

The MO Diagram for Water

Revision

- molecular orbitals are combinations of atomic orbitals
- atomic orbitals:
 - atomic orbitals have a radial and angular component, **Figure 1**
 - the radius of maximum density increases with quantum shell, there are inner nodes
 - but we only represent the **outer portion** in our MO diagrams
 - **shaded part** of diagram is the negative part of wavefunction, **Figure 2**
 - the **angular nature** is represented by the shaded lobes, s, p, d shapes, **Figure 3**

$$\psi_{1s}$$

$$R_{1s} Y_{1s}$$

$$\left[2Z^{3/2} e^{-\rho/2} \right] \left[(1/4\pi)^{1/2} \right]$$

R_{1s} Y_{1s}

Figure 1 Equation for the 1s atomic orbital

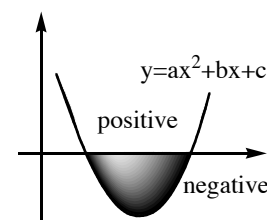
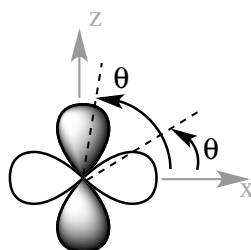


Figure 2 Negative portion of the function is shaded



sign change with θ

Figure 3 Angular part of the wavefunction

confused? there is an additional document on the web-site covering the very basics

Introduction

- In this lecture we will go through forming the MO diagram for a simple molecule together. Next lecture we will come back and I will explain many of the steps in more detail
- the first steps in forming a MO diagram have already been covered in lecture 1: determine the shape of the molecule, identify the molecular point group, define an axial system and find all of the symmetry elements of the point group, **Figure 4**.

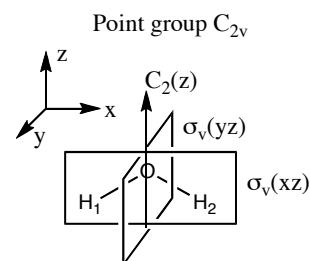


Figure 4 Symmetry elements for H_2O

Determine the fragments

- the fragments for water are the central O atomic orbitals and the H_2 fragment (more on how to choose the fragments later)
 - draw the structure of the whole molecule, explicitly write in the fragment atoms and leave **place holders** for the other atoms
 - this will form the bottom of your MO diagram

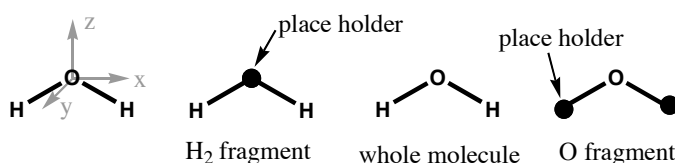


Figure 5 Drawing the fragments

Set up the MO diagram

- set up for the MO diagram as shown in **Figure 6** below:

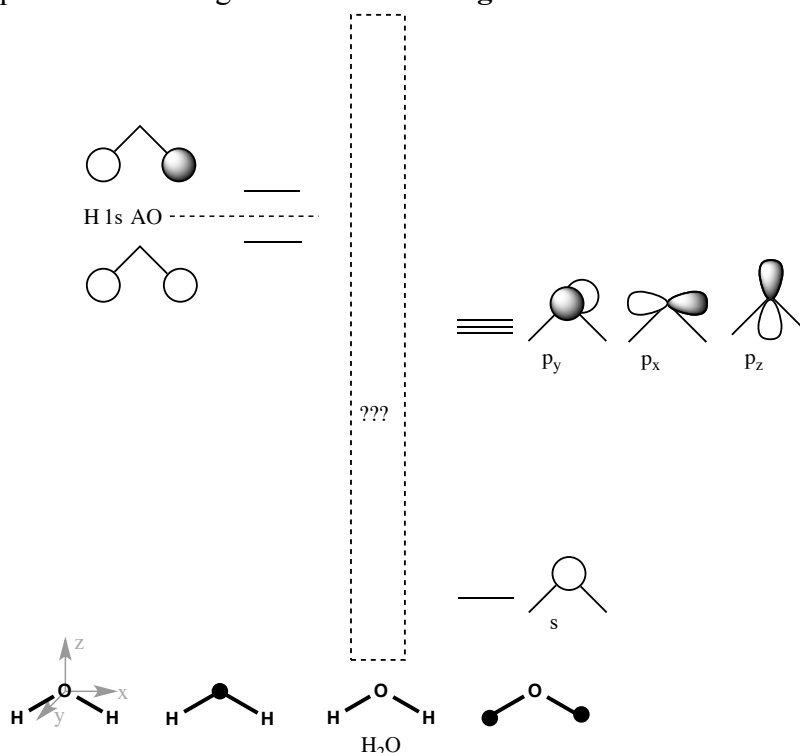


Figure 6 Bare MO diagram

- the vertical axis is an energy axis
- first identify the relative position of the AOs, O is much more electronegative than H and so the O fragment orbitals (FOs) will lie lower than the H AOs
- in water the hydrogen atoms are **further apart** than they would be in H_2 and therefore they **interact less**, stabilisation of the bonding, and destabilisation of the antibonding FOs is less and thus the overall splitting energy or **energy gap is small**.

IMPORTANT

Determine the symmetry of the fragment orbitals

- we could determine the symmetry of these fragments as we did last lecture: by examining how the orbitals transform under the symmetry operations of the C_{2v} point group, **Figure 7**.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	
$\Gamma \left\{ \begin{array}{c} \text{H}_2 \text{ bonding} \\ \text{H}_2 \text{ antibonding} \end{array} \right\}$	1	1	1	1	$\Rightarrow a_1$
$\Gamma \left\{ \begin{array}{c} \text{H}_2 \text{ bonding} \\ \text{H}_2 \text{ antibonding} \end{array} \right\}$	1	-1	1	-1	$\Rightarrow b_1$

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	
$\Gamma \left\{ \begin{array}{c} \text{O } 2s \\ \text{O } 2p_x \end{array} \right\}$	1	-1	-1	1	p_y
$\Gamma \left\{ \begin{array}{c} \text{O } 2p_y \\ \text{O } 2p_z \end{array} \right\}$	1	-1	1	-1	p_x
$\Gamma \left\{ \begin{array}{c} \text{O } 2p_z \\ \text{O } 2p_x \end{array} \right\}$	1	1	1	1	p_z

Figure 7 Symmetry of H_2 molecular orbitals and O atomic under the C_{2v} point group

- However there are some important **short-cuts** that you should be using
 - totally bonding orbitals and sAOs are always **totally symmetric** and have the highest symmetry, which is always the first symmetry listed in the character table, in this case a_1

IMPORTANT

- on the far right of the character table there are two extra columns, these identify the symmetry labels of the axes (and pAOs) and the dAOs
- the x-axis and p_x orbital transform in the same way because they have the same phase pattern (pattern of + and - or light and dark) as the vector T_x which is b_1 , **Figure 8**
- thus the y-axis and p_y AO transform as the vector T_y which is b_2 and the z-axis and p_z AO transform as the vector T_z which is a_1
- you will learn more about the T_i and R_i and the dAO column next term in my Spectroscopy and Characterisation course.
- the antibonding H_2 orbital has the same phase pattern as the p_x AO or x-axis and therefore belongs to the b_1 irreducible representation **Figure 8**
- add the symmetry labels of the AOs to the diagram, **Figure 9**

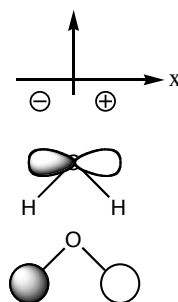


Figure 8 These all have the same phase pattern

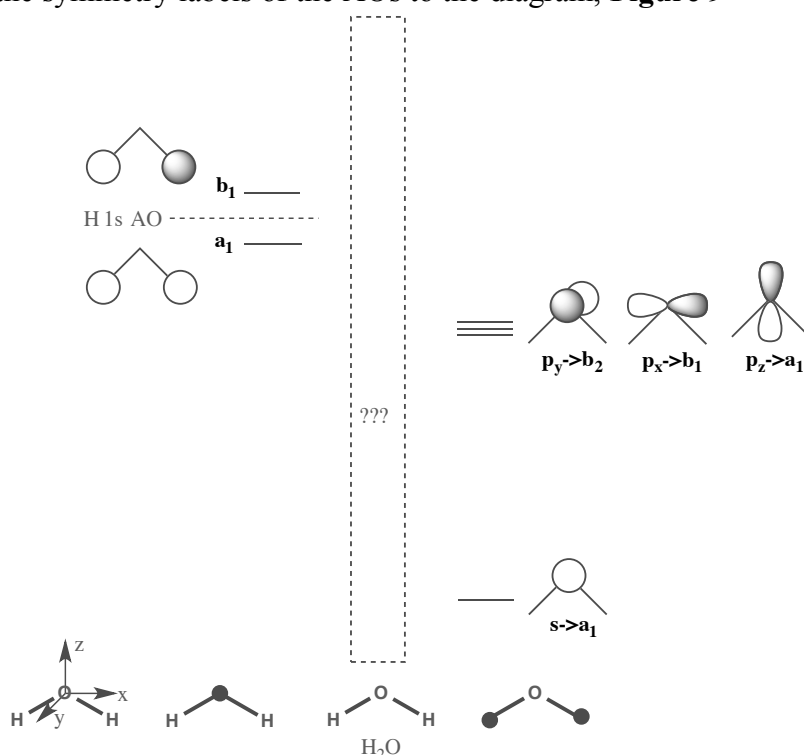


Figure 9 Adding AO symmetry labels

Form the molecular orbitals for the basic or first stage MO diagram

- **first work out the MOs** and then determine from their interactions the energy splitting for the final MO energy level
- only fragment orbitals of the same symmetry can combine thus for water we combine first the orbitals of a_1 and then b_1 symmetry.
- fragment orbitals only interact once
 - if there is more than one fragment orbital of the same symmetry, we generally combine the lowest energy orbitals first leaving the extra one non-bonding
 - this is only a loosely applied rule, sometimes one orbital will be too deep in energy to interact (more on this next lecture)
 - for water this case lowest energy a_1 FOs on O ($2s$ a_1 FO) and H_2 (totally bonding a_1) are combined, leaving the O " p_z " a_1 FO non-bonding

IMPORTANT

- to form a bonding/antibonding pair, take orbitals of one fragment and "add" them to the orbitals of the other fragment, do this once "as is", and once with the phase of all components reversed (ie adding the negative)
 - formation of the a_1 and b_1 symmetry MOs are shown in **Figure 10**
 - in-phase interactions lead to bonding MOs and out-of-phase interactions lead to anti-bonding MOs

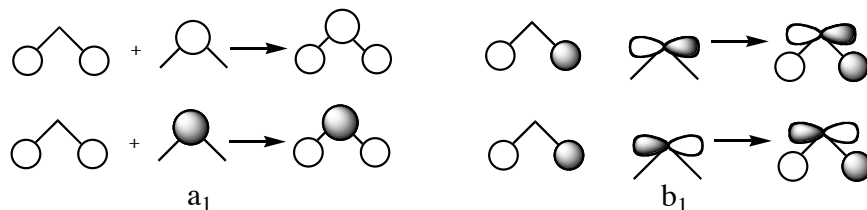


Figure 10 Forming bonding and antibonding MOs

- then we determine the **splitting energy**, ie the extent to which a pair of MOs is stabilised and destabilised relative to their FOs by evaluating the energy difference between the FOs, and the overall bonding characteristics of the final MO (more on this next lecture)
 - FOs that are far apart do not interact strongly and the MOs formed are stabilised and destabilised less (ie a_1 FOs interact weakly, b_1 strongly)
 - antibonding MOs are destabilised more than bonding MOs are stabilised
 - orbitals with better overlap interact more

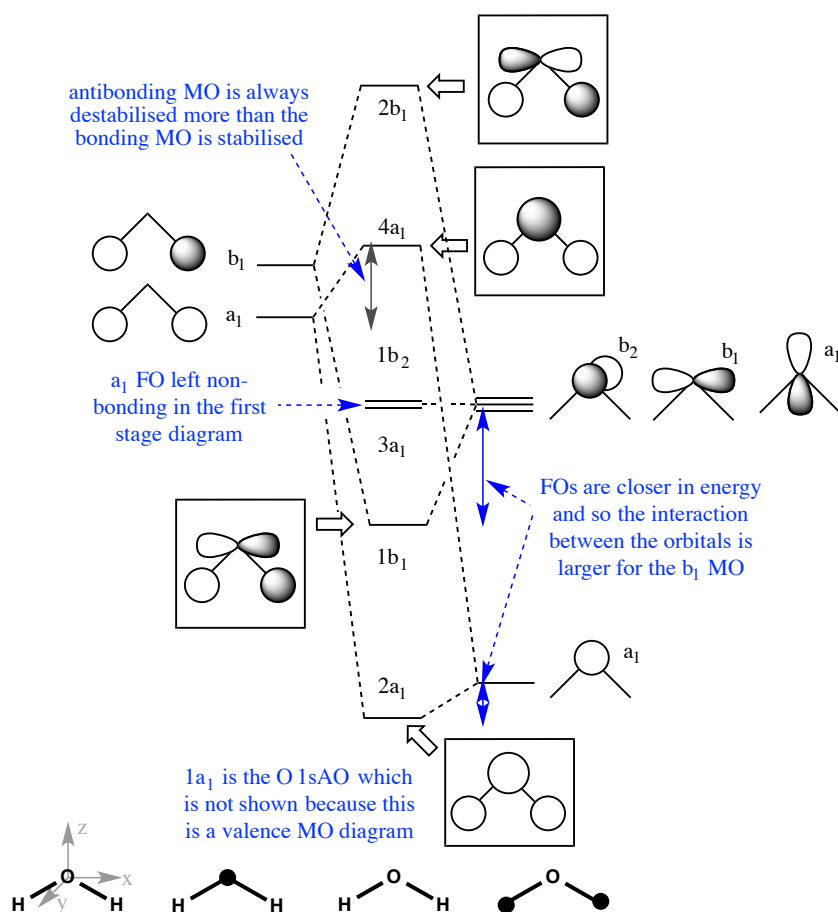


Figure 11 Basic MO diagram

- MOs are labelled by their symmetry, and sequentially starting with the lowest energy orbitals

- this is a valence MO diagram so the core 1sAO of oxygen is not explicitly drawn, but it is counted when determining the numbering for the MOs
- this is an example of an orbital that was too deep in energy to interact.

IMPORTANT

- I have **annotated** this MO diagram. I expect you to annotate your MO diagrams in the exam, explaining key features.

Add the electrons

- determine the number of electrons for each fragment
 - in this case each H contributes one 1s electron so these go in the lowest energy H_2 fragment orbital.
 - The oxygen atom contributes 6 valence electrons, these go in the lowest energy AOs

- then fill the central MOs sequentially starting at the lowest energy MOs,

Figure 12

- there is a total of 8 electrons available for the central MOs.
- the filling of these energy levels follows both the Pauli exclusion principal and Hund's rule.
- each MO is filled from the lowest energy up and holds only two electrons of opposite spin.
- if orbitals are degenerate fill them with parallel spin electrons until they are half-fill, and then start pairing the electrons.

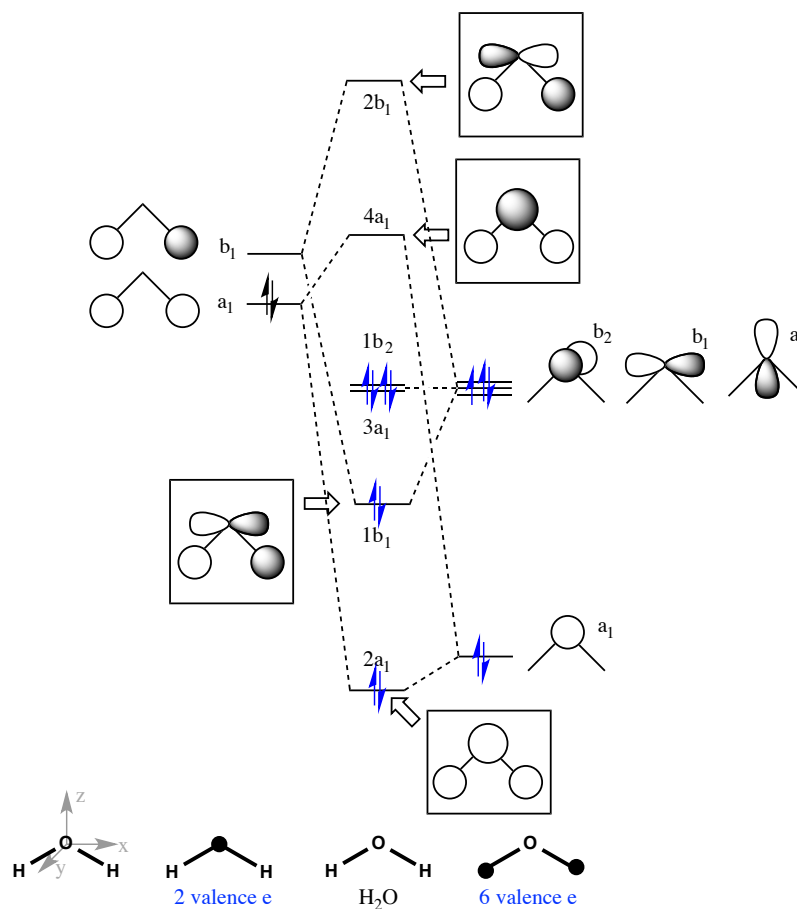


Figure 12 Including the electrons

IMPORTANT

Molecular orbital mixing

- **necessary** conditions for MO mixing to occur:
 - only MOs of the same symmetry can mix
 - mixing must stabilise the total energy of the molecule
- mixing tends to be **large** when at least one of these criteria are met:
 - MOs are close in energy
 - one of the MOs is non-bonding or unoccupied
 - MOs are in the HOMO-LUMO region
- MOs that mix form a new bonding/antibonding pair.
 - take one MO and then "add" the other MO once "as is", and once with the phase reversed
 - then examine the resultant MOs to determine which is bonding (lowered in energy) and which is antibonding (raised in energy)
- the $3a_1$ and $4a_1$ MOs of water exhibit significant mixing, **Figure 13**, as they fulfil all of the items listed above!
 - notice how mixing produces "sp" hybrid like orbitals on the O atom, this is a common feature of mixing
 - only occupied MOs contribute to the total energy of the molecule, because the $4a_1$ MO is unoccupied its destabilisation does not effect the total energy of the molecule, while the stabilisation of the $3a_1$ MO stabilises the whole molecule, this is why MO mixing tends to be large for orbitals in the HOMO-LUMO region and where one orbital is occupied and the other unoccupied

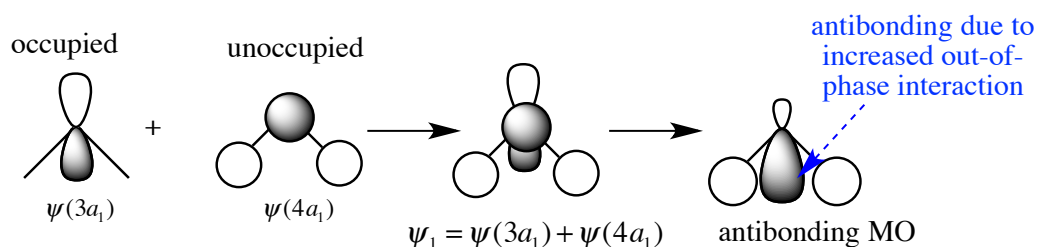


Figure 13a Mixing MOs (once as is)

In-Class Activity

- following the format of the diagram in **Figure 13a**, determine the other mixed orbital by forming $-\psi(3a_1) + 4\psi(a_1)$, note that the first orbital is the negative of $\psi(3a_1)$

Figure 14 Mixing MOs (once with phase reversed)

- add the effects of mixing into the MO diagram, **Figure 15**

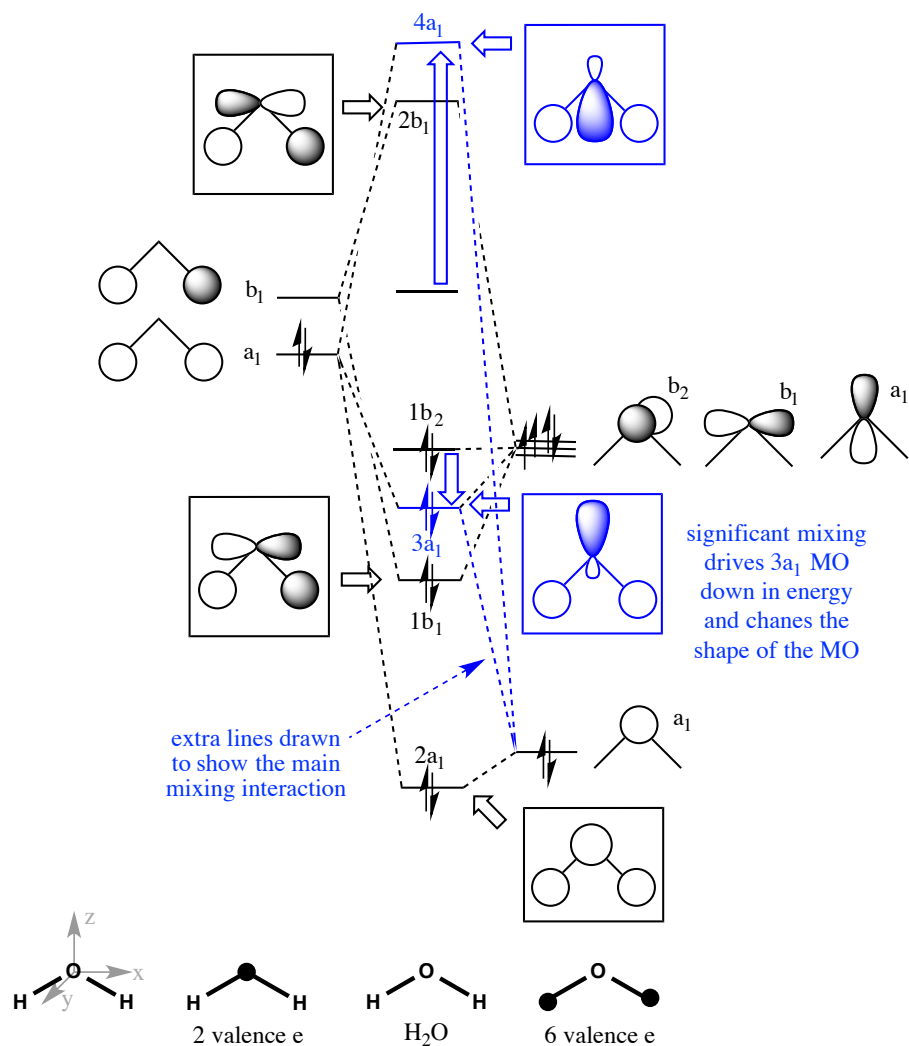


Figure 15 MO diagram including mixing

- some more comments on mixing
 - in reality all orbitals of the same symmetry mix very slightly but we only represent the largest effects that stabilise the molecule the most.
 - when we mix MOs we are really making MOs out of all the FOs that contribute to these MOs, there is a general rule: **n FOs make n MOs**
 - for water 3FOs have produced 3MOs, the FOs are the H₂ a₁ FO, and the O 2s AO and 2p_z AO, the final mixed MOs are the 2a₁, 3a₁ and 4a₁. The effect on the deep 2a₁ MO is very small and is not shown on MO diagrams
 - we sometimes add extra connection lines in the MO diagram

The final or second stage MO diagram for H₂O

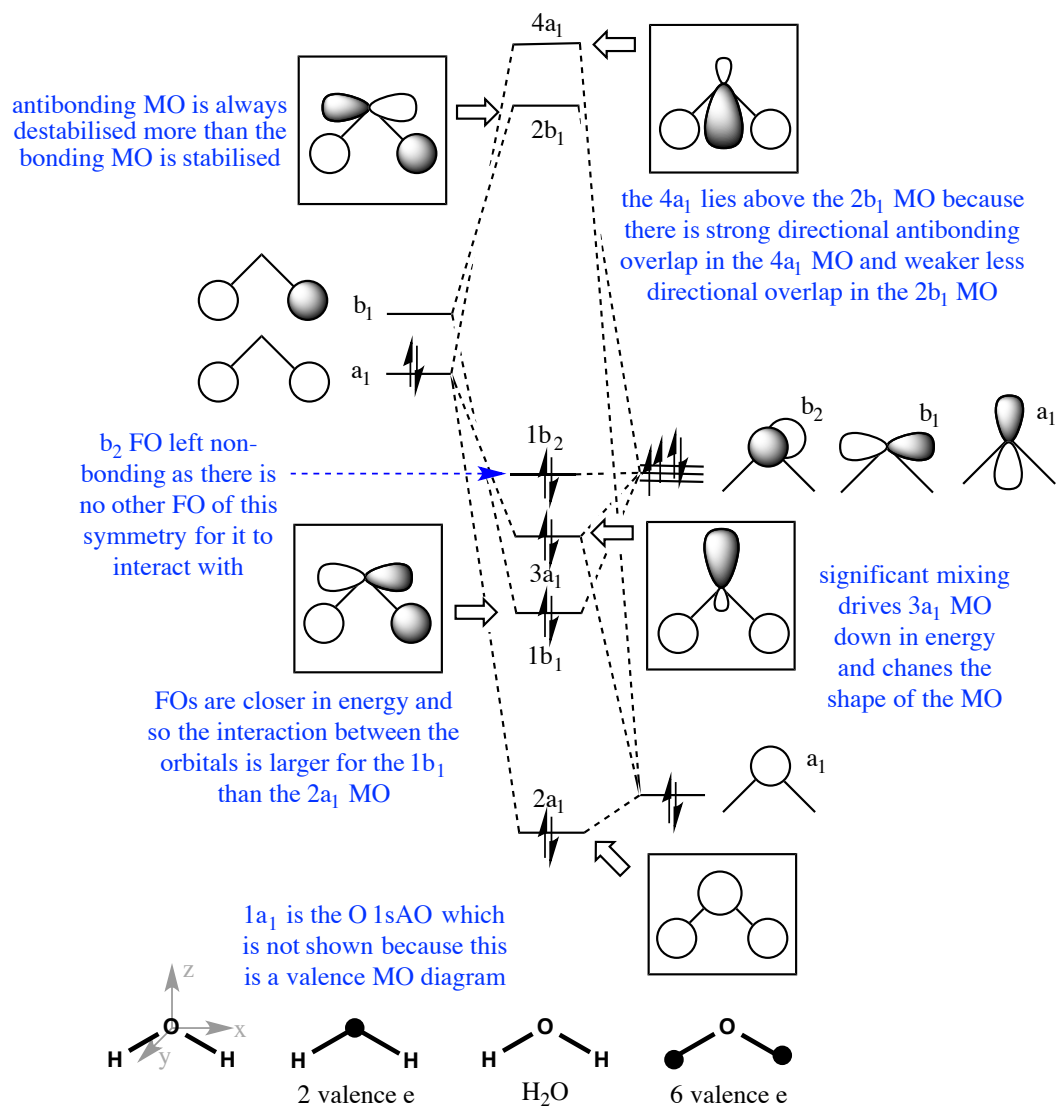


Figure 16 Final MO diagram

- note the annotations!

How realistic are the MOs?

- In forming the MO diagram you are "solving" the Schrödinger equation!!!
- The computed MOs for water are shown in **Figure 17** below, our qualitative MOs are mostly correct!

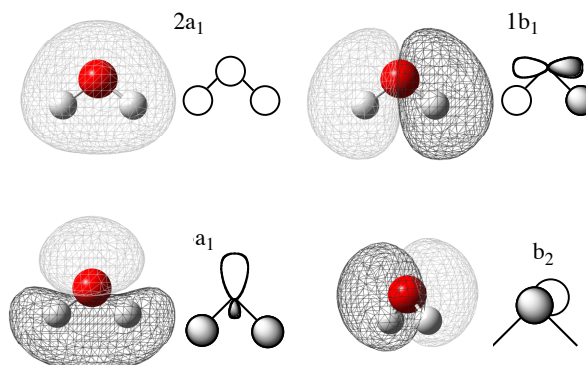


Figure 17 Real MOs

- Experimental evidence backs us up.
 - a photoelectron spectrum PES measures the energy required to eject an electron from its orbital
 - if water was formed two identical O-H bonds and two lone pairs on the oxygen atom (**Figure 18**) then the PES would have two (degenerate) peaks, one for the two bonds and one for the two lone pairs
 - The photoelectron spectrum (PES) of liquid water is shown below (**Figure 19**) it clearly shows 3 peaks in the positions we expect for the MOs we have derived.
 - the peaks are not "lines" because each individual water molecule experiences a slightly different environment due the random orientation of other surrounding water molecules, there will also be vibrational fine structure. This spectrum does not go to high enough energy to show the deep $2a_1$ MO.

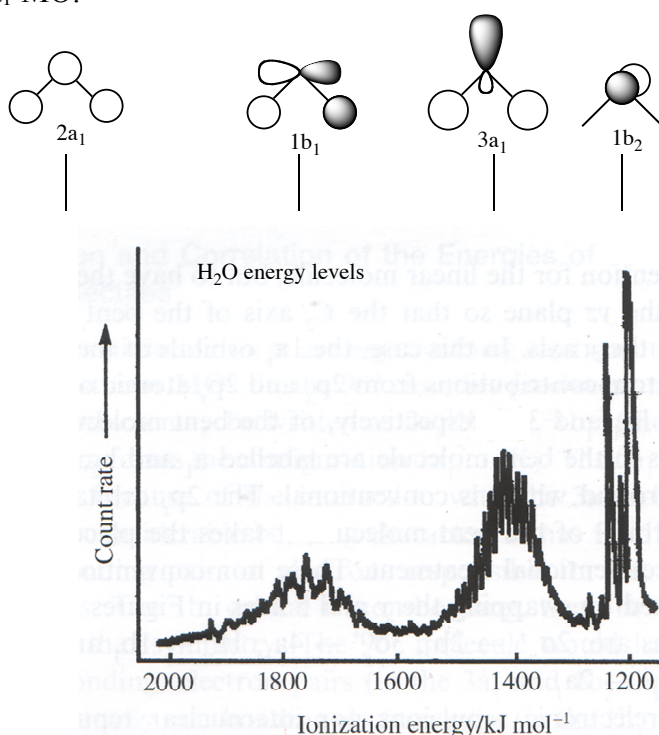
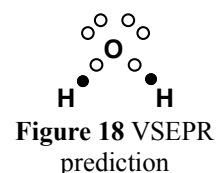


Figure 19 Photoelectron spectrum of water vapour.¹

- But if these MOs represent the **real** electronic structure, where have the bonds gone???
 - these MOs are **delocalised**, they bare little relationship to the familiar 2-center 2-electron (2c-2e) bonds we are used to
 - for example the $2a_1$ $1b_1$ and $3a_1$ MOs all have contributions from 3 atoms, they are 3 centre 2 electron MOs.
 - bonds however can be thought of as representing a build up of the *total* electron density which loosely put is a *total of all the orbital contributions*.
 - we keep the ideas of (sp) hybridisation and 2c-2e bonds because they are useful NOT because they represent reality

¹ Source: Fig 5.13 from "Structure and Bonding" by J. Barrett

Using the MO Diagram

- one MO diagram is suitable (with minor modifications) for a whole group of molecules.
 - for example the H_2O diagram can be used as a basis for ALL molecules of the form AH_2 where A is a main group element, a couple of examples include BeH_2 , NH_2 (fragments), H_2S .
 - for different central atoms, different numbers of electrons are added to the MO diagram, for example for an NH_2 fragment the total number of electrons is $7e=2$ (from H_2) +5 (from N)
 - adjustments are required if the relative electronegativity of the atoms changes significantly (more on this next lecture)
 - metals can also be included if dAOs are introduced into the diagram.

Special Note

- some text books overemphasise the contribution of the Op AO to the $3a_1$ MO, **Figure 20**, you should be aware of this, and in your diagrams draw the MO properly polarized
- if you want to know more see the “Questions answered” section on the website

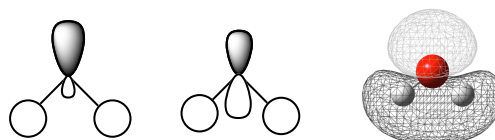


Figure 20 $3a_1$ MO for water (a) polarised (b) some text books (c) real MO

- we like to think of O in water as having a tetrahedral of electron density, 2 O-H bonds are formed and 2 lone pairs on the oxygen (VSEPR theory). MO theory shows us that the electronic structure of something as simple as water is far more complex than has traditionally been recognised.

my research involves understanding the electronic structure of water, some links to relevant research papers are provided on the website

Correlation Diagrams

- We can form **correlation diagrams**, sometimes called Walsh diagrams after Professor Walsh (**Figure 21**).
 - in a correlation diagram one geometric parameter (distance or angle) is varied and the effect on the form and energy of the MOs is monitored.
 - for example we can answer questions like: Why is H_2O bent?
 - normally we start by constructing the MO diagram for the high symmetry molecule, then we allow the symmetry to lower
 - I've produced the correlation diagram for water in **Figure 22**



Figure 21 Prof. Walsh²

²source: <http://www.dundee.ac.uk/museum/scientists.htm> accessed 27 Sept 2007

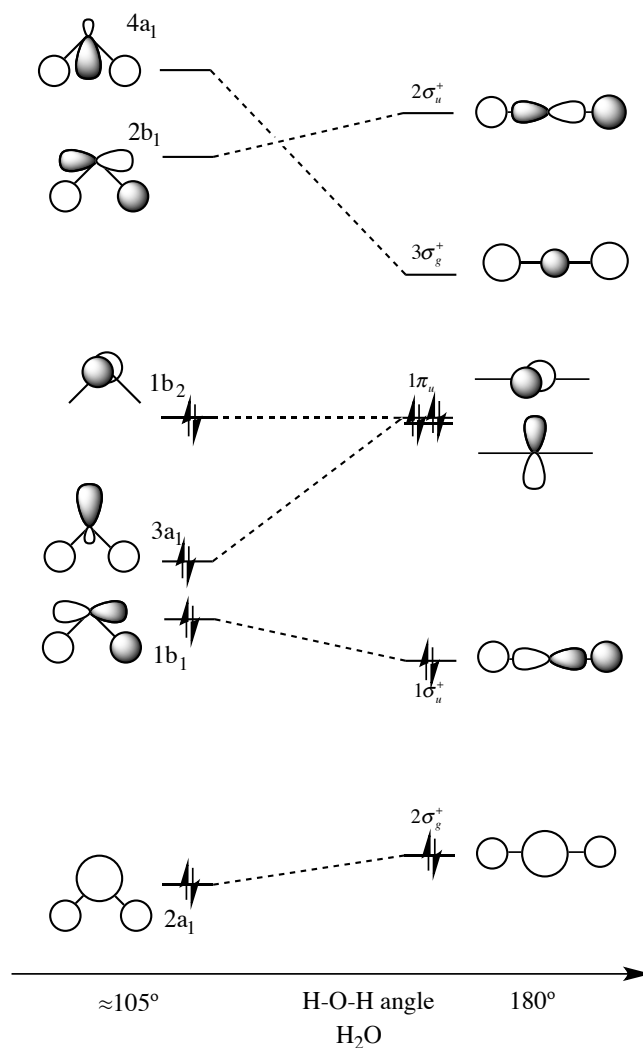


Figure 22 Correlation diagram for H₂O

- by examining the "bonding" vs "antibonding" character of orbitals we can determine if they are stabilised or destabilised on the drop in symmetry.
 - the $2\sigma_g^+$ (goes to $2a_1$) MO is stabilised due to an increase in the (through space) H-H sAO bonding overlap
 - the $1\sigma_u^+$ (goes to $1b_1$) MO is destabilised due to a reduction in the Op-Hs bonding interaction, and an increase H-H antibonding interaction
 - one of the $1\pi_u$ MOs (goes to $1b_2$) is non-bonding and thus has no change in energy

In-Class Activity

- A **socratic quiz**
 - Why is the $2\sigma_u^+$ (goes to $2b_1$) MO stabilised (go down in energy)?

- the other $1\pi_u$ and the $3\sigma_g^+$ MOs are special (goto the $3a_1$ and $4a_1$ MOs)
 - in the linear $D_{\infty h}$ molecule the Op_x MO has π_u symmetry and therefore cannot mix with the $3\sigma_g^+$ MO, and thus cannot be stabilised.
 - as soon as the linear molecule is distorted slightly it takes on C_{2v} symmetry, the symmetry label of the Op FO changes from $Op_x \rightarrow Op_z$ and the MO changes from $1\pi_u \rightarrow 3a_1$, and the symmetry label of the $3\sigma_g^+$ MO changes to $4a_1$, these orbitals are now allowed to mix and the occupied $3a_1$ MO is substantially stabilised.
 - watch the axes they must **formally re-orientate** on the symmetry change!

IMPORTANT

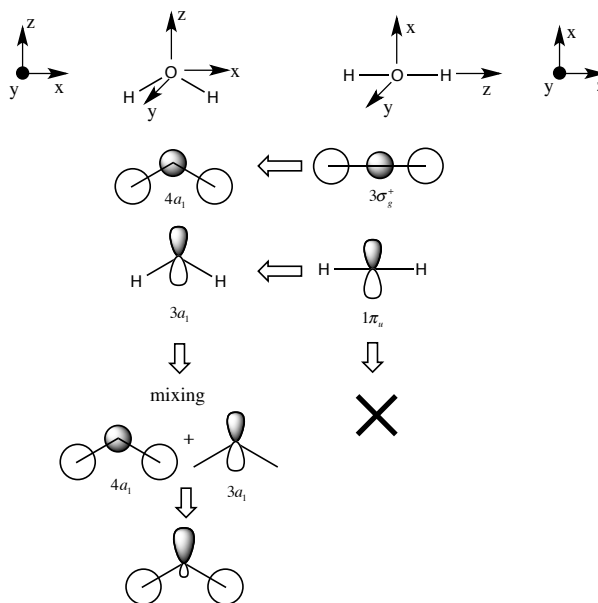


Figure 23 Mixing is “switched on” by the drop in symmetry

- MO changes
 - notice that the AOs move with their nuclear centres
 - for most MOs the contributing AOs remain similar irrespective of the geometry the molecule takes on.
 - however if mixing occurs then **the shape of MO changes**.
- the geometry of a molecule is determined by ALL of the MO interactions
 - examine all the MOs, but one or two occupied orbitals may dominate in terms of stability changes
 - for water one interaction clearly dominates over the others, and H_2O is bent because of the stabilisation of the $3a_1$ MO
 - thus the geometry of the water molecule is determined by the electronic structure and the greater the mixing the greater the distortion from linear and the smaller the H-E-H angle

IMPORTANT

Symmetry Breaking

- no mixing occurs until the molecule is infinitesimally distorted from linear
 - one way this can occur is via coupling of the electronic structure with internal vibrations, this is called **vibronic coupling**
 - vibronic coupling ONLY occurs when there has been a breakdown of the Born-Oppenheimer approximation
- once the symmetry is lowered degeneracy breaking occurs, allowing mixing of previously non-interacting orbitals.

- the Jahn-Teller theorem: "any non-linear molecule with a degenerate electronic ground state will undergo a geometrical distortion to remove the degeneracy and lower the total energy of the molecule" is a special case of this kind of vibronic coupling
- thus we have seen that **symmetry breaking** involves the collapse of a very fundamental approximation, and it results in some very fundamental changes with respect to the electronic and nuclear structure of a molecule
- symmetry breaking is a very wide ranging concept that spans all of physics and chemistry and which is important in philosophy. It is a key component, in magnetization, in Jahn-Teller distortions, in Einstein's theory of general relativity, in electroweak theories, and it is also required for the "existence" of the Higgs boson! See my web-site for some links to interesting sites.
- symmetry requires invariance under a (group) transformation and can be applied to molecules, bananas (ie objects), and abstract objects, (ie mathematical equations, functions).
- for example if a molecule remains the same under small translations in space, then it conserves linear momentum. If a molecule remains the same over short spans of time then it conserves energy. These are all continuous symmetries which underpin fundamental physical "laws".
- how symmetry is considered and the relationship with physical reality, plays an important role in the historical development of physics, chemistry and the philosophy of science.

MO diagram check list

- The focus of this course is to understand and be able to carry out the **process** of forming MO diagrams, not in memorising MO diagrams for a few specific examples. This has an advantage that when faced with a new challenging molecule, you know the process to be applied.
- Below is my MO diagram checklist, you could also design your own
 1. determine the molecular shape and identify the point group
 2. define the axial system find all of the symmetry operations
 3. identify the chemical fragments; put them on the bottom of the diagram
 4. determine the energy levels and symmetry labels of the fragment orbitals (use H1s as a reference level)
 5. combine fragment orbitals of the same symmetry, determine the MOs and then estimate the splitting energy, draw in the MO energy levels and MOs (in pencil!)
 6. determine the number of electrons in each fragment and hence the central MO region; add them to the diagram
 7. identify if any MO mixing occurs, determine the mixed orbitals and redraw the MO diagram with shifted energy levels and the mixed MOs
 8. Annotate your diagram
 9. Use your MO diagram to understand the structure, bonding and chemistry of the molecule

IMPORTANT

Key Points

- be able to form a MO diagram for molecules with the general formula AH_2 and AH_3 (tutorial problem)
- be able to explain and illustrate MO mixing
- be able to critically evaluate VSEPR theory, localised 2c-2e bonding and the delocalised MO pictures of bonding
- be able to describe how a PES spectrum is formed and be able to relate a spectrum to the MOs, and MO diagram, for a molecule
- be able to form correlation diagrams and explain why a particular geometry is more stable than another with reference to the stability of its MOs
- be able to discuss symmetry breaking and vibronic coupling
- be able to describe the process of forming an MO diagram (ie the MO checklist!)

Self-Study Problems / Exam Preparation

model answers are on the
web-site

- revise your computational chemistry workshop from last year:
http://www.huntresearchgroup.org.uk/teaching/year1_lab_start.html
- use qualitative MO theory to predict if BeH_2 will be bent or linear.
- optimise BeH_2 using the B3LYP method and 6-311G(d,p) basis set, confirm you have a minimum structure. Compute the MOs using pop=(full,nbo), visualise orbitals 1-7 and compare them to your qualitative MO diagram
- draw and annotate the MO diagram for linear water HOH, using your diagram explain if linear CH_2 is expected to be diamagnetic or paramagnetic
- (do AFTER the problems class) draw a MO diagram for planar D_{3h} NH_3
- (do AFTER the problems class) draw the correlation diagram for the distortion of NH_3 from D_{3h} to C_{3v}
- (do AFTER the problems class) discuss the bonding and structure of the acid-base adduct H_3BNH_3
- (do AFTER lecture 4) compare and contrast the bonding within H_3BNH_3 to that of ethane.