**Bond Length and Bond Order**

**Bond order** indicates whether a covalent bond is **single** (b.o. = 1), **double** (b.o. = 2), or **triple** (b.o. = 3).

**Bond length** is the distance (in pm or Å) between the nuclei of two atoms joined by a covalent bond.

*Bond length depends on the particular atoms in the bond and on the bond order*.

---

**Bond Energies**

**Bond-dissociation energy** \((D)\) is the amount of energy required to break one mole of covalent bonds between atoms in a molecule in the *gas* phase.

\[
\text{atom} + 436 \text{ kJ} \rightarrow \text{atom} + \text{atom}
\]

\[
\text{atom} + 499 \text{ kJ} \rightarrow \text{atom} + \text{atom}
\]

\[
\text{atom} + 428 \text{ kJ} \rightarrow \text{atom} + \text{atom}
\]

When a certain bond may exist in different molecules (O–H, N–H, C–N, etc.), its bond dissociation energy represents an average value.
Representative Bond Lengths

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Length, pm</th>
<th>Bond Energy, kJ/mol</th>
<th>Bond</th>
<th>Bond Length, pm</th>
<th>Bond Energy, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>H—H</td>
<td>74</td>
<td>436</td>
<td>C—O</td>
<td>143</td>
<td>360</td>
</tr>
<tr>
<td>H—C</td>
<td>110</td>
<td>414</td>
<td>C==O</td>
<td>129</td>
<td>736</td>
</tr>
<tr>
<td>H—N</td>
<td>100</td>
<td>389</td>
<td>C—Cl</td>
<td>178</td>
<td>339</td>
</tr>
<tr>
<td>H—O</td>
<td>97</td>
<td>464</td>
<td>N—N</td>
<td>145</td>
<td>163</td>
</tr>
<tr>
<td>H—S</td>
<td>132</td>
<td>368</td>
<td>N==N</td>
<td>123</td>
<td>418</td>
</tr>
<tr>
<td>H—F</td>
<td>92</td>
<td>365</td>
<td>N==N</td>
<td>110</td>
<td>946</td>
</tr>
<tr>
<td>H—Cl</td>
<td>127</td>
<td>431</td>
<td>N—O</td>
<td>136</td>
<td>222</td>
</tr>
<tr>
<td>H—Br</td>
<td>141</td>
<td>364</td>
<td>N==O</td>
<td>129</td>
<td>590</td>
</tr>
<tr>
<td>H—I</td>
<td>161</td>
<td>297</td>
<td>O—O</td>
<td>145</td>
<td>142</td>
</tr>
<tr>
<td>C—C</td>
<td>154</td>
<td>347</td>
<td>O==O</td>
<td>121</td>
<td>498</td>
</tr>
<tr>
<td>C==C</td>
<td>134</td>
<td>613</td>
<td>F—F</td>
<td>143</td>
<td>159</td>
</tr>
<tr>
<td>C==Cl</td>
<td>120</td>
<td>837</td>
<td>Cl—Cl</td>
<td>199</td>
<td>243</td>
</tr>
<tr>
<td>C==N</td>
<td>147</td>
<td>305</td>
<td>Br—Br</td>
<td>228</td>
<td>193</td>
</tr>
<tr>
<td>C==N</td>
<td>128</td>
<td>615</td>
<td>I==I</td>
<td>266</td>
<td>151</td>
</tr>
<tr>
<td>C==N</td>
<td>116</td>
<td>891</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Electronegativity affects bond energy & length

In heteronuclear molecules, bond length equals the sum of covalent radii

1 Å = 100 pm

Bond order affects bond energy & length

Calculations Using Bond Energies

The sum of the energy changes for breaking the old bonds and forming the new bonds is the energy change for the reaction
Summary of Concepts

• Bond length depends on the type of atoms and the bond order
  – Higher b.o. ⇒ shorter bonds!

• Bond energy is the energy required to break the bond
  – Every bond contains energy!

Molecular Geometry

The molecular geometry is the shape of the molecule formed by joining the atomic nuclei in straight lines.
**VSEPR**

- *Valence-Shell Electron-Pair Repulsion (VSEPR)* is a simple method for determining geometry.

- Basis: **pairs of valence electrons** (bonding or non-bonding) in the atom **repel one another**.

- These mutual repulsions push electron pairs as far from one another as possible.

When the electron pairs (bonds) are as far apart as they can get, what will be the B-A-B angle?

**Electron-Group Geometries**

How can electrons on the central atom be arranged so they are as far apart as possible?

- 2 electron groups – linear
- 3 electron groups – trigonal planar
- 4 electron groups – tetrahedral
- 5 electron groups – trigonal bipyramidal
- 6 electron groups – octahedral
A VSEPR Summary

The optimal repulsion arrangement is opposite ends of a line

**What happens when there are lone pairs?**

Example: \( \\text{NO}_2^- \)

---

**Structures with Lone Pairs**

- Electron groups on the central atom repel one another, whether they are shared pairs or lone pairs.
- However, the geometry of the *molecule* is determined by the bonded atoms.

Nitrite ion is *bent* or *angular*, with a bond angle of 120°.

Three electron groups are 120° apart, regardless of what is (or isn’t) attached.
A VSEPR Summary

<table>
<thead>
<tr>
<th>Number of Electron Groups</th>
<th>Electron-Group Geometry</th>
<th>Number of Lone Pairs</th>
<th>VSEPR Notation</th>
<th>Molecular Geometry</th>
<th>Ideal Bond Angles</th>
<th>Example</th>
<th>Molecular Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Trigonal planar</td>
<td>0</td>
<td>AX₃</td>
<td>X—A</td>
<td>120°</td>
<td>BF₃</td>
<td><img src="image" alt="BF₃" /></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The optimal repulsion arrangement is the corners of a triangle—note the planarity.

With a lone pair, the geometry is essentially the same.

| 3                         | Trigonal planar         | 1                    | AX₂            | X—A               | 120°             | SO₂     | ![SO₂](image)   |
|                           |                         |                      |                |                   |                  |         |                |

What happens with AX₄ molecules?

| 4                         | Tetrahedral             | 0                    | AX₄            | X—X               | 109.5°           | methane | ![CH₄](image)    |
|                           |                         |                      |                |                   |                  |         |                |

The optimal repulsion arrangement is the corners of a regular tetrahedron—four equal triangular faces.
Geometry of Methane

A VSEPR Summary

<table>
<thead>
<tr>
<th>Number of Electron Groups</th>
<th>Electron-Group Geometry</th>
<th>Number of Lone Pairs</th>
<th>VSEPR Notation</th>
<th>Molecular Geometry</th>
<th>Ideal Bond Angles</th>
<th>Example</th>
<th>Molecular Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>Tetrahedral</td>
<td>1</td>
<td>$\tilde{\text{AX}}_3$</td>
<td>Trigonal pyramidal</td>
<td>109.5$^\circ$</td>
<td>$\text{NH}_3$</td>
<td>ammonia</td>
</tr>
<tr>
<td>4</td>
<td>Tetrahedral</td>
<td>2</td>
<td>$\tilde{\text{AX}}_2$</td>
<td>Angular</td>
<td>109.5$^\circ$</td>
<td>$\text{H}_2\text{O}$</td>
<td>water</td>
</tr>
</tbody>
</table>

Never underestimate the lone pairs…!
Molecular Geometry of Water

Is the water molecule tetrahedral?

No; its electron groups are tetrahedrally arranged. The molecule is _______.

A VSEPR Summary

<table>
<thead>
<tr>
<th>Number of Electron Groups</th>
<th>Electron-Group Geometry</th>
<th>Number of Lone Pairs</th>
<th>VSEPR Notation</th>
<th>Molecular Geometry</th>
<th>Ideal Bond Angles</th>
<th>Example</th>
<th>Molecular Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Trigonal pyramidal</td>
<td>0</td>
<td>AX₃</td>
<td>90°, 120°, 180°</td>
<td>PCl₅</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The optimal repulsion arrangement is a triangle with a bisecting line through the triangle face
A VSEPR Summary

<table>
<thead>
<tr>
<th>Number of Electron Groups</th>
<th>Electron-Group Geometry</th>
<th>Number of Lone Pairs</th>
<th>VSEPR Notation</th>
<th>Molecular Geometry</th>
<th>Ideal Bond Angles</th>
<th>Example</th>
<th>Molecular Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>Trigonal Bipyramidal</td>
<td>1</td>
<td>$\text{AX}_2$</td>
<td>T-shaped</td>
<td>90°, 180°</td>
<td>SF$_6$</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Trigonal Bipyramidal</td>
<td>2</td>
<td>$\text{AX}_3$</td>
<td>Linar</td>
<td>90°, 180°</td>
<td>CHF$_3$</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Trigonal Bipyramidal</td>
<td>3</td>
<td>$\text{AX}_4$</td>
<td></td>
<td>180°</td>
<td>XeF$_2$</td>
<td></td>
</tr>
</tbody>
</table>

The optimal repulsion arrangement is an octahedron
A VSEPR Summary

<table>
<thead>
<tr>
<th>Number of Electron Groups</th>
<th>Electron-Group Geometry</th>
<th>Number of Lone Pairs</th>
<th>VSEPR Notation</th>
<th>Molecular Geometry</th>
<th>Ideal Bond Angles</th>
<th>Example</th>
<th>Molecular Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>Octahedral</td>
<td>1</td>
<td>AX₄</td>
<td>Tetrahedral</td>
<td>90°</td>
<td>BrF₅</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Octahedral</td>
<td>2</td>
<td>AX₅</td>
<td>Trigonal bipyramidal</td>
<td>90°</td>
<td>XeF₄</td>
<td></td>
</tr>
</tbody>
</table>

Structures with No Lone Pairs

- AX₂ ⇒ linear.
- AX₃ ⇒ trigonal planar
- AX₄ ⇒ tetrahedral
- AX₅ ⇒ trigonal bipyramidal
- AX₆ ⇒ octahedral

require an expanded valence shell ⇒ central atom is a third-period or higher element (i.e., has valence d orbitals).
Some Structures with Lone Pairs

- ÆX$_2$ ⇒ electron-group geometry: *trigonal planar*  
  molecular geometry: *bent*
- ÆX$_2$ ⇒ electron-group geometry: *tetrahedral*  
  molecular geometry: *bent*
- ÆX$_3$ ⇒ electron-group geometry: *tetrahedral*  
  molecular geometry: *trigonal pyramidal*
- ÆX$_4$ ⇒ electron-group geometry: *trigonal bipyramidal*  
  molecular geometry: *seesaw*
- ÆX$_4$ ⇒ electron-group geometry: *octahedral*  
  molecular geometry: *square planar*

Polar Molecules and Dipole Moments

- A *polar bond* has separate centers of positive and negative charge.
- A *molecule* with separate centers of positive and negative charge is a *polar molecule.*
- The *dipole moment* (µ) of a molecule:  
  \[ \mu = \delta \cdot d \]
- A unit of dipole moment is the *debye (D).*
- One debye (D) is equal to $3.34 \times 10^{-30}$ C m.
Polar Molecules in an Electric Field

An electric field causes polar molecules to align with the field.

(a)
(b)

Bond and Molecular Dipoles

• A dipole is a vector: it has a magnitude and direction
  – Dipoles in a molecule can cancel each other!

\[
\begin{align*}
\text{O} & \quad \text{C} \quad \text{O} \\
\mu &= 0
\end{align*}
\]

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{O} & \quad \text{H} \\
\text{H} & \quad 104.5^\circ \\
\mu &= 1.84 \text{ D}
\end{align*}
\]
How to Determine if a Molecule is Polar

• Use electronegativity values to predict bond dipoles
• Use the VSEPR method to predict the molecular shape
• From the molecular shape, determine whether bond dipoles cancel to give a nonpolar molecule or combine to produce a resultant dipole moment for the molecule

Summary of Concepts

• The VSEPR method is used to predict the shapes of molecules and polyatomic ions
  – Electron groups repel each other
  – Lone pairs repel more
• The bond’s dipole moment can be estimated from the electronegativity values of the atoms
  – The net dipole moment of a molecule depends on its shape