Thoughts for the Day
CH301 Fall 2010
10/19/10

Molecules

Now we have to think about Quantum mechanics of molecules.

Overview of what we will look at

Simplest problem.

H_2^+. A one electron system. We can solve this exactly in the limit of the Born-Oppenheimer approximation (see below)

H_2^+ with molecular orbitals. We will use this system to look at how to approximate the molecular wavefunctions using a linear combination of atomic orbitals (LCAO).

Then we will look at homonuclear diatomics (same atoms) with MO.

Then we will look at heteronuclear diatomics (different atoms) with MO.

Finally we will look at polyatomics and start organic molecules

How do deal with molecules? What do we want to know?
We are now going to use QM to look at bonding. How will we define a bond. This is a tricky ideas as strictly speaking there is not rigorous definition. However, we can intuitively decide on what we mean by a "bond". Two atoms will be bonded together when we find there exists a small distance at which the electrons in the atoms have a lower energy compared to the atoms separated by a large distance. That is the lowest energy state for the system is when the two nuclei are close (at a distance of the bond length) compared to infinitely separated (distinct atoms). As such we need to do a lot of QM calculations to explore this distance.

For starters we are again confronted by the fact that there are a lot of coordinates. Before we ran into trouble when we had two or more electrons. Now we have the nuclei to deal with as well. We can write down the Hamiltonian. It is the kinetic energy of the electrons, the kinetic energy of the nuclei, and Coulomb's law. The coulomb part as the electron-nucleus attraction (now there is a term for each electron and each nucleus), the is the electron-electron repulsions (unless

we are talking about 1 electron systems like H_2^+), and then there is nuclear-nuclear repulsions. To deal with this we are forced to make an approximation. We assume that the nuclear positions are fixed relative to the electrons. That is we say that the electrons can adjust infinitely fast to changes in the nuclear coordinates. It is not that the electron (or molecular) energy is not dependent on the position of the nuclear, they are strongly affected. What we say it that as far as the electrons are concerned the nuclei are not moving. We will then solve the electronic part of the problem at different nuclear separations. This is the Born-Oppenheimer approximation. (actually it is my hand wavy description of the B.O. approximation that actually states that we can separate the wavefunction into electronic and nuclear parts and that the kinetic energy operator for the nuclei does not operate on the electronic part of the wavefuction).

Thus in the B.O. approximation we find the energy of the molecule at a particular geometry for the nuclei. This is in fact one of the great uses of quantum chemistry. If you want to know something about the geometry of the molecule, we can compute the energy at every possible geometry to find the lowest (most stable) one. We can see what the barrier is to conversion to other geometries, etc… As you might imagine this gets to be a big problem very quickly as the more atoms you have the more possible geometries you have. Thankfully today we have large computers. Still big molecules are a problem for calculations with very high energies.

What will we do. For H_2^+ we can solve the Schrödinger equation (in the BO limit). These solutions are shown in the book and we looked at them in class. What do they look like? They have several key characteristics.

First, they have either "bonding" or "anitbonding" character. Bonding wavefunction do not have a node between the two nuclei. Anti-bonding have a node.

Next, they can have angular momentum along the bond axis. This is best understood in terms of the shape (just like the different between atomic orbitals with different angular momentum s,p,d..). If the shape is such that there is electron density along the bond axis, this is a sigma orbital. If it is off axis we have a pi orbital. Higher angular momentum states are delta, …

Finally, the wavefunctions have a symmetry based on reflection of the function through the origin (the point half way between the two nuclei). If you reflect the function and get the same sign it is even or gerade (g). If you get the opposite sign it is odd or ungerade (u). Note: they are all symmetric. You'll get the same amplitude. The only difference is the sign.

Also, they each have an energy. As you increase in energy you get more nodes. The lowest state has zero nodes. The first excited state has one. Etc…. The ground state has a lower energy than separated atoms at a small distance, it has an even symmetry, it is a sigma orbital, and it does not have a node between the atoms and is thus "bonding". The first excited state is sigma, its symmetry is u, and it is antibonding as it has a node between the nuclei. Moreover, this state has an energy that is higher than the separated nuclei at all distances.

Now we look at the exact same problem, but we solve it with approximate wavefunctions. Why? Because this is how we will solve multi-electron molecules, and it is the simplest problem to

looks at. What do we do? We do the same thing we did with multielectron atoms. First we make the orbital approximations. That is the total wavefunction is the product of one electron wavefunctions. Now these wavefunctions describe the whole molecule not just one atom. The molecular orbitals (MO) that we will use are linear combinations of atomic orbital (LCAO). That is they are the AO added or substracted from each other.

What would we guess is the lowest energy solution? A 1s on each H atom. Why? That is the lowest energy on the atoms. That is what the molecule should look like at large internuclear separation. It turns out that we are correct. The lowest energy solution is a $1s_A + 1s_B$. That is a 1s wavefunction on nucleus A and a 1s wavefunction on nucleus B. There are some constants to keep the functions properly normalized. When we bring these two together what does the MO look like? The two orbitals have the same sign. Thus when they overlap the constructively interfere (they add up together). Thus the MO has a greater electron density between the two nuclei than you would have from two non-interaction H-atoms. There is an excellent picture of this in the book that we looked at in class. What about the energy. It turns out this function has an energy that is lower than two separate H-atoms at some distance. At large distances it is the same, at very short distances the repulsion of the nuclei leads to a very high energy, but at slightly larger distance the energy is significantly lower than the separate atoms. Just like the lowest energy solution for H_2^+ that we found directly.   Just the exact solution, this solution is sigma and even (g) and bonding.

What do the other solutions look like. There is a combination in which the two 1s function have a different sign (phase). The sign of the wavefunction only matters when we have two that interact. There are only two choices. They are the same (the lower energy solution we discussed moments ago) or they are different. The one with different signs we can think of as $1s_A - 1s_B$. This now has destructive interference when we bring the two together. This leads to a node between the two nuclei. This on must be anti-bonding. Just like the exact solutions this one is sigma, u, and anti-bonding.

We can now think about similar calculations for H_2^+, H_2, He_2^+, and He_2.

It turns out that just like the multi-electron atoms, the orbital energy ordering is the same. Thus we now have a set of MO that we can start to fill up in the same way that we has a set of atomic orbitals that we filled for looking at different elements. The lowest energy state is the σ_{g1s} the next highest state is the σ_{u1s}^* .

If you start to put the electrons in these H_2^+ has only 1 electron and thus it goes in the lowest energy orbital. H_2 has two electrons. Both can go in the lowest energy orbital. Thus we now have two electrons in a MO with a lower energy compared to the AO. Thus we would predict that H_2 would have a stronger bond than H_2^+. If we look at He_2^+ it has three electrons. We cannot put a third electron in the lowest energy MO so we are force to put an electron in the anti-bonding σ_{u1s}^* orbital.   The total energy depends on all three electrons. Thus the energy for He_2^+ should be higher than that of H_2 as it now has two bonding electrons and one antibonding. In the simple limit where the anti-bonding are higher in energy by the same amount that the bonding are lower in energy they cancel. Thus we would expect this to be similar to H_2^+ as it would effectively have only one bonding eletron (2 bonding – 1 antibonding). Finally, we would

predict that He_2 does not exist as it would have to have the same number of bonding and anti-bonding electrons. Thus it would have the same energy as the separated atoms. Thus no bond.