6.13: The Covalent Bond

Formation of an ionic bond by complete transfer of an electron from one atom to another is possible only for a fairly restricted set of elements. Covalent bonding, in which neither atom loses complete control over its valence electrons, is much more common. In a **covalent bond** the electrons occupy a region of space *between* the two nuclei and are said to be *shared* by them.

The simplest example of a covalent bond is the bond between the two H atoms in a molecule of H_2. Suppose that two H atoms approach each other until their two 1*s* electron clouds interpenetrate. You can see what would happen to each 1s electron in the figure below by clicking on 1s left atom to show a 1s atomic orbital on the left H atom.

In such a situation the electron does not continue to move about its own nucleus only. The electron initially associated with the left-hand H atom, for example, will feel the attractive pull of the right-hand nucleus as well as the left-hand nucleus. Since both nuclei have the same charge, the electron is unable to discriminate between them. Accordingly it adopts a new *symmetrical* probability cloud. You can see this by clicking on the Sigma 1 button in *the third row* of the figure. (Also click on the 1s button to remove the 1s atomic orbital.)

The same argument applies to the electron initially associated with the right-hand H atom. (Use the figure to show what happens to that electron when it is attracted by two H nuclei.) Each electron is said to be *delocalized* over both nuclei and each electron has an equal probability of being found in the vicinity of either nucleus.

An orbital, like Sigma 1, that extends over a whole molecule rather than being restricted to a single atom is called a molecular orbital. We can consider it to be the result of a combination or overlap of the two 1s atomic orbitals. In fact, if you follow the instructions for part c of the figure, you can see how the overall molecular orbital overlaps with the densities of the two Sigma electrons, and how the molecular orbital has adopted a new shape from the densities shown by the two 1s orbitals.

A molecular orbital formed in this way must conform to the Pauli exclusion principle. Only two electrons of opposite spin can occupy each orbital, denoted here as the two electrons in the Sigma orbital. Since the second electron (seen by clicking on the "Sigma 2" button) from the other H atom is available, it occupies the molecular orbital together with the original (Sigma 1) electron. The result is a shared pair of electrons moving around both nuclei and holding them together (the orange color).

The overlap of two 1*s* electron clouds and their spreading over both nuclei when the H_2 molecule forms has the effect of concentrating the electron density *between* the protons. When the molecule forms, the negative charges move *closer* to positive charges than before. This is represented by the fact that the extent of dots in the molecular orbital is less than the spread due to the individual 1*s* electrons. There is thus a reduction in potential energy.

Since the virial theorem guarantees that a reduction in the *potential* energy means that the total energy (kinetic + potential) is also reduced, we can conclude that the H_2 molecule is *lower in energy* and hence more stable under normal conditions than two separate H atoms. Alternatively we can say that energy is *required* to break apart an H_2 molecule and separate it into two H atoms. This energy (called the **bond energy**) can be measured experimentally. It is found to have a value of 436 kJ mol^{-1} for the H_2 molecule.

Example 6.13.1 : Molecular Orbitals

Below is a Jmol applet, a 3-D interactive view of H_2. There are a set of commands to the left where you can play around with appearances, viewing the molecule as ball and stick, a wire, or see the van der Waals radii. You can also label the atoms, radii, and bond length. Take a bit to play around with the applet if you are unfamiliar with Jmol.

Now focus on the molecular orbital commands to the right. These allow you to visual the orbitals discussed earlier on this page. Set the MO cut off to 0.05. This will produce a surface that encloses 95% (0.95) of the electron density.

(a) Click on HOMO. This stands for **H**ighest **O**ccupied **M**olecular **O**rbital. This is the highest-energy orbital with any electrons in it. The HOMO contains two electrons, one from each H atom.

Try to see the relationship between the two-dimensional dot-density diagram above and the three-dimensional representation in the Jmol window. The Jmol shows a surface that encloses 95% of the electron density (95% of the dots in the figure above).

Rotate the HOMO diagram until you are looking along a line that passes through both H atoms (end-on to the molecule). What can you observe about the shape of the MO? Now rotate the diagram so that you are looking along a line perpendicular to the H-H bond. What do you observe now?

What does the shape of the HOMO tell you about H_2?

(b) Now click on LUMO. this stands for **L**owest **U**noccupied **M**olecular **O**rbital. This is the next higher energy molecular orbital in the molecule--the orbital that electrons would fill if more electrons were added. Based on the shape of the LUMO, what would be the consequence of placing electrons in this orbital?

Solution

a) The orbital is symmetrical about the center of the H_2 molecule. As was discussed on this page, the two electrons in this orbital are now equally shared by both atoms. The orbital is centered between the two atoms, so electron density is highest there. Again, as said above, this reduced the total energy of the system, and electrons in this orbital will thus lead to a covalent bond between the two atoms. This orbital is referred to as a bonding orbital.

b)With the LUMO of H_2 there is *zero* electron density half way between the two hydrogen atoms. The two protons repel each other, and without much electron density between them to attract them together the LUMO has a higher energy than the two separate hydrogen atoms. If electrons occupied this orbital, it would lead to the repulsion of the atoms and breaking of the covalent bond. The point exactly half way the two atoms where the electron denisty is zero is called a node. Because the atoms would fly apart if the LUMO were occupied, this molecular orbital with a node is referred to as an anti-bonding orbital.