Polar and non-polar bonds

In homonuclear diatomic molecules such as H$_2$ or Cl$_2$, electrons are shared equally between equal atoms. The result is that the electron distribution in such molecules is symmetrical with the centre of the molecule intercepting a mirror plane that is perpendicular to the inter-nuclear axis (perpendicular to the bond). There is an equal amount of charge (electron charge density) distributed on either side of this mirror plane (on either side of the molecule) resulting in a non-polar covalent bond.

In heteronuclear molecules such as HCl or IBr the electrons are not shared equally resulting in a polar bond. Recall from earlier that each atom is characterized by an atomic property we called electron affinity, which was the energy change that occurred when an isolated gaseous atom gained an electron. In general atoms with a greater electron affinity attract the shared electron pair more strongly. In molecules, however we do not have isolated gas phase atoms and it is therefore not appropriate to refer to electron affinity. **A measure that describes the ability of an atom in a molecule to attract shared electrons to itself is known as electronegativity.** A widely used scale is the Pauling electronegativity scale. From the table below you can see that electronegativity correlates extremely well with electron affinity. It generally decreases from the top to the bottom in a group and increases from the left to the right within a period making fluorine the most electronegative atom.

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
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<th>11</th>
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<tbody>
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</tr>
<tr>
<td>2</td>
<td>Li</td>
<td>Be</td>
<td>0-1.9</td>
<td>2-2.9</td>
<td>3.0-4.0</td>
<td>B</td>
<td>C</td>
<td>N</td>
<td>O</td>
<td>F</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>3</td>
<td>Na</td>
<td>Mg</td>
<td>0.9</td>
<td>1.2</td>
<td>Al</td>
<td>Si</td>
<td>P</td>
<td>S</td>
<td>Cl</td>
<td></td>
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</tr>
<tr>
<td>4</td>
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<td>Ca</td>
<td>Sc</td>
<td>Ti</td>
<td>V</td>
<td>Cr</td>
<td>Mn</td>
<td>Fe</td>
<td>Co</td>
<td>Ni</td>
<td>Cu</td>
<td>Zn</td>
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<td>Ge</td>
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<td>Sr</td>
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<td>Ru</td>
<td>Rh</td>
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<td>Ag</td>
<td>Cd</td>
<td>In</td>
<td>Sn</td>
<td>Sb</td>
<td>Te</td>
<td>I</td>
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<td>Ba</td>
<td>La</td>
<td>Hf</td>
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<td>W</td>
<td>Re</td>
<td>Os</td>
<td>Ir</td>
<td>Pt</td>
<td>Au</td>
<td>Hg</td>
<td>Tl</td>
<td>Pb</td>
<td>Bi</td>
<td>Po</td>
<td>At</td>
</tr>
<tr>
<td>7</td>
<td>Fr</td>
<td>Ra</td>
<td>Ac</td>
<td>Lanthanides: 1.1-1.3</td>
<td>Actinides: 1.3-1.5</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Nonpolar covalent bonds (e.g. H$_2$) and ionic bonds (e.g. NaCl) represent extremes of types of chemical bonds. Polar covalent bonds have both, covalent and ionic character.

The greater the difference in electronegativity between two atoms that are chemically bound the more polar is the bond and the closer it will be to an ionic bond.
**Dipole Moments**

We can actually measure how polar a bond is.

When two atoms share electrons unequally a **bond dipole** results. Two equal but opposite charges $Q$ that are separated by a distance $r$ produce a dipole moment $\mu$ which is calculated: $\mu = Q \times r$

![Dipole Moment Diagram](image)

The dipole moment can be measured by introducing molecules between the plates of a capacitor. Without an electric field the molecules orient randomly. When an electric field is applied the polar molecules will align in the field so that the positive ends of the molecules point to the negative plate and vice versa. This weakens the applied electric field and the greater the dipole moment in the molecules the greater the effect.

The unit of the dipole moment is the Debye (D). 1D $= 3.34 \times 10^{-30}$ coulomb $\times$ meter (Cm).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond Length (pm)</th>
<th>$\Delta$ Electronegativity</th>
<th>Dipole Moment (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>92</td>
<td>1.9</td>
<td>1.82</td>
</tr>
<tr>
<td>HCl</td>
<td>127</td>
<td>0.9</td>
<td>1.08</td>
</tr>
<tr>
<td>HBr</td>
<td>141</td>
<td>0.7</td>
<td>0.82</td>
</tr>
<tr>
<td>HI</td>
<td>161</td>
<td>0.4</td>
<td>0.44</td>
</tr>
</tbody>
</table>

Positive or negative fractional charges also known as **partial charges** arising from the unequal sharing of bonding electron pairs are indicated as $\delta^+$ and $\delta^-$ above the atom which gives rise to the partial charge.

**Class exercise**: Calculate the partial charges $\delta^+$ and $\delta^-$ on the hydrogen and chlorine atom in HCl. Use the dipole moment and the bond length for HCl provided in the table above.

Considering that the charge of an electron is $1.602 \times 10^{-19}$ C what is the % ionic character of the HCl bond?
Polar molecules

Polarity is of immense importance. It affects a wide range of chemical and physical properties including reactivity, states of matter, vapour pressure, surface tension, solubility, cohesion, viscosity, capillary forces, melting point depression, osmosis and many more. We will cover some of the properties that are more relevant to engineering chemistry in chapter 4. Before we can proceed it is essential to easily distinguish polar from non-polar molecules.

In diatomic molecules the case is trivial. There is only one bond and thus if the bond is polar the molecule will be polar.

In tri or polyatomic molecules the decision if a molecule is polar or not, does not solely rest on the presence of polar bonds within the molecule but critically depends on the orientation of these polar bonds with respect to each other.

Carbon dioxide for example contains two C=O double bonds which are clearly polar. The shared electron pairs are attracted to the electronegative oxygens more so than to the less electronegative carbon. If one measures the dipole moment of CO\(_2\) one finds though that the molecule is non-polar with a dipole moment of exactly 0 Debye. How can this be? The answer lies in the shape of the molecule. CO\(_2\) is a linear molecule. The two polar C=O bonds are aligned much like two equal teams in a tug o war.

\[
\begin{align*}
\text{Sulfur dioxide on the other hand is a polar molecule. The molecule is bent with an OSO bond angle of approximately 120°. This means the individual bond dipoles in SO}_2 \text{ do not cancel as in CO}_2 \text{ but add up to give resultant dipole moment (\textbf{bold vertical arrow}).}
\end{align*}
\]
The shape of molecules.

How did we know that CO$_2$ is linear and SO$_2$ is bent? Is there a simple theory out there that allows us to make predictions about the shape of molecules and ions? The answer is yes: VSEPR or Valence Shell Electron Pair Repulsion theory. The Theory only makes four assumptions:

1. Electron pairs, called electron groups repel another whether they are in chemical bonds (X) or lone pairs (E).
2. Valence electron pairs are oriented to be as far apart as possible to minimize repulsion (achieve lowest energy)
3. Multiple bonds count as one electron group only.
4. Lone pair-lone pair repulsions are stronger than lone pair-bonding pair repulsion and lone pair-bonding pair repulsion is stronger than bonding pair-bonding pair repulsion (Simply put, lone pairs need more space than bonding pairs)

So how do 2,3,4,5 and 6 electron groups arrange around a central atom to minimize repulsion? They give rise to linear, trigonal planar, tetrahedral, trigonal bipyramidal and octahedral electron group geometry (EGG, also known as parent shape) respectively. You must know the names of these shapes and be able to draw them!
Now that you know how to derive the electron group geometry (determined by the number of electron groups around the central atom) it is possible to predict the shape of the molecule. Remember: It is the EGG that determines the molecular shape.

To determine the shape of a molecule or ion:

1. Draw the Lewis structure
2. Determine the number of bonding pairs (X). Remember to count multiple bonds as one bonding pair only!
3. Determine the number of lone pairs (E).
4. EGG = X + E
5. Once EGG is known place lone pairs (E) in positions to minimize E-E and E-X repulsions.
6. The molecular geometry (SHAPE) is determined by the position of the bond pairs (X) (e.g. we only see the atoms, not the electron pairs)

Class Exercises and example.

Determine the shape of the species bellow. Start by drawing a valid Lewis structure showing all valence electrons and all nonzero formal charges. Draw and name both the parent shape and the molecular shape. Finally indicate if the species is polar or not.

SO$_2$, BF$_3$, [SO$_4$]$^{2-}$, H$_2$O, NH$_3$, PBr$_5$, SF$_4$, ClF$_5$, [I$_3$]$,^-$, SF$_6$, BrF$_5$, XeF$_4$.

<table>
<thead>
<tr>
<th>Lewis Structure</th>
<th>EGG</th>
<th>Parent shape</th>
<th>Molecular shape</th>
<th>Polar (Yes or No)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_2$</td>
<td>3</td>
<td>Trigonal planar</td>
<td>Bent</td>
<td>Yes</td>
</tr>
</tbody>
</table>

SO$_2$
$[\text{SO}_4]^{2-}$

$\text{H}_2\text{O}$

$\text{NH}_3$

$\text{PBr}_5$

$\text{SF}_4$

$\text{ClF}_3$
*) remember that there is more than one valid Lewis structure that can be drawn for the sulfate ion (class exercise). Do the non-equivalent Lewis structures produce the same shape?