $s$ orbital can also mix with all 3 $p$ orbitals in the same subshell

**NOTE:** $sp^2$ refers to a hybrid orbital being constructed from one $s$ orbital and two $p$ orbitals. Although it looks like an electron configuration notation, the superscript '2' DOES NOT refer to the number of electrons in an orbital.
Thus, using **valence bond theory**, we would describe the bonds in methane as follows: each of the carbon $sp^3$ hybrid orbitals can overlap with the $1s$ orbitals of a hydrogen atom to form a bonding pair of electrons.

**NOTE:** $sp^3$ refers to a **hybrid orbital** being constructed from one $s$ orbital and three $p$ orbitals. Although it looks like an electron configuration notation, the superscript '3' DOES NOT refer to the number of electrons in an orbital.

**ANOTHER NOTE:** the two steps often observed when constructing hybrid orbitals is to 1) promote a valence electron from the ground state configuration to a higher energy orbital, and then 2) hybridize the appropriate valence electron orbitals to achieve the desired valence electron geometry (i.e. the correct number of hybrid orbitals for the appropriate valence electron geometry).

$H_2O$

**Oxygen**
Hybridization Involving $d$ Orbitals

Atoms in the third period and higher can utilize $d$ orbitals to form hybrid orbitals

$\text{PF}_5$

![Diagram showing hybridization and octahedral geometry](image)

**Trigonal Bipyramidal**

Similarly hybridizing one $s$, three $p$ and two $d$ orbitals yields six identical hybrid $sp^3d^2$ orbitals. These would be oriented in an **octahedral geometry**.

- Hybrid orbitals allows us to use **valence bond theory** to describe covalent bonds (sharing of electrons in overlapping orbitals of two atoms)
- When we know the molecular geometry, we can use the concept of hybridization to describe the electronic orbitals used by the central atom in bonding.

Steps in predicting the hybrid orbitals used by an atom in bonding:

1. Draw the Lewis structure
2. Determine the electron pair geometry using the VSEPR model
3. Specify the hybrid orbitals needed to accommodate the electron pairs in the geometric arrangement

**NH$_3$**

1. **Lewis structure**

   \[
   \begin{array}{c}
   H \\
   \mid \\
   N \\
   \mid \\
   H
   \end{array}
   \]

2. **VSEPR** indicates *tetrahedral geometry* with one non-bonding pair of electrons (structure itself will be *trigonal pyramidal*)

3. Tetrahedral arrangement indicates four equivalent electron orbitals
**Valence Electron Pair Geometry** | **Number of Orbitals** | **Hybrid Orbitals**
---|---|---
Linear | 2 | $sp$
Trigonal Planar | 3 | $sp^2$
Tetrahedral | 4 | $sp^3$
Trigonal Bipyramidal | 5 | $sp^3d$
Octahedral | 6 | $sp^3d^2$

**In the case of methane**, the three 2p orbitals of the carbon atom are combined with its 2s orbital to form four new orbitals called "$sp^3$" hybrid orbitals. The name is simply a tally of all the orbitals that were blended together to form these new hybrid orbitals. Four hybrid orbitals were required since there are four atoms attached to the central carbon atom. These new orbitals will have an energy slightly above the 2s orbital and below the 2p orbitals as shown in the following illustration. Notice that no change occurred with the 1s orbital.
These hybrid orbitals have 75% p-character and 25% s-character which gives them a shape that is shorter and fatter than a p-orbital. The new shape looks a little like...

A stick and wedge drawing of methane shows the tetrahedral angles...(The wedge is coming out of the paper and the dashed line is going behind the paper. The solid lines are in the plane of the paper.)

A space-filling model of methane would look like...

In the case of ammonia, the three 2p orbitals of the nitrogen atom are combined with the 2s orbital to form four sp$^3$ hybrid orbitals. The non-bonded electron pair will occupy a hybrid orbital. Again we need a hybrid orbital for each atom and pair
of non-bonding electrons. Ammonia has three hydrogen atoms and one non-bonded pair of electrons when we draw the electron-dot formula. In order to determine the hybridization of an atom, you must first draw the electron-dot formula.

A stick and wedge drawing of ammonia showing the non-bonding electrons in a probability area for the hybrid orbital...

A space-filling model of ammonia would look like...(Note the non-bonded electron pair is not shown in this model.)

In the case of water, the three 2p orbitals of the oxygen atom are combined with the 2s orbital to form four sp³ hybrid orbitals. The two non-bonded electron pairs will occupy hybrid orbitals. Again we need a hybrid orbital for each atom and each pair of non-bonding electrons. Water has two hydrogen atoms and two non-bonded pairs of electrons when we draw the electron-dot formula.
A stick and wedge drawing of water showing the non-bonding electron pairs in probability areas for the hybrid orbital...

A space-filling model of water would look like...(Note the non-bonded electron pairs are not shown in this model.)

Now let's look at something a bit different. In the boron trifluoride molecule, only three groups are arranged around the central boron atom. In this case, the 2s orbital is combined with only two of the 2p orbitals (since we only need three hybrid orbitals for the three groups...thinking of groups as atoms and non-bonding pairs) forming three hybrid orbitals called $sp^2$ hybrid orbitals. The other p-orbital remains unhybridized and is at right angles to the trigonal planar arrangement of the hybrid orbitals. The trigonal planar arrangement has bond angles of $120^\circ$. 
In the following stick model, the empty p orbital is shown as the probability area...one end shaded blue and the other is white...there are no electrons in this orbital!

A space-filling model of boron trifluoride would look like...

**Finally let's look at beryllium dichloride.** Since only two groups are attached to beryllium, we only will have two hybrid orbitals. In this case, the 2s orbital is combined with only one of the 2p orbitals to yield two sp hybrid orbitals. The two hybrid orbitals will be arranged as far apart as possible from each other with the result being a linear arrangement. The two unhybridized p-orbitals stay in their respective positions (at right angles to each other) and perpendicular to the linear molecule.
In the following stick model, the empty p orbitals are shown as the probability areas...one green and one blue.

A space-filling model of beryllium dichloride would look like...

**Hybridization Involving d-Orbitals**

As we discussed earlier, some 3rd row and larger elements can accommodate more than eight electrons around the central atom. These atoms will also be hybridized and have very specific arrangements of the attached groups in space. The two types of hybridization involved with d orbitals are $sp^3d$ and $sp^3d^2$.

The groups will be arranged in a trigonal bipyramidal arrangement with $sp^3d$ hybridization...bond angles will be 120° in the plane with two groups arranged vertically above and below this plane.
There will be an octahedral arrangement with \( \text{sp}^3\text{d}^2 \) hybridization...all bond angles are at 90°.

Non-bonded electron pairs are always placed where they will have the most space...in the trigonal plane for \( \text{sp}^3 \text{d} \) hybridization.

Try drawing the 3-dimensional electron-dot picture for each of the following molecules...First draw an electron-dot formula. Remember to put all the extra electrons on the central atom as pairs when drawing this initial electron-dot formula. Now count the groups around the central atom. If there are six groups (Remember to count non-bonding electron pairs as groups.) it will have \( \text{sp}^3\text{d}^2 \) hybridization. If it has five groups it will have \( \text{sp}^3 \text{d} \) hybridization.

- \( \text{SF}_6 \) sulfur hexafluoride
- \( \text{PF}_5 \) phosphorus pentafluoride
- \( \text{SF}_4 \) sulfur tetrafluoride
- \( \text{ClF}_3 \) chlorine trifluoride
- \( \text{XeF}_2 \) xenon difluoride