Bonding Theories for Covalent Molecules (1):

Valence Bond Theory

\( \text{VSEPR} \rightarrow \) predicts the 3-dimensional molecular (\( MG \)) and electron pair (\( EPG \)) geometries of a large number of covalent compounds and polyatomic anions.

Valence Bond (\( VB \)) theory describes these geometries in terms of the bonding orbitals used by the atoms in these molecules.

Valence bond theory states that bonding in covalent compounds occurs via the overlap of two half-filled orbitals of the bonding atoms.

In order to achieve the correct bond angles as predicted by VSEPR, the atomic orbitals on each bonding atom “mix” to form new “hybrid” bonding orbitals.

Valence Bond Terminology:

- **Overlap**: two orbitals existing in the same region of space
- **lp**: lone pair of electrons (non-bonding)
- **bp**: bonding pair of electrons (result of orbital overlap)
- **Central atom**: the atom of concern in a molecule
- **hybridization**: the linear combination of atomic orbitals
- **hybrid orbital**: bonding orbitals that arise from the mixing of AO’s.
- **\( \sigma \)-bond**: (sigma bond) overlap of orbitals along the bond axis
- **\( \pi \)-bond**: (pi bond) overlap of orbitals above and below the bond axis.
- **single bond**: one \( \sigma \)-bond
- **double bond**: one \( \sigma \)-bond & one \( \pi \)-bond
- **triple bond**: one \( \sigma \)-bond & two \( \pi \)-bonds
• **PH₃ (phosphorous trihydride)**

Phosphorous has 5 valence electrons with an electron configuration of $3s^23p^3$. Each H-atom has one 1s electron.

![Bonding orbitals of P atom](image)

Each 1s orbital can overlap with one of the half-filled $p$ orbitals.

The result shows that the molecule will have 3 bonds and 1 lone pair of electrons. The H-P-H bond angles are 90° (from the original $p$-orbitals on P).

![Covalent bonds formed](image)

However, VESPR tells us that we should have a *trigonal pyramid* MG (H-P-H) bond angles ~95° with a *tetrahedral* EPG. Why don’t the two agree exactly?
Consider the valence electrons on Phosphorous:

When the atomic orbitals are combined, four new orbitals result that are “Hybrids” of the original atomic orbitals.

The four new bonding orbitals are given the designation $sp^3$ since they are a linear combination of one $s$-orbital and 3 $p$-orbitals.

Now each of the three H-atoms can overlap to form one bond and the electron pair in the filled $sp^3$ corresponds to the lone pair.
An *s-orbital* combines with 3 *p-orbitals* to form 4 new sp$^3$ hybrid orbitals that have a *tetrahedral EPG*. 
Methane: $CH_4$

The $2s$ and (3) $2p$ orbitals in methane overlap to form 4 new $sp^3$ hybrid orbitals. Each of the $1s$ electrons on hydrogen overlap to form $\sigma$-bonds and the expected tetrahedral MG and EPG is seen.

**Conclusion:**

When tetrahedral electron pair geometry (EPG) is seen on a central atom, the atom is most likely bonding through $sp^3$ hybrid orbitals.

Other examples of $sp^3$ hybrid molecules are:
**sp² hybridization**

When an “s” orbital mixes with two “p” orbitals, three sp² orbitals result leaving one “p” orbital behind.

\[ \text{2s} \rightarrow \text{2p} \rightarrow \text{new sp}² \text{ hybrid orbitals} \]

The sp² orbitals spread out to form a *trigonal planar* geometry leaving the p orbital perpendicular to the plane. The sp² orbitals can form *σ*-bonds or hold lone pairs and the p orbital forms the *π*-bond in a double bond.
The head on overlap of two sp² orbitals produces a σ-bond whereas the overlap of the p orbitals above and below the bond axis produces a π-bond.

An example of sp² hybridization is given by C₂H₄ (ethene)

Each carbon atom undergoes sp² hybridization

The 4 valence electrons redistribute amongst the orbitals, placing one in each of the sp² orbitals and one in the left over p orbital.
**Bonding in C₂H₄**

One of the sp² orbitals on each carbon form the C-C σ-bond, while the other two form the C-H σ-bonds via overlap with the 1s electrons in H. The two half-filled p orbitals on each carbon overlap to form the π-bond.

Other examples of molecules with sp² hybridization are:

**CH₂O formaldehyde**

**SO₂ sulfur dioxide**
**Conclusion**: When a central atom has a trigonal planar electron pair geometry (EPG), it is most likely to bond through sp² hybridization. Compounds containing double bonds (\(\sigma + \pi\)) have sp² hybridization.

**sp Hybridization**:
When an “s” orbital mixes with one “p” orbital, two sp orbitals result leaving two “p” orbital behind.

\[
\begin{array}{c}
\text{2s} \\
\text{2p} \\
\text{sp} \\
\end{array}
\rightarrow
\begin{array}{c}
\text{2p} \\
\text{2p} \\
\text{new sp hybrid orbitals} \\
\end{array}
\]

The sp orbitals spread out to form a linear geometry (directed away from one another) leaving the p orbitals perpendicular to the molecular axis.

The sp orbitals can form \(\sigma\)-bonds or hold lone pairs and one of the p orbital forms the \(\pi\)-bond in a double bond or the two form the \(\pi\)-bonds in a triple bond.

*An example of sp² hybridization is given by \(C_2H_2\) (acetylene)*

\[
\begin{array}{c}
\uparrow \\
\text{2p} \\
\downarrow \\
\text{sp} \\
\end{array}
\rightarrow
\begin{array}{c}
\uparrow \\
\text{2p} \\
\uparrow \\
\end{array}
\]

Each carbon atom undergoes sp hybridization

The 4 valence electrons redistribute amongst the orbitals, placing one in each of the sp orbitals and one in each of the left over p orbitals.
One of the sp orbitals on each carbon forms the C-C $\sigma$-bond, while the other forms the C-H $\sigma$-bonds via overlap with the 1s electrons in H. The two half-filled p orbitals on each carbon overlap to form the $\pi$-bonds (perpendicular to one another).

**Bonding in $C_2H_2$:**

On each carbon, one of the two sp hybrid orbitals overlaps with the H-atom and the other with the C-atom forming $\sigma$-bonds. The two perpendicular p orbitals on each carbon overlap to form the two $\pi$-bonds.

**Other examples of molecules with sp hybridization are:**

$N_2$

$:\text{N}\equiv\text{N}:$

$\text{CN}^-$ (cyanide anion)

$[\cdot:\text{C}\equiv\text{N}:]^-$
**Conclusion:** When a central atom has a *linear* electron pair geometry (EPG) with no lone pairs, it is most likely to bond through sp hybridization.

Compounds containing triple bonds ($\sigma + 2\pi$) or adjacent double bonds ($\text{CO}_2$) have sp hybridization.

*Valence Bond Theory (2): Expanded Valence*

- For elements beyond the second period, we found several examples where the central atom in a Lewis structure had greater than 8 electrons in the valence.

- At $n = 3$, $l = 0$, 1 & 2 or there are “s, p & d” orbitals that can be filled.

- We’ve seen that when four $sp^3$ hybrid orbitals form, a central atom can accommodate only up to 8 electrons in the valence (bp & lp).

- To place more in the valence, we must bring the d orbitals into the “mix” as it were.

*Consider a molecule like PCl$_5*$

Phosphorous has a valence electron configuration of 3s$^2$3p$^3$.

Each of the five electrons forms a single bond with a chlorine atom.

How can we describe the bonding in terms of hybrid orbitals?

Each chlorine atom forms a $\sigma$-bond with a half-filled...
Each of the 5 \( sp^3d \) hybrid orbitals will distribute in such a way as to minimize repulsions. The most stable (lowest energy) configuration is a \textit{trigonal bipyramid structure}. 

\textit{Conclusion:} When any central atom in a molecule has an electron pair geometry (EPG) that is \textit{trigonal bipyramid}, the central atom is most likely bonding through \( sp^3d \) hybridized orbitals.

Additional example of \( sp^3d \) hybrid molecules:
What about molecules with 12 electrons in the valence?

In order to achieve an expanded valence that can hold six electron pairs (bp & lp) we need to form 6 new hybrid orbitals. This requires the mixing of an s, 3 p’s and 2 d atomic orbitals.

\[ \text{new } sp^3d^2 \text{ hybrid orbitals} \]
Each of the 5 $sp^3d$ hybrid orbitals will distribute in such a way as to minimize repulsions. The most stable (lowest energy) configuration is a trigonal bipyramid structure.

Consider a molecule like $SF_6$
Sulfur has a valence electron configuration of $3s^23p^4$.
Each of the five electrons forms a single bond with a fluorine atom forming an octahedral MG and EPG.
The bonding can be described in terms of $sp^3d^2$ hybrid orbitals.
Each fluorine atom forms a \( \sigma \)-bond with a half-filled \( 3d \) \( sp^3d^2 \) orbital.

\[
\begin{array}{cccc}
\uparrow & \downarrow & \uparrow & \uparrow \\
3p & \downarrow & 3d & \downarrow \\
\uparrow & \uparrow & \uparrow & \uparrow \\
& & & \text{new } sp^3d^2 \text{ hybrid orbitals}
\end{array}
\]

Conclusion:
Molecules with an \textit{octahedral} EPG have \( sp^3d^2 \) hybridization at the central atom.

\textit{Additional examples are:}

SbCl\textsubscript{5}\textsuperscript{2-} (antimony pentachloride ion)

\[
\left[ \begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{Sb} \\
\text{Cl} \\
\text{Cl} \\
\end{array} \right]^{2-}
\]

XeF\textsubscript{4} (xenon tetra fluoride)
Determining the hybridization of a molecule:

Since Carbon (1) & (3) are identical, each must have the same hybridization.
Trigonal planar EPG, double bond… The bonding is $sp^2$

Carbon (2) has a linear EPG and two double bonds. To do so there must be two p-orbitals forming two $\pi$-bonds. Linear + two $\pi$-bonds… $sp$
Additional Examples of hybridization:

\[
\begin{align*}
\sigma &: \text{H}(1s) - C(sp^2) \\
\pi &: C(2p) - O(2p) \\
\end{align*}
\]

\[
\begin{align*}
\sigma &: C(sp^2) - O(2p) \\
\end{align*}
\]

\[
\begin{align*}
\pi &: C(2p) - O(2p) \\
\sigma &: C(sp^2) - H(1s) \\
\sigma &: C(sp^2) - O(sp^3) \\
\sigma &: O(sp^3) - H(1s) \\
\end{align*}
\]