Unit 1
Inorganic and Physical Chemistry
Shapes of Molecules and Polyatomic Ions

\[
\begin{align*}
\text{CH}_3 & \quad 109.5^\circ \\
\text{NH}_3 & \quad 107^\circ \\
\text{H}_2\text{O} & \quad 104.5^\circ
\end{align*}
\]
Shapes of molecules

Bonding and Electronegativity - Revision

A Covalent Bond will form when atoms can rearrange their electrons (by sharing) to produce an arrangement of lower energy. An Ionic Bond will form when atoms can rearrange their electrons (transfer) to produce an arrangement of lower energy.

Ionic and Covalent are, in fact, rather arbitrary labels and it is no longer enough to simply look to see if a metal element is involved or not. Ionic and Covalent are just opposite ends of a bonding continuum. Most bonds lie between these two extremes. Electronegativity values are a useful guide but properties will still need to be studied to provide confirmation.

A simple summary of bonding covered in Higher Chemistry is shown below, where $\Delta EN = \text{difference in electronegativity values between the two atoms forming the bond.}$

This illustrates that non-polar covalent bonding and ionic bonding are considered as being at opposite ends of a bonding continuum with polar covalent bonding lying between these two extremes. This is very much a simplified summary with metallic
bonding being ignored. There are also well-known exceptions such as carbon in the form of graphite, which can conduct electricity.

Electronegativity differences between atoms of different elements are helpful but do not always predict the type of bonding correctly. For example, consider the two compounds sodium hydride (NaH) and water (H2O):

sodium hydride: $EN$ for Na = 0.9  $EN$ for H = 2.2
so $\Delta EN = 2.2 - 0.9 = 1.3 $

water: $EN$ for H = 2.2  $EN$ for O = 3.5
so $\Delta EN = 3.5 - 2.2 = 1.3$

It might therefore be expected that both compounds will have the same type of bonding, most likely polar covalent. However, sodium hydride is a solid at room temperature and when melted and electrolysed, hydrogen gas is produced at the positive electrode. This demonstrates that sodium hydride is ionic and also that it contains the hydride ion, $H^-$. Water, of course, has polar covalent bonding.

Electronegativity values and their differences are useful indicators of the type of bonding but it is also necessary to study the properties of the substance for confirmation or otherwise.

**VSEPR Rules**

In order to predict molecular shape, we consider that all outer shell electrons (valence electrons) of the central atom repel each other. Therefore, the molecule adopts whichever 3D
geometry minimizes this repulsion. Both bonding and non-bonding electron pairs must be considered.

We call this process the Valence Shell Electron Pair Repulsion (VSEPR) theory.

\[ \text{NH}_3 \rightarrow \text{H} - \text{N} \cdots \text{H} \rightarrow \text{H} - \text{N} - \text{H} \rightarrow \]

Lewis structure

Electron-pair geometry (tetrahedral)

Molecular geometry (trigonal pyramidal)

The shapes of molecules or polyatomic ions (e.g. \( \text{NH}_4^+ \)) can be predicted from the number of bonding electron pairs and the number of non-bonding electron pairs (lone pairs). This is because the direction which covalent bonds take up in space is determined by the number of orbitals occupied by electron pairs and the repulsion between these orbitals. The repulsive effect of a nonbonded pair or lone pair of electrons is greater than that of a bonded pair and so the trend in repulsive effect is:

\[ \text{bonded pair:bonded pair} < \text{bonded pair:lone pair} < \text{lone pair:lone pair} \]

The shape adopted by the molecule or polyatomic ion is the one in which the electron pairs in the outer shell get as far apart as possible. In other words, the shape in which there is the minimum repulsion between the electron pairs.
It is important not to confuse the number of atoms with the number of electron pairs.

For example, CF$_4$ and XeF$_4$ may, at first sight, appear likely to be the same shape.

Electron pairs = \( \frac{\text{electrons of central atom} + \text{no. of atoms attached}}{2} \)

\[
\text{CF}_4 = \frac{4 + 4}{2} = 4 \text{ pairs.}
\]

\[
\text{XeF}_4 = \frac{8 + 4}{2} = 6 \text{ pairs.}
\]

To minimise repulsion, the electron pairs arrange themselves in given shapes:

<table>
<thead>
<tr>
<th>Number of Electron Pairs</th>
<th>Arrangement of Electron Pairs</th>
<th>Electron-Pair Geometry</th>
<th>Predicted Bond Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td></td>
<td>Linear</td>
<td>180°</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>Trigonal planar</td>
<td>120°</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>Tetrahedral</td>
<td>109.5°</td>
</tr>
</tbody>
</table>
Bonding electrons, because they are attracted by two nuclei, do not repel as much as non-bonding electrons. This can cause 'distortions' in the shapes of molecules:

Since lone pairs repel more than bonding pairs, this leads to a wide range of shapes within different molecules:

Electron pair repulsions decrease in strength in the order:
- non-bonding/non-bonding
- non-bonding/bonding
- bonding/bonding
Placing the non-bonding lone pairs at the Axial positions would appear to give least repulsion but they would only be 90° away from the 3 bonding pairs. To minimize $e^-\text{--} e^-$ repulsion, lone pairs are always placed in equatorial positions, so ...

The final shape of the bonds in the molecule are T-shaped, although the electron pairs take up an octahedral shape.

<table>
<thead>
<tr>
<th>Total number of electron pairs</th>
<th>Arrangement of electron pairs</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Linear</td>
</tr>
<tr>
<td>3</td>
<td>Trigonal</td>
</tr>
<tr>
<td>4</td>
<td>Tetrahedral</td>
</tr>
<tr>
<td>5</td>
<td>Trigonal bipyramidal</td>
</tr>
<tr>
<td>6</td>
<td>Octahedral</td>
</tr>
<tr>
<td>Steric No.</td>
<td>Basic Geometry</td>
</tr>
<tr>
<td>-----------</td>
<td>---------------</td>
</tr>
<tr>
<td>2</td>
<td>Linear</td>
</tr>
<tr>
<td>3</td>
<td>Bent or Angular</td>
</tr>
<tr>
<td>4</td>
<td>Bent or Angular</td>
</tr>
<tr>
<td>5</td>
<td>Bent or Angular</td>
</tr>
<tr>
<td>6</td>
<td>Bent or Angular</td>
</tr>
</tbody>
</table>