Molecular Structure Properties

The electron was discovered in the year of 1900, and it took about twenty years for the electronic nature of the chemical bond to come into wide acceptance. Particle-based models for atomic and molecular structure soon gave way to the quantum mechanical view, in which electrons are not treated as localized, discrete particles (electrons orbiting around a nucleus), but as delocalized areas of wavelike charge, each possessing a given probability of being found in a given location near an atomic nucleus (an orbital). The chemical bonding in molecules, which began the twentieth century as shared electron pairs between atoms, evolved to become a matter of molecular orbitals. Molecular orbitals describe three-dimensional arrangements of the atomic nuclei in a molecule and the probability that any given electron of a given energy will occupy a given location with respect to those nuclei. Single bonds are explained by the overlap of atomic orbitals along the internuclear axis of two atoms. Multiple bonds are the combination of sigma plus pi bonding, the latter corresponding to the overlap of atomic orbitals that is not along the internuclear axis. A rough guide to the bonding molecular orbitals in methane is depicted in Figure 6. The eight valence shell electrons (four from carbon, four from the four hydrogens) are distributed among four molecular orbitals.

Molecules are built of permanent numbers of atoms joined together by covalent bonds, and can variety from the very small (even down to single atoms, as in the noble gases) to the very large (as in polymers, proteins or even DNA).

The covalent bonds keeping the molecules together are very strong, but these are largely immaterial to the physical properties of the substance. Physical properties are ruled by the intermolecular forces - forces attracting one molecule to its neighbours - van der Waals attractions or hydrogen bonds.

Formal Charges:

The formal charge is an idea of accounting for the distribution of electrons in an atom. This can help in two ways.

1. It can help us decide which of several Lewis dot structures is closest to representing the properties of the real compound.

2. It can help us envision where there might be regions of positive or negative charge in a molecule.

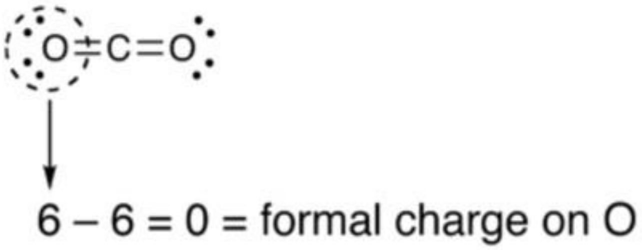
First, how does it help to decide between different structures? Our general rule is that the best structure minimizes the formal charges. This is because minimizing the formal charges leads to the electrons being most evenly distributed about the different atomic centers in a molecule. Having electrons concentrated in one area will lead to regions of negative charge. The atoms that are now "missing" electrons will be positive in charge. Separating positive and negative charges costs energy and thus we conclude that the lowest energy (best structure) would minimize having separated charges.

How do we find these charges? We look at how many valence electrons the atoms "has" in the molecule compared to how many it has on its own. It is important to know that this is a very general idea that grossly over simplifies the quantum mechanics. The electrons in a molecule have no memory of where they came from or to which atom they "belong". They are simply spread throughout the molecule. None the less, these simple ideas can help us to arrive at the best structures as well as understand something about the charge distributions.

In a molecule, we assign each atom a formal charge. This charge is the number of electrons it had as valence electrons minus the number it "has" in the molecule. The number it has in the molecule is a combination of the lone pair electrons and the shared bonding electrons. For each atom, we will count all of the lone pair electrons but only half of the bonded electrons (as they are shared). This is easiest to account for by just counting the number of bonds. So the formal charge is

Formal charge = Valence Electrons - [Lone Pair Electrons + (# of Bonds)]

So for example if we look at CO_2 each oxygen has two lone pairs (4 electrons) and 2 bonds (double bond). Oxygen has 6 valence electrons. So the formal charge on each oxygen atom will be 6-(4+2)=0.

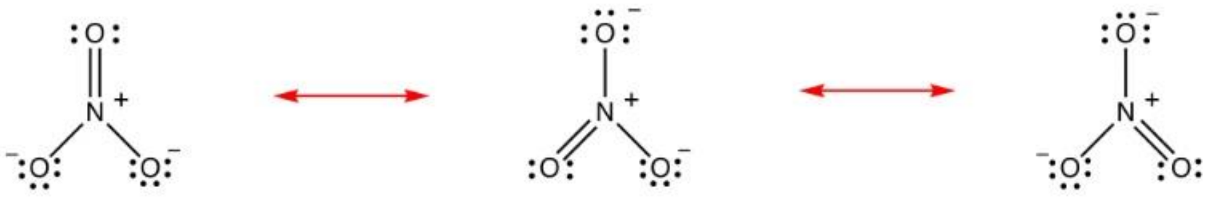


You need to find the formal charge on each atom in a compound. However, there are some short cuts that will help. The sum of all the formal charges must be the charge on the molecule. For neutral compounds this will be zero. Since each oxygen in CO_2 is zero, and the total charge is zero, the formal charge on carbon must be zero.

Resonance Theory:

Resonance theory is an attempt to explain the structure of a species, like the nitrate ion or benzene, no Lewis diagram of which is consistent with the observed properties of the species. The major advantage of resonance theory is that, although based on rigorous mathematical analysis, resonance theory can be applied successfully invoking little or no math. Resonance theory is explained below using the nitrate ion as the example.

According to resonance theory, the structure of the nitrate ion is not 1 nor 2 nor 3 but the average of all three of them, weighted by stability. Lewis diagrams 1, 2, and 3 are called resonance forms, resonance structures, or resonance contributors of the nitrate ion. The structure of the nitrate ion is said to be a resonance hybrid or, simply, hybrid of resonance forms 1, 2, and 3. Whenever it is necessary to show the structure of the nitrate ion, resonance forms 1, 2, and 3 are drawn, connected by a double-headed arrows.



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Introduction to Molecular Orbital Theory:

Modern chemistry has depended upon the use of models of increasing comlexity. Atoms can be represented as spheres connected by cyclinders or sticks. In order to understand the mechanism of many reactions, Lewis Theory, developed by Robinson and Ingold, can provide a succesful answer.

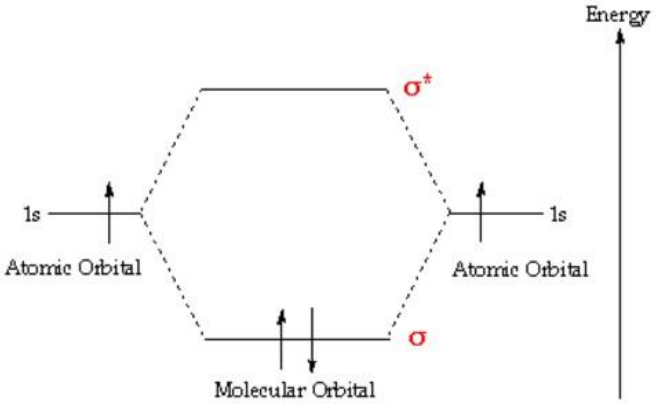
Lewis Theory uses curly arrows to denote electron migration during a chemical reaction and has led to a greater understanding of the factors controlling chemical reactions.

Pauling with others, developed Resonance Theory, which provided the rationale to an all-embracing orbital theory. The use of "canonical forms" and "resonance hybrids", alonng with extensive use of curvy arrows has provided the fundamental background to modern organic theory, but for eg. Diels-Alder and pericyclic reactions, the curly arrow format is not very clear and in some instances the reactions are described as no-machanism reactions. Woodward and Hoffmann showed that by examining the interaction of the frontier molecular orbitals (ie. the Highest Occupied, HOMO and Lowest Unoccupied, LUMO) both the regio- and stereospecificity could be accountred for. By sharing electron, molecules can form bonds, and it is possible to regard the sharing of two electrons by two atoms as constituting a chemical bond. Atoms can share one, two or three electrons (forming single, double and triple bonds).

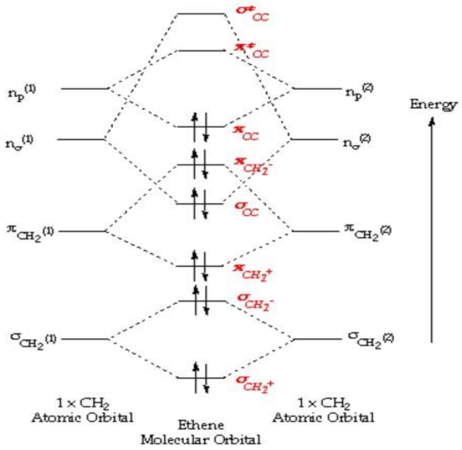
A hydrogen atom consists of a nucleus (a proton) and an electron. It is not possible to accurately determine the position of the electron, but it is possible to calculate the probability of findng the electron at any point around the nucleus. With a hydrogen atom the probability distribution is spherical around the nucleus and it is possible to draw a spherical boundary surface, inside which there is a 95% possibility of finding the electron. The electron has a fixed energy and a fixed spatial distribution called an orbital. In the helium atom there are two electrons associated with the helium nucleus. The electrons have the same spatial distribution and energy (ie. they occupy the same orbital), but they differ in their spin (Pauli exlusion principle). In general: electrons in atomic nuclei occupy orbitals of fixed energy and spatial distribution, and each orbital only contains a maximum of two electrons with anti-parallel spins.

In atoms, electrons occupy atomic orbitals, but in molecules they occupy similar molecular orbitals which surround the molecule. The simplest molecule is hydrogen, which can be considered to be made up of two seperate protons and electrons. There are two molecular orbitals for hydrogen, the lower energy orbital has its greater electron density between the two nuclei. This is the bonding molecular orbital - and is of lower energy than the two 1s atomic orbitals of hydrogen atoms making this orbital more stable than two seperated atomic hydrogen orbitals. The upper molecular orbital has a node in the electronic wave function and the electron density is low between the two positively charged nuclei. The energy of the upper orbital is greater than that of the 1s atomic orbital, and such an orbital is called an antibonding molecular orbital.

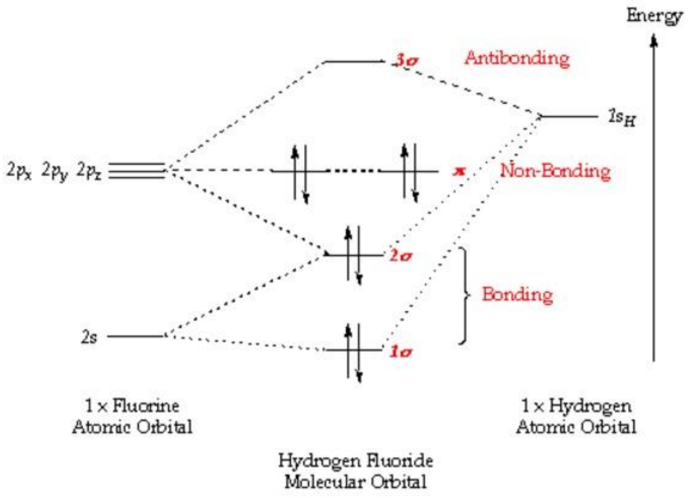
Normally, the two electrons in hydrogen occupy the bonding molecular orbital, with anti-parallel spins. If molecular hydrogen is irradiated by ultra-violet (UV) light, the molecule may absorb the energy, and promote one electron into its antibonding orbital (s*), and the atoms will seperate. The energy levels in a hydrogen molecule can be represented in a diagram - showing how the two 1s atomic orbitals combine to form two molecular orbitals, one bonding (s) and one antibonding (s*). This is shown below - by clicking upon either the s or s* molecular orbital in the diagram - it will show graphically in a window to the right:



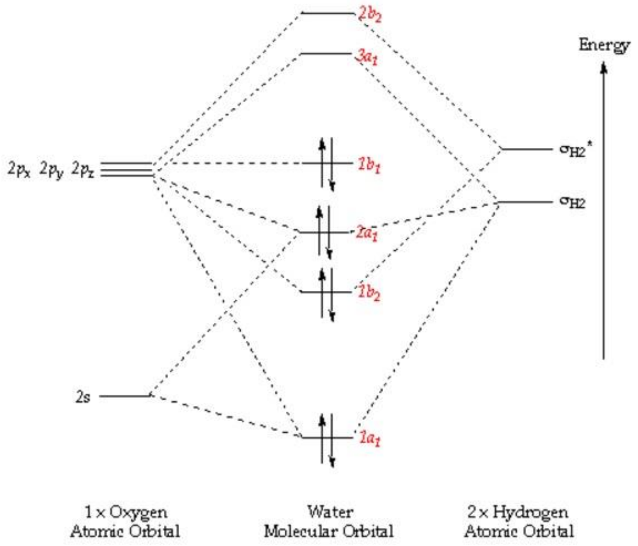
In molecules where the number of bonding electron pairs exceeds the number of unions between atoms, the extra electrons occupy higher energy molecular orbitals than the orbitals found in molecules where the number of bonding electron pairs equals the number of unions between atoms. These are double bonds, and the orbitals have a nodal plane containig the atoms sharing these p-type orbitals. The simplest alkene is ethene. Its chemistry is dominated by two "frontier orbitals", that is the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO). For the ethene orbital energy diagram these are shown as pCC for the HOMO, and p*CC for the LUMO. An important property of the ethene molecule, and alkenes in general is the existence of a high barrier to rotation about the C=C which tends to hold the molecule flat. For the energy diagram and pictorial view of the orbitals.



A simple diatomic molecule is Hydrogen fluoride. There are eight valence electrons which occupy four molecular orbitals. The two highest energy MO's are degenerate, are p-type and have no electron density associated with the hydrogen atom, ie. they are Non-Bonding Orbitals (NBO) and in Lewis Theory are represented as two "Lone Pairs". Another important difference between Hydrogen Fluoride and previous molecules is that the electron density is not equally distributed about the molecule. There is a much greater electron density around the fluorine atom. This is because fluorine is an exremely electronegative element, and in each bonding molecular orbital, fluorine will take a greater share of the electron density.



In the water molecule the highest occupied orbital, (1b1) is non-bonding and highly localized on the oxygen atom, similar to the non-bonding orbitals of hydrogen fluoride. The next lowest orbital (2a1) can be thought of as a non-bonding orbital, as it has a lobe pointing away from the two hydrogens. From the lower energy bonding orbitals, it is possible to see that oxygen also takes more than its "fair share" of the total electron density.



Hybridization:

Hybridization is a concept that allows us to account for certain key structural issues that are not easily accounted for in other bonding theories when starting from the ground state of a carbon atom 2s2 2p2.

The concept involves the "cross breeding" of atomic orbitals to create "new" orbitals. Hence the use of the term "hybrid" : think of a hybrid animal which is a cross breed of two species.

Let's pose the bonding problems in the context of methane, CH4

despite the fact that C has only 2 unpaired electrons, it forms 4 bonds

all 4 C-H bonds are of equal strength

tetrahedral shape (i.e. H-C-H bond angle = 109.5 degrees)

The number of orbitals in the hybrid set is determined by the number of s bonds required at that centre.

4 s bonds => sp3 hybridised (e.g. alkanes)

3 s bonds => sp2 hybridised (e.g. alkenes)

2 s bonds => sp hybridised (e.g. alkynes)

sp3occurs when a C has 4 attached groups

sp3 has 25% s and 75% p character

the 4 sp3 hybrids point towards the corners of a tetrahedron at 109.5o to each other

each sp3hybrid is involved in a σ bond