Molecular Shapes

• The shape of a molecule plays an important role in its reactivity.

• By noting the number of bonding and nonbonding electron pairs we can easily predict the shape of the molecule.
What Determines the Shape of a Molecule?

- Simply put, electron pairs, whether they be bonding or nonbonding, repel each other.
- By assuming the electron pairs are placed as far as possible from each other, we can predict the shape of the molecule.
Electron Domains

- We can refer to the electron pairs as **electron domains**.
- In a double or triple bond, all electrons shared between those two atoms are on the same side of the central atom; therefore, they count as one electron domain.
- The central atom in this molecule, A, has four electron domains.
Valence Shell Electron Pair Repulsion Theory (VSEPR)

“The best arrangement of a given number of electron domains is the one that minimizes the repulsions among them.”
**Electron-Domain Geometries**

These are the electron-domain geometries for two through six electron domains around a central atom.
Electron-Domain Geometries

- All one must do is count the number of electron domains in the Lewis structure.
- The geometry will be that which corresponds to the number of electron domains.

![Lewis structure and electron-domain geometry (tetrahedral)](image)
Molecular Geometries

- The electron-domain geometry is often *not* the shape of the molecule, however.
- The molecular geometry is that defined by the positions of *only* the atoms in the molecules, not the nonbonding pairs.
Within each electron domain, then, there might be more than one molecular geometry.
Linear Electron Domain

- In the linear domain, there is only one molecular geometry: linear.
- **NOTE:** If there are only two atoms in the molecule, the molecule will be linear no matter what the electron domain is.
There are two molecular geometries:

- Trigonal planar, if all the electron domains are bonding,
- Bent, if one of the domains is a nonbonding pair.
Nonbonding Pairs and Bond Angle

- Nonbonding pairs are physically larger than bonding pairs.
- Therefore, their repulsions are greater; this tends to decrease bond angles in a molecule.
Multiple Bonds and Bond Angles

• Double and triple bonds place greater electron density on one side of the central atom than do single bonds.

• Therefore, they also affect bond angles.
There are three molecular geometries:

- Tetrahedral, if all are bonding pairs,
- Trigonal pyramidal if one is a nonbonding pair,
- Bent if there are two nonbonding pairs.
Trigonal Bipyramidal Electron Domain

- There are two distinct positions in this geometry:
  - Axial
  - Equatorial
Trigonal Bipyramidal Electron Domain

Lower-energy conformations result from having nonbonding electron pairs in equatorial, rather than axial, positions in this geometry.
Trigonal Bipyramidal Electron Domain

- There are four distinct molecular geometries in this domain:
  - Trigonal bipyramidal
  - Seesaw
  - T-shaped
  - Linear
Octahedral Electron Domain

- All positions are equivalent in the octahedral domain.
- There are three molecular geometries:
  - Octahedral
  - Square pyramidal
  - Square planar
Larger Molecules

In larger molecules, it makes more sense to talk about the geometry about a particular atom rather than the geometry of the molecule as a whole.
Larger Molecules

This approach makes sense, especially because larger molecules tend to react at a particular site in the molecule.
Bond Polarity

- Electronegativity difference
- Nonpolar $<$ 0.5 $<$ polar $<$ 1.7 $<$ ionic

- Use chart on page 273
Polarity

• In Chapter 8 we discussed bond dipoles.
• But just because a molecule possesses polar bonds does not mean the molecule as a whole will be polar.
Polarity

By adding the individual bond dipoles, one can determine the overall dipole moment for the molecule.
Polarity

- Polar: H-Cl
- Nonpolar: F-B, Cl-C-Cl
- Polar: N-H, H-N-H

Molecular Geometries and Bonding
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Overlap and Bonding

- We think of covalent bonds forming through the sharing of electrons by adjacent atoms.
- In such an approach this can only occur when orbitals on the two atoms overlap.
Overlap and Bonding

- Increased overlap brings the electrons and nuclei closer together while simultaneously decreasing electron-electron repulsion.
- However, if atoms get too close, the internuclear repulsion greatly raises the energy.
But it’s hard to imagine tetrahedral, trigonal bipyramidal, and other geometries arising from the atomic orbitals we recognize.
Hybrid Orbitals

• Consider beryllium:
  – In its ground electronic state, it would not be able to form bonds because it has no singly-occupied orbitals.
Hybrid Orbitals

But if it absorbs the small amount of energy needed to promote an electron from the $2s$ to the $2p$ orbital, it can form two bonds.
Hybrid Orbitals

- Mixing the $s$ and $p$ orbitals yields two degenerate orbitals that are hybrids of the two orbitals.
  - These $sp$ hybrid orbitals have two lobes like a $p$ orbital.
  - One of the lobes is larger and more rounded as is the $s$ orbital.
Hybrid Orbitals

- These two degenerate orbitals would align themselves $180^\circ$ from each other.
- This is consistent with the observed geometry of beryllium compounds: linear.
Hybrid Orbitals

With hybrid orbitals the orbital diagram for beryllium would look like this.

- The $sp$ orbitals are higher in energy than the $1s$ orbital but lower than the $2p$. 
Hybrid Orbitals

Using a similar model for boron leads to...

1

2s

1

2p

Promote

1

2s

1

1

2p

Hybridize

1

1

1

sp^2

2p
Hybrid Orbitals

...three degenerate $sp^2$ orbitals.
Hybrid Orbitals

With carbon we get...

\[ \text{2s} \quad \text{1} \quad \text{1} \quad \text{2p} \quad \text{Promote} \quad \text{1} \quad \text{2s} \quad \text{1} \quad \text{1} \quad \text{1} \quad \text{Hybridize} \quad \text{1} \quad \text{1} \quad \text{1} \quad \text{1} \quad \text{sp}^3 \]
Hybrid Orbitals

...four degenerate \( sp^3 \) orbitals.
Hybrid Orbitals

For geometries involving expanded octets on the central atom, we must use $d$ orbitals in our hybrids.
Hybrid Orbitals

This leads to five degenerate $sp^3d$ orbitals…

…or six degenerate $sp^3d^2$ orbitals.
Hybrid Orbitals

Once you know the electron-domain geometry, you know the hybridization state of the atom.
Valence Bond Theory

• Hybridization is a major player in this approach to bonding.
• There are two ways orbitals can overlap to form bonds between atoms.
Sigma (σ) Bonds

• Sigma bonds are characterized by
  – Head-to-head overlap.
  – Cylindrical symmetry of electron density about the internuclear axis.
Pi ($\pi$) Bonds

- Pi bonds are characterized by
  - Side-to-side overlap.
  - Electron density above and below the internuclear axis.
Single Bonds

Single bonds are always $\sigma$ bonds, because $\sigma$ overlap is greater, resulting in a stronger bond and more energy lowering.
Multiple Bonds

In a multiple bond one of the bonds is a $\sigma$ bond and the rest are $\pi$ bonds.
Multiple Bonds

- In a molecule like formaldehyde (shown at left) an \( sp^2 \) orbital on carbon overlaps in \( \sigma \) fashion with the corresponding orbital on the oxygen.

- The unhybridized \( p \) orbitals overlap in \( \pi \) fashion.
Multiple Bonds

In triple bonds, as in acetylene, two $sp$ orbitals form a $\sigma$ bond between the carbons, and two pairs of $p$ orbitals overlap in $\pi$ fashion to form the two $\pi$ bonds.
Resonance

This is the Lewis structure we would draw for ozone, $\text{O}_3$. 
Resonance

- But this is at odds with the true, observed structure of ozone, in which...
  - ...both O-O bonds are the same length.
  - ...both outer oxygens have a charge of -1/2.
Resonance

• One Lewis structure cannot accurately depict a molecule like ozone.
• We use multiple structures, resonance structures, to describe the molecule.
Resonance

Just as green is a synthesis of blue and yellow...

...ozone is a synthesis of these two resonance structures.
Resonance

- In truth, the electrons that form the second C-O bond in the double bonds below do not always sit between that C and that O, but rather can move among the two oxygens and the carbon.
- They are not localized; they are delocalized.
Resonance

- The organic compound benzene, C\textsubscript{6}H\textsubscript{6}, has two resonance structures.
- It is commonly depicted as a hexagon with a circle inside to signify the delocalized electrons in the ring.
Delocalized Electrons: Resonance

When writing Lewis structures for species like the nitrate ion, we draw resonance structures to more accurately reflect the structure of the molecule or ion.

\[
\begin{align*}
\text{[O=\text{N}=\text{O}^-]} & \quad \leftrightarrow \quad \text{[O=\text{N}=\text{O}^-]} & \quad \leftrightarrow \quad \text{[O=\text{N}=\text{O}^-]} \\
\text{[O=\text{N}=\text{O}^-]} & \quad \leftrightarrow \quad \text{[O=\text{N}=\text{O}^-]} & \quad \leftrightarrow \quad \text{[O=\text{N}=\text{O}^-]}
\end{align*}
\]
Delocalized Electrons: Resonance

- In reality, each of the four atoms in the nitrate ion has a $p$ orbital.
- The $p$ orbitals on all three oxygens overlap with the $p$ orbital on the central nitrogen.
Delocalized Electrons: Resonance

This means the $\pi$ electrons are not localized between the nitrogen and one of the oxygens, but rather are delocalized throughout the ion.
Resonance

The organic molecule benzene has six $\sigma$ bonds and a $\rho$ orbital on each carbon atom.
Resonance

• In reality the $\pi$ electrons in benzene are not localized, but delocalized.
• The even distribution of the $\pi$ electrons in benzene makes the molecule unusually stable.
Covalent Bond Strength

\[
\begin{align*}
:\text{Cl} & \equiv \text{Cl}\,(g) \\
\rightarrow & \\
2 \cdot \text{Cl}\,(g)
\end{align*}
\]

• Most simply, the strength of a bond is measured by determining how much energy is required to break the bond.
• This is the bond enthalpy.
• The bond enthalpy for a Cl-Cl bond, \(D(\text{Cl-Cl})\), is measured to be 242 kJ/mol.
Average Bond Enthalpies

- This table lists the average bond enthalpies for many different types of bonds.
- Average bond enthalpies are positive, because bond breaking is an endothermic process.

<table>
<thead>
<tr>
<th>Single Bonds</th>
<th>Average Bond Enthalpies (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C—H</td>
<td>413</td>
</tr>
<tr>
<td>C—C</td>
<td>348</td>
</tr>
<tr>
<td>C—N</td>
<td>293</td>
</tr>
<tr>
<td>C—O</td>
<td>358</td>
</tr>
<tr>
<td>C—F</td>
<td>485</td>
</tr>
<tr>
<td>C—Cl</td>
<td>328</td>
</tr>
<tr>
<td>C—Br</td>
<td>276</td>
</tr>
<tr>
<td>C—I</td>
<td>240</td>
</tr>
<tr>
<td>C—S</td>
<td>259</td>
</tr>
<tr>
<td>Si—H</td>
<td>323</td>
</tr>
<tr>
<td>Si—Si</td>
<td>226</td>
</tr>
<tr>
<td>Si—C</td>
<td>301</td>
</tr>
<tr>
<td>Si—O</td>
<td>368</td>
</tr>
<tr>
<td>Si—Cl</td>
<td>464</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Multiple Bonds</th>
<th>Average Bond Enthalpies (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=C</td>
<td>614</td>
</tr>
<tr>
<td>C≡C</td>
<td>839</td>
</tr>
<tr>
<td>C≡N</td>
<td>615</td>
</tr>
<tr>
<td>C≡N</td>
<td>891</td>
</tr>
<tr>
<td>C=O</td>
<td>799</td>
</tr>
<tr>
<td>C≡O</td>
<td>1072</td>
</tr>
</tbody>
</table>
NOTE: These are average bond enthalpies, not absolute bond enthalpies; the C-H bonds in methane, CH$_4$, will be a bit different than the C-H bond in chloroform, CHCl$_3$.

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<th>Average Bond Enthalpies (kJ/mol)</th>
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</thead>
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<tr>
<td>C—C</td>
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</tr>
<tr>
<td>C—O</td>
<td>358</td>
</tr>
<tr>
<td>C—F</td>
<td>485</td>
</tr>
<tr>
<td>C—Cl</td>
<td>328</td>
</tr>
<tr>
<td>C—Br</td>
<td>276</td>
</tr>
<tr>
<td>C—I</td>
<td>240</td>
</tr>
<tr>
<td>C—S</td>
<td>259</td>
</tr>
<tr>
<td>Si—H</td>
<td>323</td>
</tr>
<tr>
<td>Si—Si</td>
<td>226</td>
</tr>
<tr>
<td>Si—C</td>
<td>301</td>
</tr>
<tr>
<td>Si—O</td>
<td>368</td>
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<tr>
<td>Si—Cl</td>
<td>464</td>
</tr>
</tbody>
</table>

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<th>Average Bond Enthalpies (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=O</td>
<td>1072</td>
</tr>
<tr>
<td>C=O</td>
<td>979</td>
</tr>
<tr>
<td>C=Cl</td>
<td>891</td>
</tr>
<tr>
<td>C=N</td>
<td>615</td>
</tr>
<tr>
<td>C=N</td>
<td>941</td>
</tr>
<tr>
<td>C=N</td>
<td>615</td>
</tr>
<tr>
<td>N=O</td>
<td>607</td>
</tr>
<tr>
<td>N=O</td>
<td>594</td>
</tr>
<tr>
<td>N=O</td>
<td>594</td>
</tr>
<tr>
<td>O$_2$</td>
<td>495</td>
</tr>
<tr>
<td>S=O</td>
<td>523</td>
</tr>
<tr>
<td>S=O</td>
<td>523</td>
</tr>
<tr>
<td>S=S</td>
<td>418</td>
</tr>
</tbody>
</table>
Enthalpies of Reaction

• Yet another way to estimate $\Delta H$ for a reaction is to compare the bond enthalpies of bonds broken to the bond enthalpies of the new bonds formed.

• In other words,

$$\Delta H_{\text{rxn}} = \sum(\text{bond enthalpies of bonds broken}) - \sum(\text{bond enthalpies of bonds formed})$$
• Formal Charge
Writing Lewis Structures

• Then assign formal charges.
  – For each atom, count the electrons in lone pairs and half the electrons it shares with other atoms.
  – Subtract that from the number of valence electrons for that atom: the difference is its formal charge.

```
Valence electrons:  6  4  6
                   6  4  6
(Electrons assigned to atom):  6  4  6
                                  7  4  5

Formal charge:      0  0  0
                      -1  0  +1
```
Writing Lewis Structures

• The best Lewis structure...
  – ...is the one with the fewest charges.
  – ...puts a negative charge on the most electronegative atom.

\[
\begin{align*}
&[:\overset{\cdot}{N}\equiv C\equiv O:]^- \\
&[:\overset{\cdot}{N}=C=\overset{\cdot}{O}]^- \\
&[:\overset{\cdot}{N}=C\equiv \overset{\cdot}{O}]^- \\
\end{align*}
\]
Metallic bonding

Sea of electrons
Figure 11.45

Molecular Geometries and Bonding

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Metal ion (+)
Ionic Bonding
Energetics of Ionic Bonding

As we saw in the last chapter, it takes 495 kJ/mol to remove electrons from sodium.

<table>
<thead>
<tr>
<th>Element</th>
<th>$I_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>495</td>
</tr>
<tr>
<td>Mg</td>
<td>738</td>
</tr>
<tr>
<td>Al</td>
<td>578</td>
</tr>
</tbody>
</table>
Energetics of Ionic Bonding

We get 349 kJ/mol back by giving electrons to chlorine.
Energetics of Ionic Bonding

But these numbers don’t explain why the reaction of sodium metal and chlorine gas to form sodium chloride is so exothermic!
Energetics of Ionic Bonding

• There must be a third piece to the puzzle.
• What is as yet unaccounted for is the electrostatic attraction between the newly-formed sodium cation and chloride anion.
Lattice Energy

• This third piece of the puzzle is the lattice energy:
  – The energy required to completely separate a mole of a solid ionic compound into its gaseous ions.

• The energy associated with electrostatic interactions is governed by Coulomb’s law:

  \[ E_{el} = \kappa \frac{Q_1 Q_2}{d} \]
Lattice Energy

• Lattice energy, then, increases with the charge on the ions.
• It also increases with decreasing size of ions.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lattice Energy (kJ/mol)</th>
<th>Compound</th>
<th>Lattice Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>1030</td>
<td>MgCl₂</td>
<td>2326</td>
</tr>
<tr>
<td>LiCl</td>
<td>834</td>
<td>SrCl₂</td>
<td>2127</td>
</tr>
<tr>
<td>LiI</td>
<td>730</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaF</td>
<td>910</td>
<td>MgO</td>
<td>3795</td>
</tr>
<tr>
<td>NaCl</td>
<td>788</td>
<td>CaO</td>
<td>3414</td>
</tr>
<tr>
<td>NaBr</td>
<td>732</td>
<td>SrO</td>
<td>3217</td>
</tr>
<tr>
<td>NaI</td>
<td>682</td>
<td>ScN</td>
<td>7547</td>
</tr>
<tr>
<td>KF</td>
<td>808</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KCl</td>
<td>701</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KBr</td>
<td>671</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CsCl</td>
<td>657</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CsI</td>
<td>600</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Energetics of Ionic Bonding

By accounting for all three energies (ionization energy, electron affinity, and lattice energy), we can get a good idea of the energetics involved in such a process.
Energetics of Ionic Bonding

- These phenomena also helps explain the “octet rule.”

- Metals, for instance, tend to stop losing electrons once they attain a noble gas configuration because energy would be expended that cannot be overcome by lattice energies.