Some of you have noticed that my MO diagram for water is not exactly like that in the book. First of all well done if you have spotted this discrepancy!

Not every text book is perfect and different people have different opinions, and qualitative MO theory is no exception. In the following I'm going to give you my opinion on why I think the diagram in the book is miss leading.

Now first up we have said as a general rule, if orbitals are far apart they should not interact, and water has a deep 2sAO (-32.4 eV!) and the orbitals of H are much higher in energy (-13.6eV) they should not interact $\Delta\varepsilon$=18.8eV. Thus, using the standard rules the H_2 a_1 FO **should** interact with the a_1 p_z AO of the Oxygen atom. If this were the case we would get **diagram B** below. This is good as a general rule, but like all qualitative theories it can be moderated by experience.

Now, I have also said that we normally use MO diagrams in reverse, we compute the MOs and then try to deconstruct them. If we do this then **diagram A** below is a better fit to the "real" MOs. For example in the real MO diagram of HF the F 2sAOs do not interact with the H 1sAO, and so water appears to be "out of sync". Thus the MO diagram of water has some tricky aspects and you have picked up on one of them!

If you remember back to lectures 4 and 5 there are 3 key things that impact on orbital interactions $\Delta\varepsilon$ the energy difference between the FOs, S_{ij} the overlap which we do visually by looking at the bonding/antibonding overlap of the FOs, and H_{ij} the Hamiltonian mediated overlap which includes the quantum nature of the electrons and which cannot always be predicted by humans.

Lets address the energy issue first. When atoms start to come together, they feel the effects of the nuclear charge of the approaching atoms. Thus if I take H_2 and stretch the bond and compute the energy of the H1s atomic orbitals at 1.5Å apart (the distance they are apart in the optimised water molecule), then the energy of the H 1sAO is -9.0eV. In addition if I compute the energy of the 2sAO of Oxygen in water, but without allowing it to form a MO, I get -24.0eV and so in the "molecule" the energy of these orbitals is not as far apart $\Delta\varepsilon$=15.0 eV. But this is still not really small enough to justify the strong interaction that is observed.

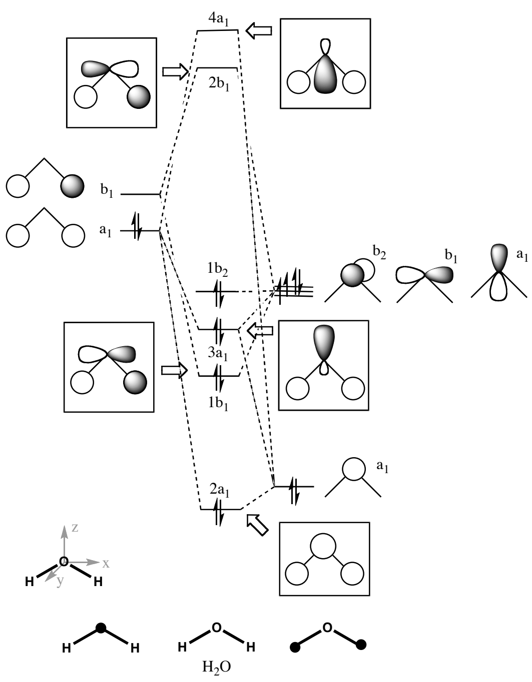


Diagram A: My MO diagram

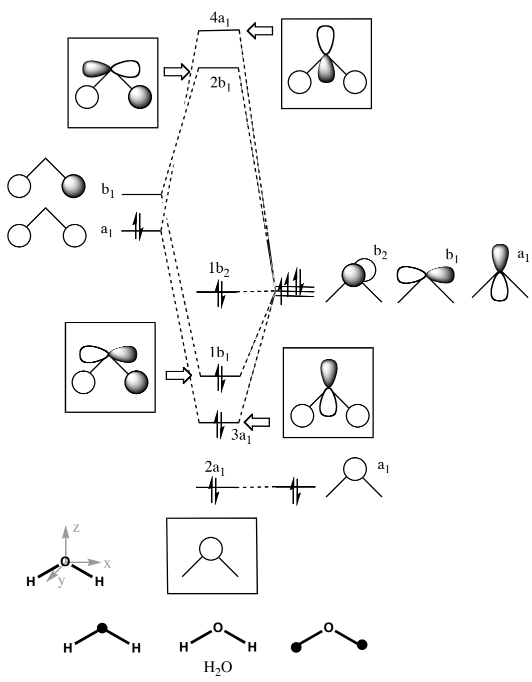
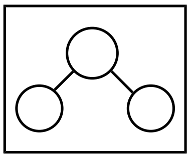
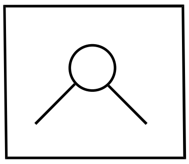
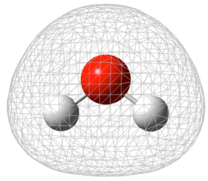


Diagram B: Standard model

Now lets consider the correlation of the above diagrams with respect to the real MO diagram computed at the B3LYP/6-31g(d,p) level.

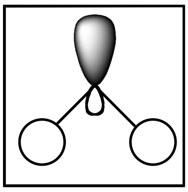
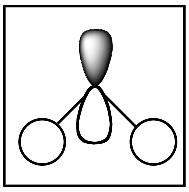
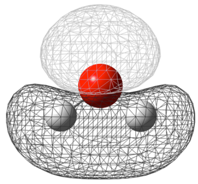
1. The $2a_1$ MOs

mine:  and the other method  and the real MO 

The real MO clearly contains sAO components from all centers and thus my MO better represents the real MO

2. If any mixing was to occur (to add sAO contributions to the H atoms) it must be between the $2a_1$ (occupied) and the $4a_1$ (unoccupied) which are very distant in energy. If such mixing were to occur it would add a "hybrid" like lobe to the oxygen, which is clearly not the case from the real $2a_1$ MO.

3. The $3a_1$ MOs

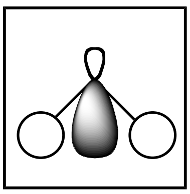
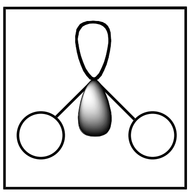
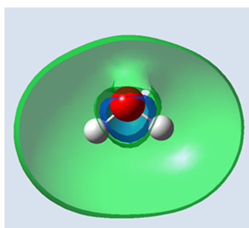
mine  and the other method  and the real MO 

The real MO could resemble either of the $3a_1$ MOs above.

4. The optimised structure energy ordering is:
-0.29 $1b_2$ MO
-0.37 $\mathbf{3a_1}$ real MO as shown above
-0.42 $\mathbf{1b_1}$ MO
-1.00 $2a_1$ real MO as shown above
-19.14 O 1sAO

Thus the energy ordering has the $3a_1$ MO *above* the $1b_1$ MO. This is not consistent with the alternative diagram B above. So why then does the $3a_1$ MO lie *below* the $1b_1$ MO in the alternative diagram? Well it should because the H_2 a_1 lies below the H_2 b_1 and so the a_1 FOs should interact more strongly because they have a smaller $\Delta\varepsilon$ between them. Moreover the bottom lobe of the p_z FO lies in the inter-nuclear region, while that for the b_1 MO is outside of the inter-nuclear region. The $3a_1$ MO is highly bonding. In considering these interactions we have been studying S_{ij} the overlap of the FOs. Thus we have found that the energy ordering of the orbitals is not consistent with our ideas of orbital overlap *if we take diagram B*. This clearly indicates that H_{ij} is having an impact on this MO diagram, and that part of the interaction is not easily predicted by us. When orbital energies shift from the expected ordering there is a good chance that "mixing" is occurring. Mixing shifts orbital energies and changes MO shapes.

5. The $4a_1$ MOs

mine  and the other method  and the real MO 

In the real MO I have sliced the MO in half so we can see inside it. Clearly the MO does not exactly reflect my $4a_1$ MO, but it does show an internal antibonding component polarized between the O and H centers. What it does not show is a clear lobe (like the $3a_1$ MO above) pointing up and away from the oxygen, which is prediced by the alternative method. My MO is much closer to the real MO.

Thus I have built the MO diagram of water using a little bit of extra information (which you did get but right at the end of lecture 3) I did it this way because I was focussing on how to build diagrams with you. Now that you are far more experienced you are noticing the discrepancy, and are much better placed to understand the arguments outlined above.

Were does this leave you the poor student! In a research or lab situation you would (like me) carry out a calculation (all of the computers in the department have the required program available to you to do this), and from this year onwards all the 1st years are shown how to use it. If you want to have a go, here is the online lab that the 1st years undertake, it takes them about 2hrs http://www.huntresearchgroup.org.uk/teaching/year1_lab_start.html

In the exam: you should **know "my" MO diagram for water**. However, if you are given a new molecule in the exam you should **use the standard rules**, because that is all you have to work with without access to the final MOs. When I create the model answers, I do it following the standard rules (then I do a calculation to see if there are any differences).