Class #22
Molecular Geometry

CHEM 107
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$sp^3$ Hybrid Orbitals

• Mix 4 orbitals, get 4 new identical orbitals
• Energy between $s$ and $p$
• Angles of 109.5°
• Tetrahedral shape
• Let’s us explain bonding in methane (and lots of other molecules, too)
Other Hybridizations

• We can form other hybrids
  
  \[ s + 3p\text{'s} \rightarrow sp^3 \]
  
  \[ s + 2p\text{'s} \rightarrow sp^2 \]
  
  \[ s + p \rightarrow sp \]

• Same ideas, but get orbitals at different angles

Steric Number & Hybridization

<table>
<thead>
<tr>
<th>Steric Number</th>
<th>Hybridization</th>
<th>Orbital Orientation</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>(sp)</td>
<td>linear</td>
</tr>
<tr>
<td>3</td>
<td>(sp^2)</td>
<td>trigonal planar</td>
</tr>
<tr>
<td>4</td>
<td>(sp^3)</td>
<td>tetrahedral</td>
</tr>
</tbody>
</table>
Orbital Orientation vs. Molecular Geometry

- Molecular shape based on position of ATOMS
- All hybrids used for bonds → molecular geometry same as orbital orientation
- Lone pairs on central atom → molecular shape differs from orbital orientation

Steric Number of 2

- sp hybrids, linear orientation
- No lone pairs → linear molecule CO₂
Steric Number of 3

- \( sp^2 \) hybrids, trigonal planar orientation
- **No lone pairs** → trigonal planar molecule
  - \( BF_3, NO_3^- \)
- **One lone pair** → bent triatomic molecule
  - \( O_3, NO_2 \)

Steric Number of 4

- \( sp^3 \) hybrids, tetrahedral orientation
- **No lone pairs** → tetrahedral
  - \( CH_4, NH_4^+ \)
- **One lone pair** → trigonal pyramid
  - \( NH_3 \)
- **Two lone pairs** → bent
  - \( H_2O \)
Steric Number of 5

- No lone pairs $\Rightarrow$ trigonal bipyramid molecule
  - $\text{PCl}_5$
- Lone pairs: Positions not all equivalent!

Steric Number of 5

- One lone pair $\Rightarrow$ "seesaw" molecule
  - $\text{SF}_4$
- Two lone pairs $\Rightarrow$ T-shape molecule
  - $\text{ClF}_3$
- Three lone pairs $\Rightarrow$ Linear molecule
  - $\text{I}_3^-$
Steric Number of 6

- No lone pairs → octahedral
  \( \text{SF}_6 \)
- One lone pair → square pyramid
  \( \text{ClF}_5 \)
- Two lone pairs → square planar
  \( \text{XeF}_4 \)

Multiple Bonds

- How can orbitals overlap to form double or triple bonds?
- Start with a simple example: \( \text{C}_2\text{H}_4 \)
- First draw a Lewis structure
Ethylene - $\text{C}_2\text{H}_4$

- Carbons have steric number of 3 $\rightarrow$ sp$^2$
- Overlap of sp$^2$ orbitals from each carbon forms single bond.
- Double bond?

Ethylene - $\text{C}_2\text{H}_4$

- Double bond?
- “Sideways” overlap of unhybridized $p$ orbitals from carbon atoms
- “$\pi$ bond”
Orbital overlap in C$_2$H$_4$

- Carbons have steric number of 2 \(\rightarrow \) sp
- “Sigma bond” from overlap of 2 sp hybrids
- Triple bond?
Acetylene - C$_2$H$_2$

\[
\text{H} - \text{C}=\text{C} - \text{H}
\]

- Triple bond $\rightarrow$ 3 bonds
- Need 2 $\pi$ bonds in addition to $\sigma$ bond
- “Sideways” overlap of unhybridized $p$ orbitals on carbon atoms, this time using 2 $p$ orbitals from each carbon ($p_x$ and $p_y$)

Orbital overlap in C$_2$H$_2$
Multiple Bonds

- In orbital overlap (or “localized bond”) model:
  - Single bond is a $\sigma$ bond
  - Double bond consists of a $\sigma$ bond and a $\pi$ bond
  - Triple bond consists of a $\sigma$ bond and two $\pi$ bonds

Large Molecules

- Use same ideas as with small molecules
- Predict geometry around each inner atom
- Work your way up to a shape for the full molecule
Peroxyacetyl nitrate

\[
\text{H} - \text{C} - \text{C} - \text{O} - \text{O} - \text{N} - \text{O} - \text{H}
\]

- Finish Lewis structure
- Determine hybridization of all inner atoms
- Predict bond angles