3.7: Electronegativity and the Polar Covalent Bond

If we were to construct a Lewis diagram for molecular hydrogen (H_2), we would pair the single valence electrons on each atom to make a single covalent bond. Each hydrogen would now have two electrons in its valence shell, identical to helium. The mathematical equations chemists use to describe covalent bonding can be solved to predict the regions of space surrounding the molecule in which these electrons are likely to be found. A particularly useful application of these calculations generates a **molecular surface** that is color coded to show *electron density* surrounding the molecule. This type of molecular surface is called an **electrostatic potential map.** When this type of calculation is done for molecules consisting of two (or more) *different* atoms, the results can be strikingly different. Consider the molecule HF. Hydrogen, with one valance electron, can share that electron with fluorine (with seven valence electrons) to form a single covalent bond.

In this electrostatic potential map, blue is used to indicate low electron density (a relative *positive* charge) and red indicates high electron density (a relative *negative* charge); the colors light blue, green, yellow and orange indicate the increasing charge gradient. The molecule HF is clearly very **polar**, meaning that a significant difference in electron density exists across the length of the molecule. The electrostatic potential map for HF contrasts significantly with that for H_2, where the charge was quite symmetrical (a uniform green color). Hydrogen fluoride (HF) can be described as a very *polar* molecule, while hydrogen (H_2) is *nonpolar*.

The origin of the polarization of the HF covalent bond has to do with *electronegativity*, an inherent property of all atoms. Within the periodic table, there is a trend for atoms to attract electrons towards themselves when they are bonded to another atom (as in HF). Atoms that tend to strongly attract electrons have a high electronegativity, relative to atoms that have a relatively low tendency to attract electrons towards themselves. The modern electronegativity scale was devised by Linus Pauling in 1932 and, in the Pauling scale, atoms in the periodic table vary in electronegativity from a low of 0.8 for cesium to a maximum of 4.0 for fluorine.

In the molecule HF, the electronegativity of the hydrogen is 2.2 and fluorine is 4.0. This difference leads to the profound polarization of the HF covalent bond which is apparent in the electrostatic potential map.

Polarizations of covalent bonds also occur in more complex molecules. In water, the oxygen has an electronegativity of 3.5; hydrogen is 2.2. Because of this, each of the H-O bonds is polarized with greater electron density towards the oxygen. Within the molecule, H_2O, the effect of this polarization becomes apparent in the electrostatic potential map, as shown in Figure 3.18. The end of the molecule with the oxygen has a high electron density and the hydrogen ends are electron deficient. We will see in later chapters that the polarization of water, caused by the difference in electronegativities, gives water the special properties that allows it to dissolve ionic compounds, and basically support life as we know it. Within organic chemistry (the study of carbon-containing molecular compounds), you will appreciate that the relative reactivity of organic molecules with each other is largely dependent on the polarization of covalent bonds in these molecules.