Bonding and Molecular Structure - PART 2 - Valence Bond Theory and Hybridization

1. Understand and be able to describe the Valence Bond Theory description of covalent bond formation.
2. Understand and be able to describe what is meant by orbital hybridization and hybrid orbitals. Be able to identify the hybridization of an atom in a molecule or polyatomic ion and the orbitals used to form hybrid orbitals.
3. Understand and be able to draw orbital diagrams for atoms before and after hybridization.
4. Understand and be able to describe the difference between sigma (σ) and pi (π) bonds and how they are formed.
5. Understand and be able to describe why pi bonding leads to cis–trans isomerism.

Valence Bond Theory - Description

When a covalent bond is formed, there is shared electron density between the nuclei of the bonded atoms.

The simultaneous attraction of the shared electron density for both nuclei holds the atoms together, forming a covalent bond.

In valence bond theory, the shared electron density is described as occurring when a valence orbital from one atom overlaps with a valence orbital from another atom.

Two electrons with opposite spin are shared in the overlap region, forming a covalent bond.

The greater the extent of orbital overlap, the stronger the bond.

Formation of sigma (σ) bonds in H₂, HCl and Cl₂.

A σ bond is formed when the electron density is located along the inter-nuclear axis. Single bonds are always σ bonds.
Valence Bond Theory Description of Bond Formation in H\textsubscript{2}

- The electron configuration of hydrogen is 1s\textsuperscript{1}. Each hydrogen atom has an unpaired electron in its valence 1s orbital.
- As the two hydrogen atoms approach each other, their 1s orbitals begin to merge (overlap). Electron density builds up in this overlap region where two valence electrons with opposite spin are shared, forming a sigma bond.
- As the two H atoms come closer and closer together, the overlap between the 1s orbitals increases and the potential energy of the system decreases to a minimum and then starts to increase as the electrostatic repulsion between the two nuclei starts to become significant at short internuclear distances.
- The internuclear distance at the minimum potential energy corresponds to the observed bond length.
- The energy released (exothermic process) as the bond is formed corresponds to the bond energy (or bond enthalpy). An input of this amount of energy is required to break the bond (endothermic process) that has formed.

**Question:** The formation of other simple diatomic molecules with single bonds, such as HF and Br\textsubscript{2} can be described in a similar way as the formation of H\textsubscript{2}.

In the case of HF, which atomic orbitals are used to form the bond?

In the case of Br\textsubscript{2}, which atomic orbitals are used to form the bond?
How do we Explain the Bonding in Covalent Molecules To Give the Correct Shapes Predicted by VSEPR Theory?

How can we use valence bond theory to adequately describe the bonding for polyatomic molecules or ions having electron-domain geometries such as linear, trigonal planar, tetrahedral, trigonal bipyramid or octahedral? Overlap of atomic s, p and d orbitals will not yield structures with these geometries (except linear)! To explain bonding for these geometries, valence bond theory uses the concept of orbital hybridization.

**Orbital Hybridization (proposed by Linus Pauling):** To understand this concept, we need to remember that the atomic s, p, d and f orbitals are described by mathematical functions. These functions are actually probability distributions, giving the probability of finding an electron with a specific energy at a given location within an atom.

Orbital hybridization is simply the mathematical combination of two or more atomic orbitals (s, p, or d) to form new hybrid orbitals that are used for bonding.

**Valence Bond Theory (Hybridization)**

Central atoms **do not use** atomic (s, p, d, f) orbitals to form **sigma bonds**.

Central atoms mix **or hybridize** their **valence atomic orbitals** to form new bonding orbitals called hybrid orbitals.

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**Hybridization - sp, and \(\text{sp}^2\) and \(\text{sp}^3\) OVERVIEW**

- **sp**
  - Central atom uses one s orbital and one p orbital to form one bond.
  - Hybridization angle: 180°.

- **sp\(^2\)**
  - Central atom uses one s orbital and two p orbitals to form one bond.
  - Hybridization angle: 120°.

- **sp\(^3\)**
  - Central atom uses one s orbital and three p orbitals to form one bond.
  - Hybridization angle: 109.5°.
Hybrid Orbital Formation: Orbital Hybridization Basics

1. When forming hybrid orbitals, the number of hybrid orbitals formed equals the number of orbitals mathematically combined or “mixed”. For example, if an s orbital is combined with a p orbital the result is two “sp” hybrid orbitals.

2. Hybrid orbitals have orientations around the central atom that correspond to the electron-domain geometry predicted by the VSEPR Theory.

3. The hybrid orbitals have shapes that maximize orbital overlap with another atom’s orbitals. This increases bond strength.

4. Hybrid orbital overlap between atoms creates SIGMA bonds.

Correlation Between VSEPR Theory and Hybridization

The logical sequence to determine hybridization is:

Formula → Lewis Structure → VSEPR Electron Domain Geometry → Hybridization

There is a direct correlation between VSEPR electron domain geometry and the hybridization of the central atom.

<table>
<thead>
<tr>
<th>VSEPR Electron Domain Geometry</th>
<th>Hybridization</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td>sp</td>
<td>BeF$_2$</td>
</tr>
<tr>
<td>Trigonal Planer</td>
<td>sp$^2$</td>
<td>NO$_3^-$</td>
</tr>
<tr>
<td>Tetrahedral</td>
<td>sp$^3$</td>
<td>CH$_4$</td>
</tr>
<tr>
<td>Trigonal Bipyramidal</td>
<td>sp$^3$d</td>
<td>PCl$_5$</td>
</tr>
<tr>
<td>Octahedral</td>
<td>sp$^3$d$^2$</td>
<td>SF$_6$</td>
</tr>
</tbody>
</table>
Correlation Between VSEPR Theory and Hybridization

### Table 9.4-6

<table>
<thead>
<tr>
<th>Atomic Orbital Set</th>
<th>Hybrid Orbital Set</th>
<th>Geometry</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>2s</td>
<td>2p</td>
<td>Linear</td>
<td>BF₃, H₂Cl₂</td>
</tr>
<tr>
<td>3s</td>
<td>3p</td>
<td>Trigonal planar</td>
<td>BF₃SO₃</td>
</tr>
<tr>
<td>4s</td>
<td>4p</td>
<td>Tetrahedral</td>
<td>CH₄, N₂H₅⁺, N₂H₆⁺</td>
</tr>
<tr>
<td>2s, 3p</td>
<td>3s, 3p</td>
<td>Trigonal pyramidal</td>
<td>PF₃, SF₄, BrF₃</td>
</tr>
<tr>
<td>2s, 3p, 4p</td>
<td>3s, 3p, 4p</td>
<td>Octahedral</td>
<td>SF₅Cl, SF₅Br, PF₅⁻</td>
</tr>
</tbody>
</table>

Energy Diagram of Hybridization - sp³ Hybridization for Carbon (Tetrahedral Electron Domain Geometry)

**Atomic Orbitals for CARBON**

- 2s
- 2p

**Hybrid Orbitals for CARBON**

- Four equivalent sp³ hybrid orbitals for bonding.

**sp³ hybridize**

Mix the 2s and 3 2p orbitals, hence sp³ hybridization.
Carbon Hybridization in Ethane - \( sp^3 \)

Sigma bond (\( \sigma \)): the first bond formed between two atoms. All single bonds are \textit{sigma} bonds.

Valence Bond Theory Description of Bonding in H\(_2\)O

1. What is the hybridization of the oxygen atom in water?

2. Draw the orbital energy diagram for the valence shell of the oxygen atom before and after hybridization. Show the electrons before and after hybridization. For the hybridized orbitals, indicate below each orbital whether the orbital holds a lone pair or is used to form a \textit{sigma} bond.

3. Make a sketch of orbitals showing the valence bond theory description of the bonding in H\(_2\)O. Label on the sketch the orbitals used by each atom to form each bond.
Hybridization in Methanol - O $sp^3$ and C $sp^3$

Lone pairs use $sp^3$ hybrid orbitals on O atom.

C—O bond formed from O and C $sp^3$ hybrid orbitals.

C—H bond formed from C atom $sp^3$ hybrid orbital and H 1s orbital.

Expanded Octets: Using $d$-orbitals in Hybridization

For expanded octets the central atom uses $d$ orbitals to hybridize with the $s$ and $p$ orbitals.
Expanded Octets: Bonding in SF₄

1. What is the hybridization of the sulfur atom in SF₄?

2. Draw the orbital energy diagram for the valence shell of the sulfur atom before and after hybridization. Show the electrons before and after hybridization. For the hybridized orbitals, indicate below each orbital whether the orbital holds a lone pair or is used to form a sigma bond.

What about MULTIPLE BONDS?

Valence Bond Theory description of Multiple Bond Formation.

1. Multiple covalent bonds (double and triple) form when more than one orbital from each atom overlap.

2. This additional overlap occurs using UNHYBRIDIZED atomic orbitals, not hybrid orbitals. This overlap is called a π (pi) bond formation.

Sigma bond (σ): the first bond formed between two atoms.

All single bonds are sigma bonds.

Pi (π) bond: the second or third bond formed between two atoms.

Single bond = sigma bond (σ)
Double bond = sigma + pi (σ + π)
Triple bond = sigma + pi + pi (σ + π + π)
A Double Bond - sp² Hybridization of Carbon  
(Trigonal Planar Electron Domain Geometry, H₂C=CH₂)

The bonding in formaldehyde can be explained by sp² hybridization.

The H-C sigma bonds come from overlap of the 1s orbital of H with a sp² hybrid orbital on carbon.

The C-O sigma bond comes from overlap of a sp² hybrid orbital on C with another sp² hybrid orbital on oxygen.

The C-O pi bond comes from overlap of a 2p atomic orbital on C with another 2p atomic orbital on oxygen.

Give it some thought: Silicon, although in the same group as carbon, does not readily form compounds with pi bonds. Why is this? (Hint: Think about size of atoms and side-to-side p orbital overlap.)
Details: Pi Bonding Restricts Rotation Around the Inter-nuclear Axis at Room Temperature

(a) Free rotation can occur around the axis of a single (σ) bond.

(b) In contrast, rotation is severely restricted around double bonds because doing so would break the π bond, a process generally requiring a great deal of energy.

Restricted Rotation Give cis- and trans- Isomers

**Geometric Isomers:** Geometric isomers are compounds that have the same molecular formula and order of attachment of the atoms, but different special arrangement of the atoms relative to each other. Restricted rotation around a π bond results in a type of geometric isomerism known as cis-trans isomerism.

These are two DIFFERENT MOLECULES that do not interconvert. They exist separately and have different physical properties.

**cis-1,2-dichloroethylene**
- **cis isomer:** like atoms are located on the same side of the double bond.
- Density: 1.28 g/mL
- Boiling pt: 60.3 °C
- Dipole: 1.9 D

**trans-1,2-dichloroethylene**
- **trans isomer:** like atoms are located on opposite sides of the double bond.
- Density: 1.26 g/mL
- Boiling pt: 47.5 °C
- Dipole: 0 D
cis- and trans- Isomers: Vision

cis isomer: rhodopsin in the normal or “relaxed” state.

trans isomer: rhodopsin after light absorption. Molecular geometry is changed to trans-form. This stimulates our nervous system to “see” the light.

Acetylene, HCCH, a triple bonded molecule

Acetylene has two pi bonds. There are formed from atomic p orbitals on each carbon.

Two unhybridized p orbitals. Used for π bonding in C₂H₂.

Two sp hybrid orbitals. Used for C—H and C—C σ bonding in C₂H₂.
Details: Delocalized pi Bonds - Resonance!

When we have resonance the position of the pi bonds are not fixed but delocalized through the resonance structures. A classic example is benzene, C₆H₆.

<table>
<thead>
<tr>
<th>Resonance forms</th>
<th>Resonance hybrid</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Localized π bonds</td>
<td>(a) N—O π bond in one of the resonance structures of NO₃⁻.</td>
</tr>
<tr>
<td>(b) Localized π bonds</td>
<td>(b) Delocalization of the π bonds in the NO₃⁻ ion.</td>
</tr>
<tr>
<td>(c) Delocalized π bonds</td>
<td></td>
</tr>
</tbody>
</table>

How many electrons are delocalized in the pi system of benzene? Of the nitrate ion?

Which of the following molecules or ions can exhibit delocalized bonding? H₂CO, CH₃COO⁻, NH₄⁺

Summary of what you should be able to do:

1. Draw a correct Lewis Structure
   a) Expand Octets when necessary to reduce formal charges.
   b) Predict if there will be resonance:
      1. Draw all resonance forms.
      2. Use formal charges to predict the stability of any resonance form.
      3. Combine resonance forms into a resonance hybrid.
      4. Estimate the bond orders in the resonance hybrid.
      5. Predict relative bond lengths and bond strengths in the hybrid.
   c) For any Central Atom:
      1. Predict Electron Geometry - Name.
      2. Predict Molecular Geometry - Name.
      3. Predict any changes to ideal bond angles.
   d) Identify any polar bonds. Predict their direction and relative magnitude.
   e) Determine if the molecule as a whole will have a permanent dipole moment.
   f) Predict Orbital Hybridization of each Central Atom or Multiply Bonded Atom.
      1. Match the hybridization and bonding to the LEWIS STRUCTURE!
      2. Determine what orbitals overlap to form each sigma (σ) bond.
      3. If double or triple bonds exist, determine which orbitals overlap to form each pi (π) bond.
      4. For lone pairs, determine what orbitals each lone pair occupies.
      5. Draw an energy level diagram for the hybrid orbitals.

2. Draw the molecule in 3D, showing the overlap of orbitals to form bonds.
Problems

Methyl isocyanate has the molecular formula CH$_3$NCO. Methyl isocyanate has been used in the production of some pesticides and of rubbers and adhesives. A highly toxic agent, it is hazardous to human health, and was involved in the Bhopal disaster that killed nearly 8,000 people initially and approximately 20,000 - 30,000 people in total.

(a) Draw a Lewis Structure for methyl isocyanate.
(b) Give the hybridization of each central atom in methyl isocyanate.
(c) Predict the ideal bond angles around each central atom. Sketch the molecular shape.
(d) Does the molecule have a permanent dipole moment?
(e) Focusing on the nitrogen atom:
   i) Describe the bonds formed between the nitrogen atom and the carbon atoms as sigma and/or pi.
   ii) What orbitals are used to make each sigma and/or pi bond.
   iii) What orbital is used for the lone pair?
(f) Draw the orbital energy diagram for the valence shell of the nitrogen atom before and after hybridization. Show the electrons before and after hybridization. For the orbitals after hybridization, indicate below each orbital whether the orbital holds a lone pair or is used to form a sigma or pi bond.

Problems from Textbook

Text Problem 9.57:

Shown below are three pairs of hybrid orbitals, with each set at a characteristic angle. For each pair, determine the type or types of hybridization that could lead to hybrid orbitals at the specified angle.
Text Problem 9.59:
(a) Draw a picture showing how two p orbitals can combined to make a sigma bond.

(b) Sketch a $\pi$ bond that is constructed from p orbitals.

(c) Which is generally the stronger, a $\sigma$ bond or a $\pi$ bond? Explain.

(d) Can two s orbitals make a $\pi$ bond. Explain.