

Molecular Orbitals in Inorganic Chemistry

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Rm 110F (MSRH)

Feedback from Lecture 1

- Finding symmetry elements
- Finding point group
- Drawing MO diagram of a diatomic
- MO mixing?

most people are:
confident
or
can with notes



● Challenging material

minimise this!

“memorise”

practice this

point groups
finding improper rotations
visualising symmetry operations

Dominant by far!
*3 or more atoms
*heteronuclear
*MO mixing

labelling MOs
relative E of AOs
MO diagrams
MOs for metals

“dotted” lines
numbering MOs
orbital overlaps
bonding/antibonding

pure metals
solids
semi-conductors

not covered



We will cover all of these



Lecture 2 Outline

L2 build a MO diagram to show you the process

- quick revision
- stage 1: basic MO diagram for H₂O
- stage 2: include MO mixing
- real MOs (how good are qualitative diagrams)
- Walsh or correlation diagrams

L3 come back and look closely at the details

your
feedback:

3 or more atoms
hetero-nuclear
AO energy
MO mixing
labelling MOs

We will spend the next
two lectures focussing on
exactly these things!

Revision

Included because of a question from a student

MO are combinations of AOs

details:

Foundation from last year

atomic orbitals

- ◆ radial and angular components
- ◆ radial: as quantum shell increases
 - ▶ inner nodes
 - ▶ radius max density increases
- ◆ cartoons represent outer portion
- ◆ shaded part represents negative part of function
- ◆ angular nature represented by the lobes

the "Orbitron"

- ◆ link from my website

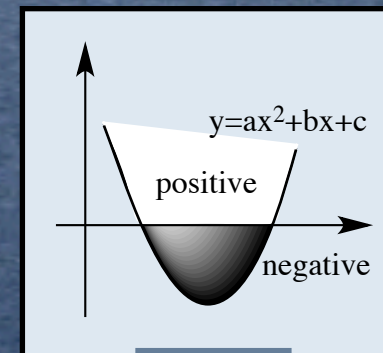
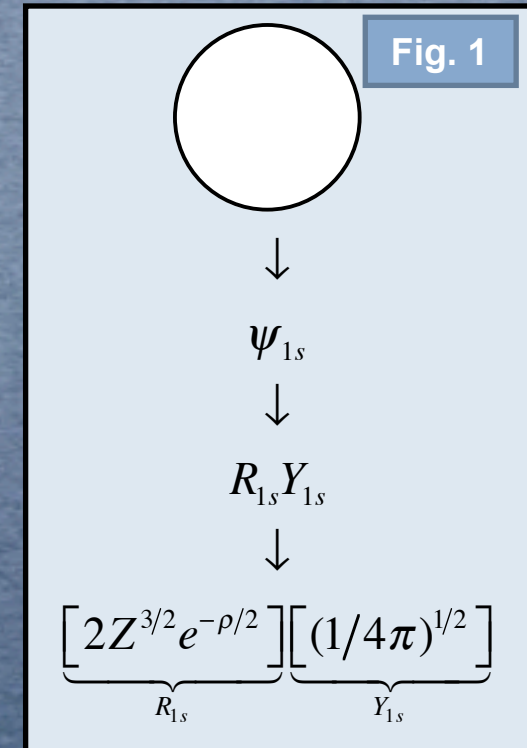
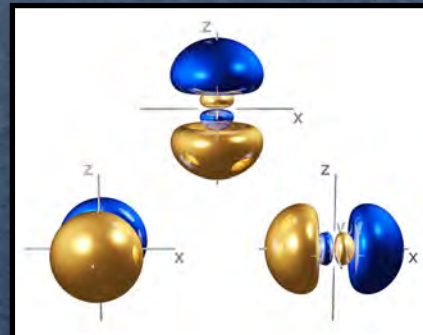


Fig. 2

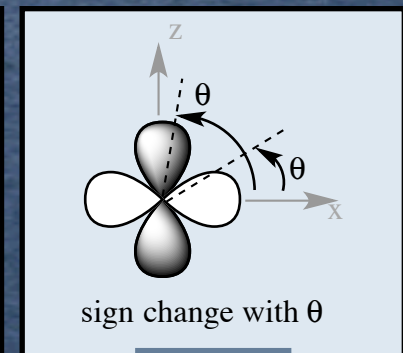


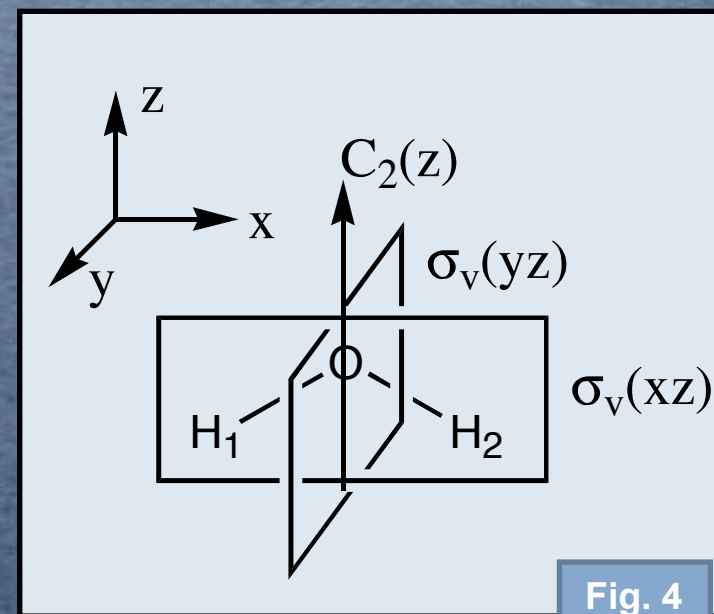
Fig. 3

Setting Up

- determine the shape of the molecule
- find the point group of the molecule: C_{2v}
- define the axial system
- find all of the symmetry elements

Lecture 1

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	$h=4$
A_1	1	1	1	1	z
A_2	1	1	-1	-1	
B_1	1	-1	1	-1	x
B_2	1	-1	-1	1	y



your character tables

Fragments

map onto each other under the symmetry operations

- ◆ H atoms map onto each other
- ◆ O atom maps onto its self
- ◆ H_2 and O atom are the fragments

use place holders!

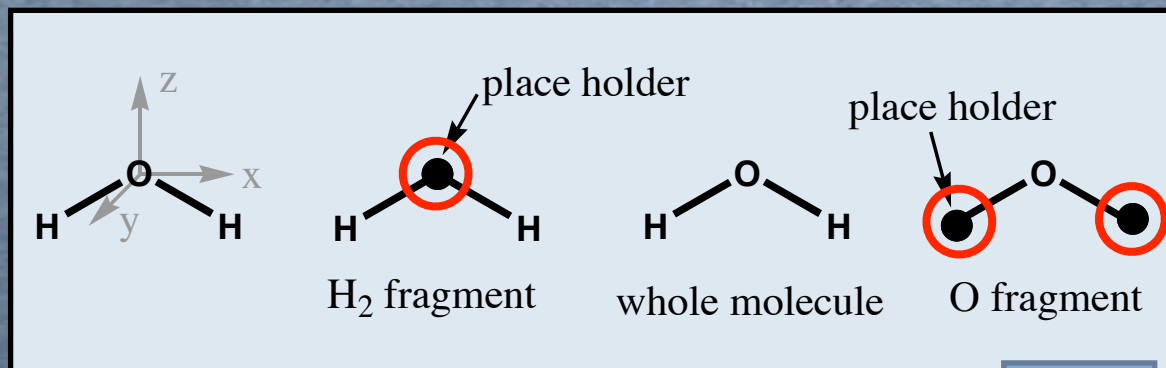


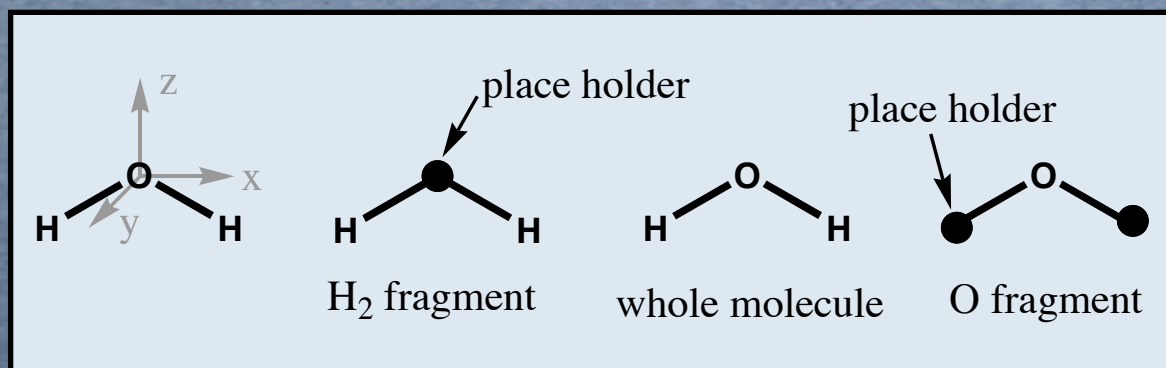
Fig. 5

Fragments

map onto each other under the symmetry operations

- ◆ H atoms map onto each other
- ◆ O atom maps onto its self
- ◆ H₂ and O atom are the fragments

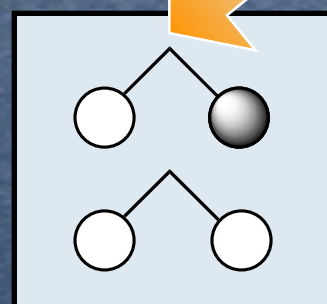
use place holders!



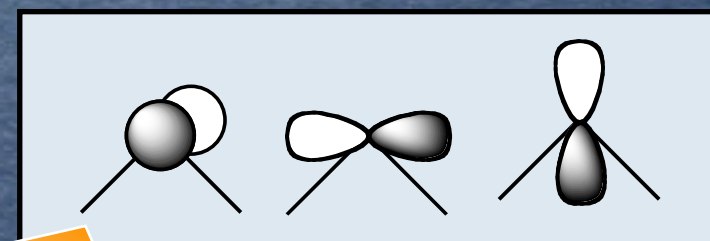
reproduce the whole of the molecular structure in the MO

fragment orbitals

- ◆ H₂ orbitals
- ◆ O atom orbitals



H₂ orbitals



O (s and p) orbitals

Fig. 6

Set Up MO Diagram

vertical axis: Energy

◆ add H 1s reference level

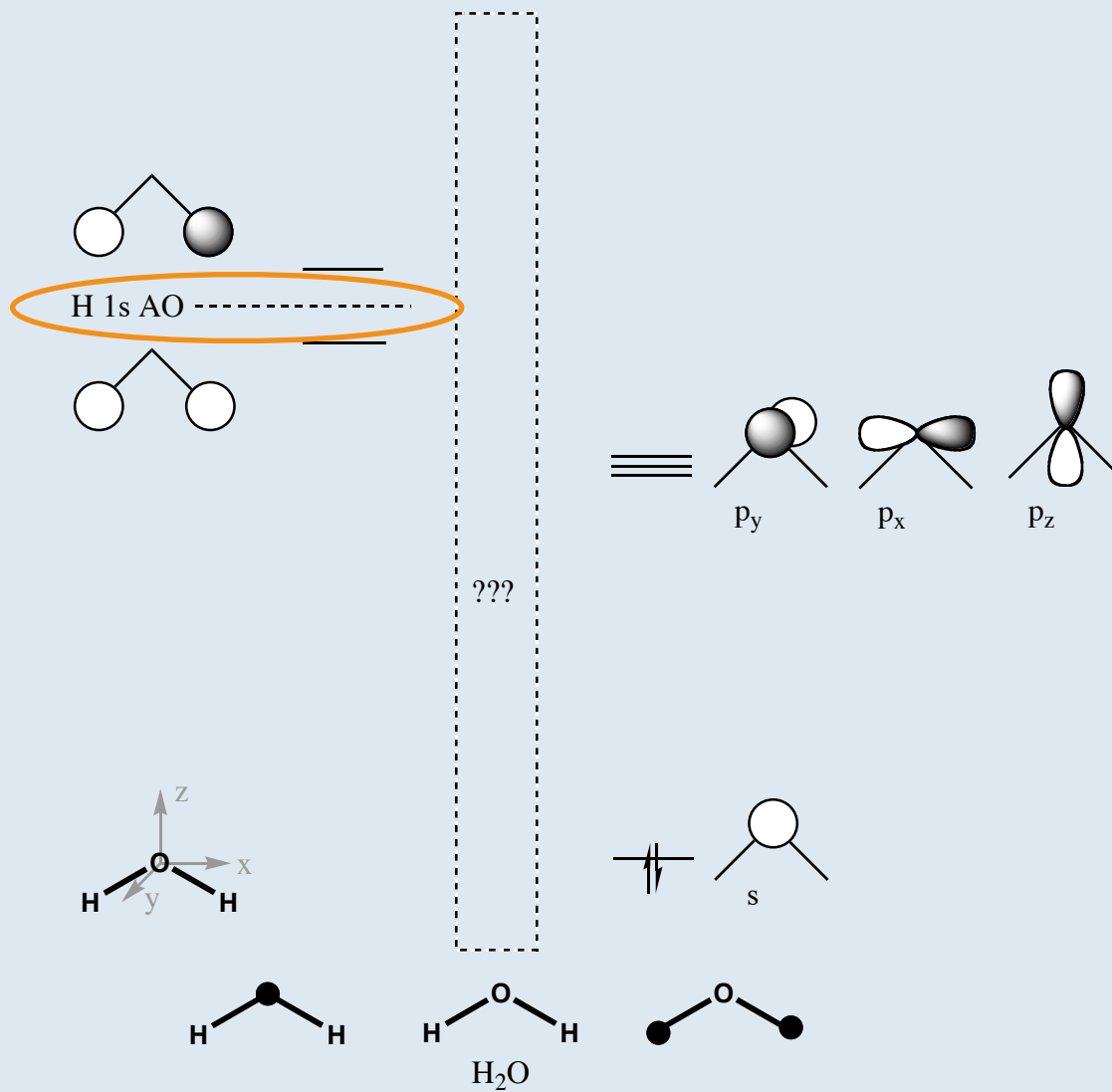


Fig. 6

Set Up MO Diagram

vertical axis: Energy

position AOs

♦ O more electronegative
=> so valence orbitals lie
below H 1s reference orbital

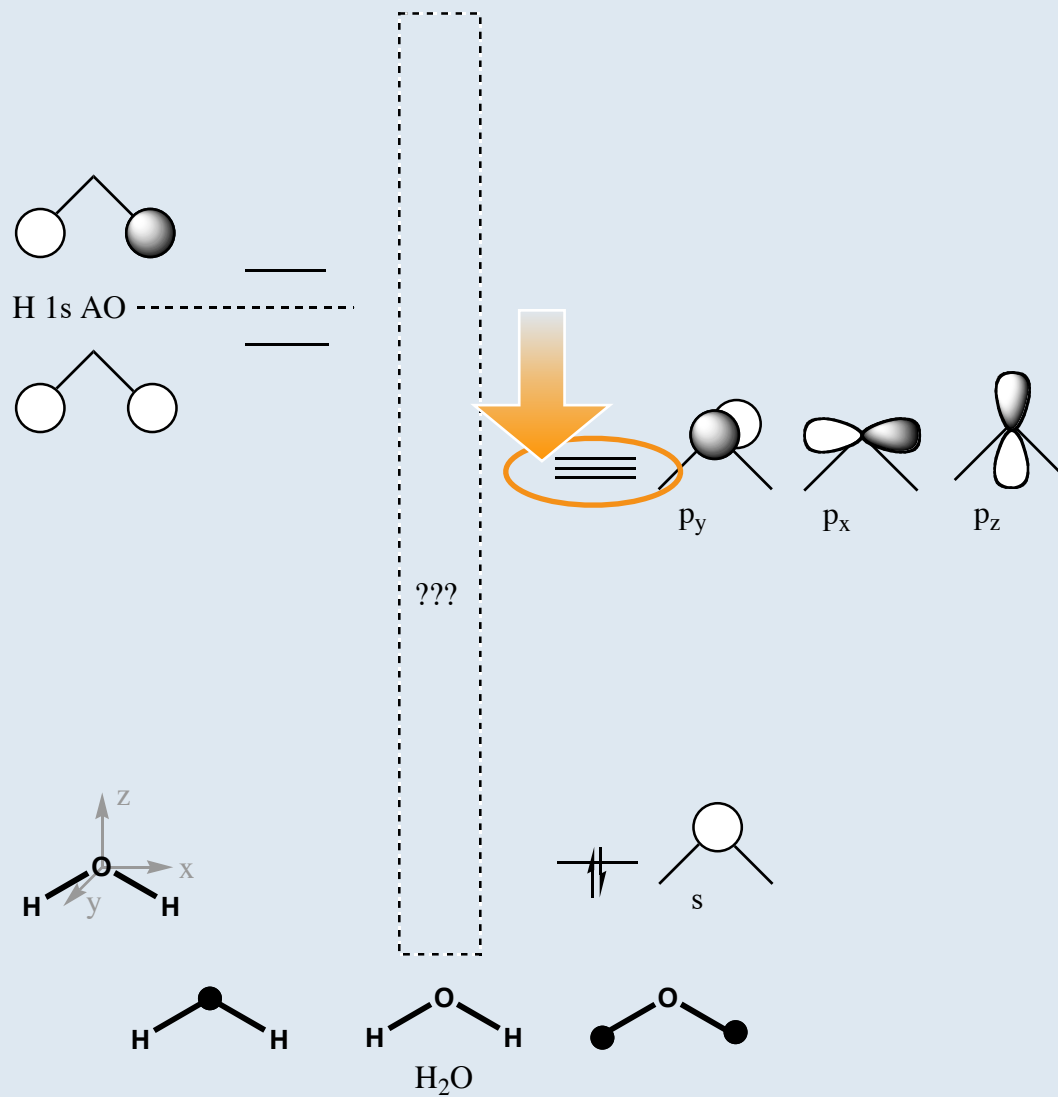


Fig. 6

Set Up MO Diagram

vertical axis: Energy

position AOs

- ♦ O more electronegative
=> so valence orbitals lie below H 1s reference orbital
- ♦ H atoms are further apart than in H₂
=> stabilisation and destabilisation are less ie splitting energy is less

more on this next lecture!

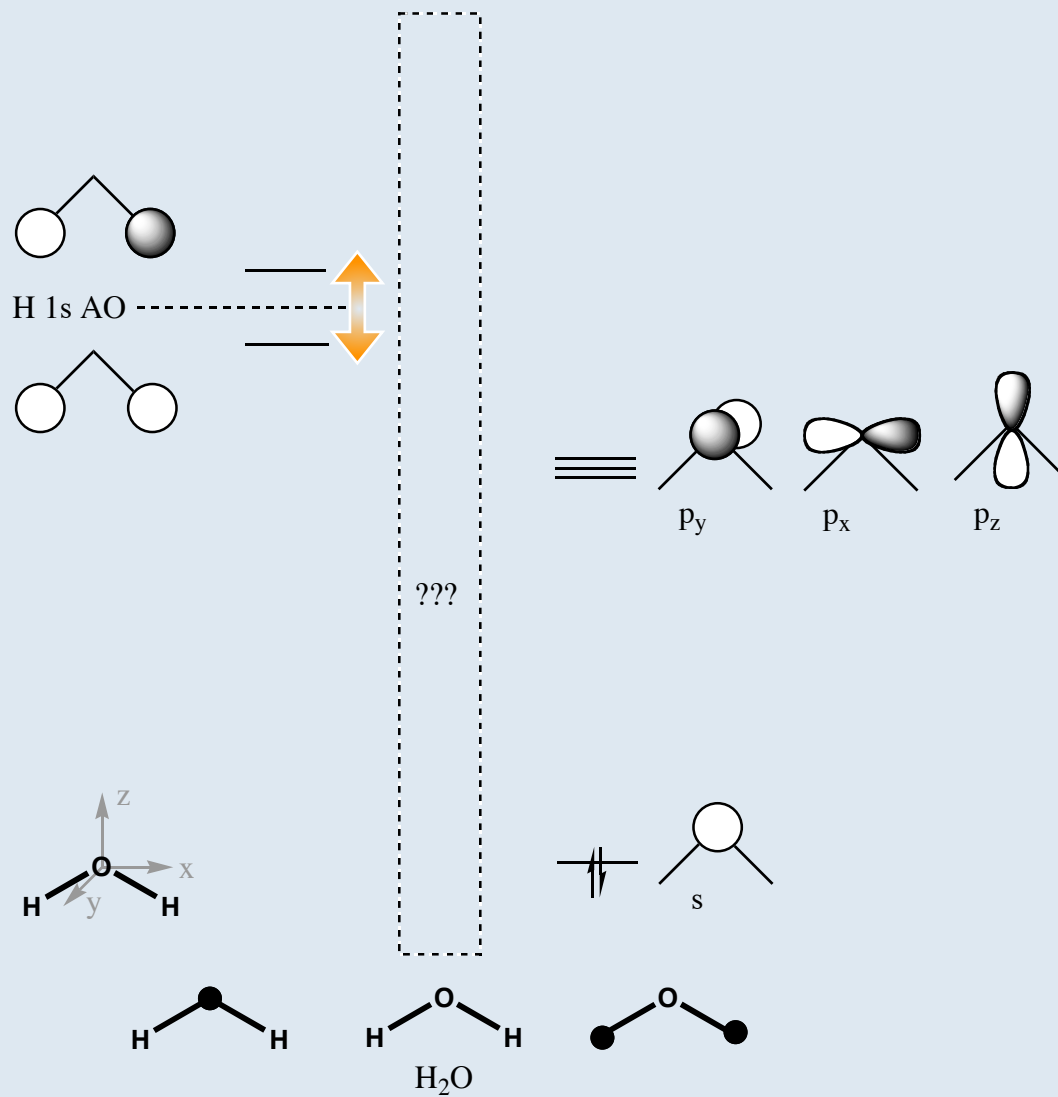
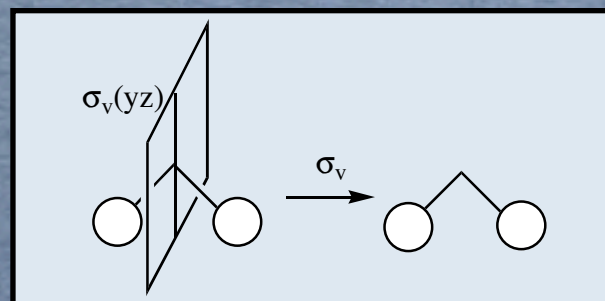


Fig. 6

Fragment Orbital Symmetry

How does each orbital transform under the symmetry operations of the group?

- ♦ orbital is unchanged \Rightarrow character = 1
- ♦ a sign change \Rightarrow character = -1
- ♦ check against the character table



Lecture 1

No change under $\sigma_v \Rightarrow \chi = 1$

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
$\Gamma \left\{ \begin{array}{c} \text{O} \\ \diagdown \quad \diagup \\ \text{O} \end{array} \right\}$	1	1	1	1

Fig. 7

a_1

Short-Cut!

totally bonding orbitals are always totally symmetric

- ♦ which is the first symmetry label listed for all point groups
- ♦ for C_{2v} this is the a_1 irreducible representation

a_1

Short Cuts!

look in the last columns of the character table

- ◆ find T_x , T_y , T_z
- ◆ sometimes also written as just x , y , z
- ◆ gives you the axis symmetry label

Important!

Short-Cut!

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	$h=4$
A_1	1	1	1	1	T_z
A_2	1	1	-1	-1	
B_1	1	-1	1	-1	T_x
B_2	1	-1	-1	1	T_y

Fig. 7

Fragment Orbitals

- look for similarities in the phase of orbitals and the cartesian axes

Short-Cut!

O

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
$\Gamma \left\{ \begin{array}{c} \text{lobe} \\ \text{lobe} \end{array} \right\}$	1	-1	-1	1	T_y	$\Rightarrow b_2$
$\Gamma \left\{ \begin{array}{c} \text{lobe} \\ \text{lobe} \end{array} \right\}$	1	-1	1	-1	T_x	$\Rightarrow b_1$
$\Gamma \left\{ \begin{array}{c} \text{lobe} \\ \text{lobe} \end{array} \right\}$	1	1	1	1	T_z	$\Rightarrow a_1$

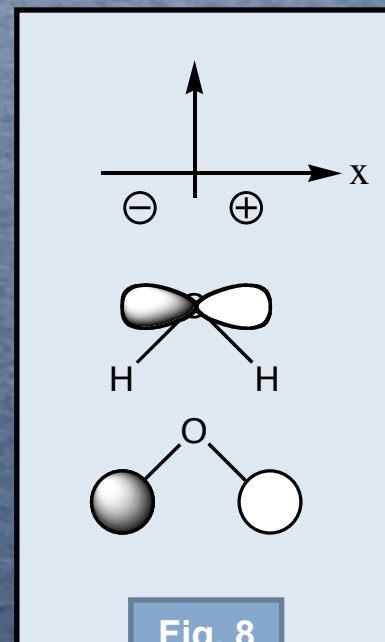
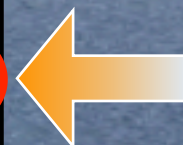


Fig. 8

H₂

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

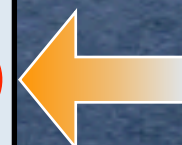


Fig. 7

look for similarity in phase patterns!

Fragment Orbitals

- look for similarities in the phase of orbitals and the cartesian axes

Short-Cut!

O

	C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	
$\Gamma \left\{ \begin{array}{c} \text{orbital} \\ \text{diagram} \end{array} \right\}$		1	-1	-1	1	$p_y \rightarrow b_2$
$\Gamma \left\{ \begin{array}{c} \text{orbital} \\ \text{diagram} \end{array} \right\}$		1	-1	1	-1	$p_x \rightarrow b_1$
$\Gamma \left\{ \begin{array}{c} \text{orbital} \\ \text{diagram} \end{array} \right\}$		1	1	1	1	$p_z \rightarrow a_1$

Fig. 7



Add symmetry labels to MO diagram

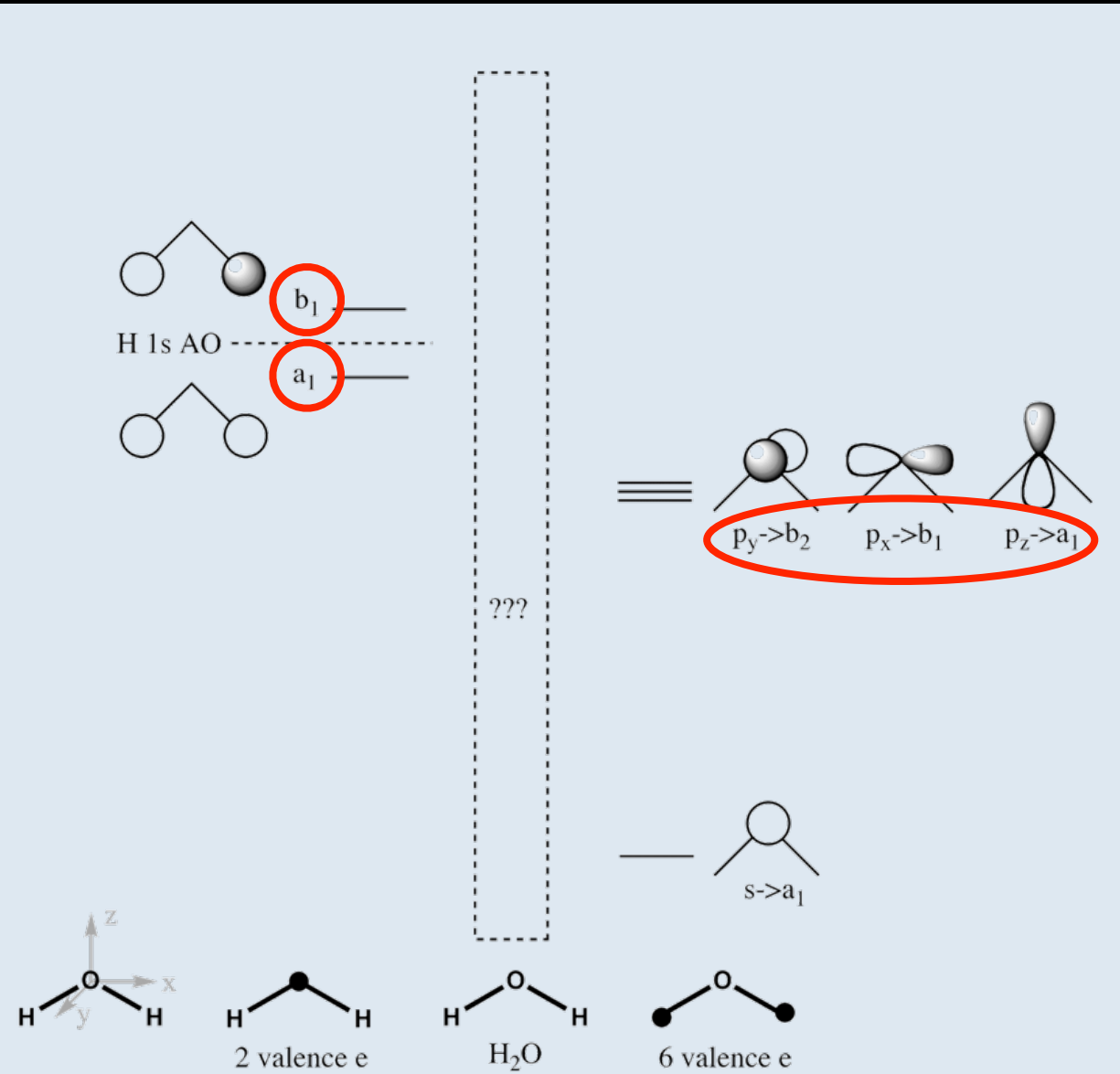


Fig. 9

Form the MOs

work out MOs first
then the splitting

Important!

● Only fragment orbitals (FOs) of the same symmetry can combine

◆ for water: a_1 and b_1

● FO can only combine ONCE

◆ more than one FO of same symmetry?

◆ then combine the lowest energy two

◆ leave the last one non-bonding (for now!)

● Form MOs by

◆ “adding” FOs together “as is”

◆ “adding” FOs with ONE FO phase inverted

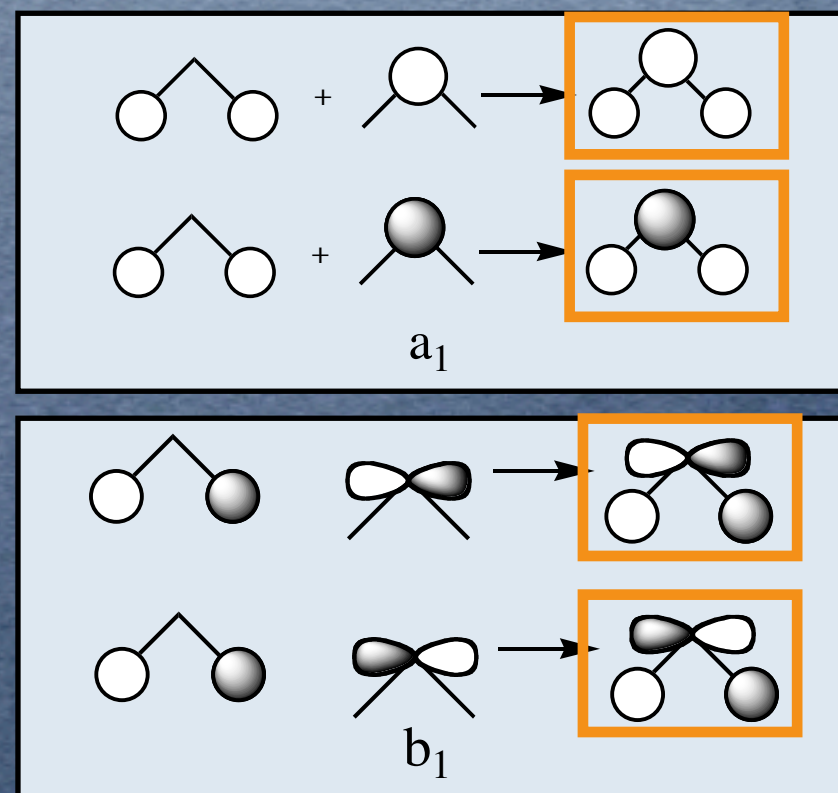


Fig 10

Stage One MO Diagram

Evaluate splitting

- ◆ FOs far apart in energy interact only weakly
- ◆ in-phase interactions are bonding
- ◆ destabilisation is always larger

more on this next
lecture!

THEN MOs on the diagram

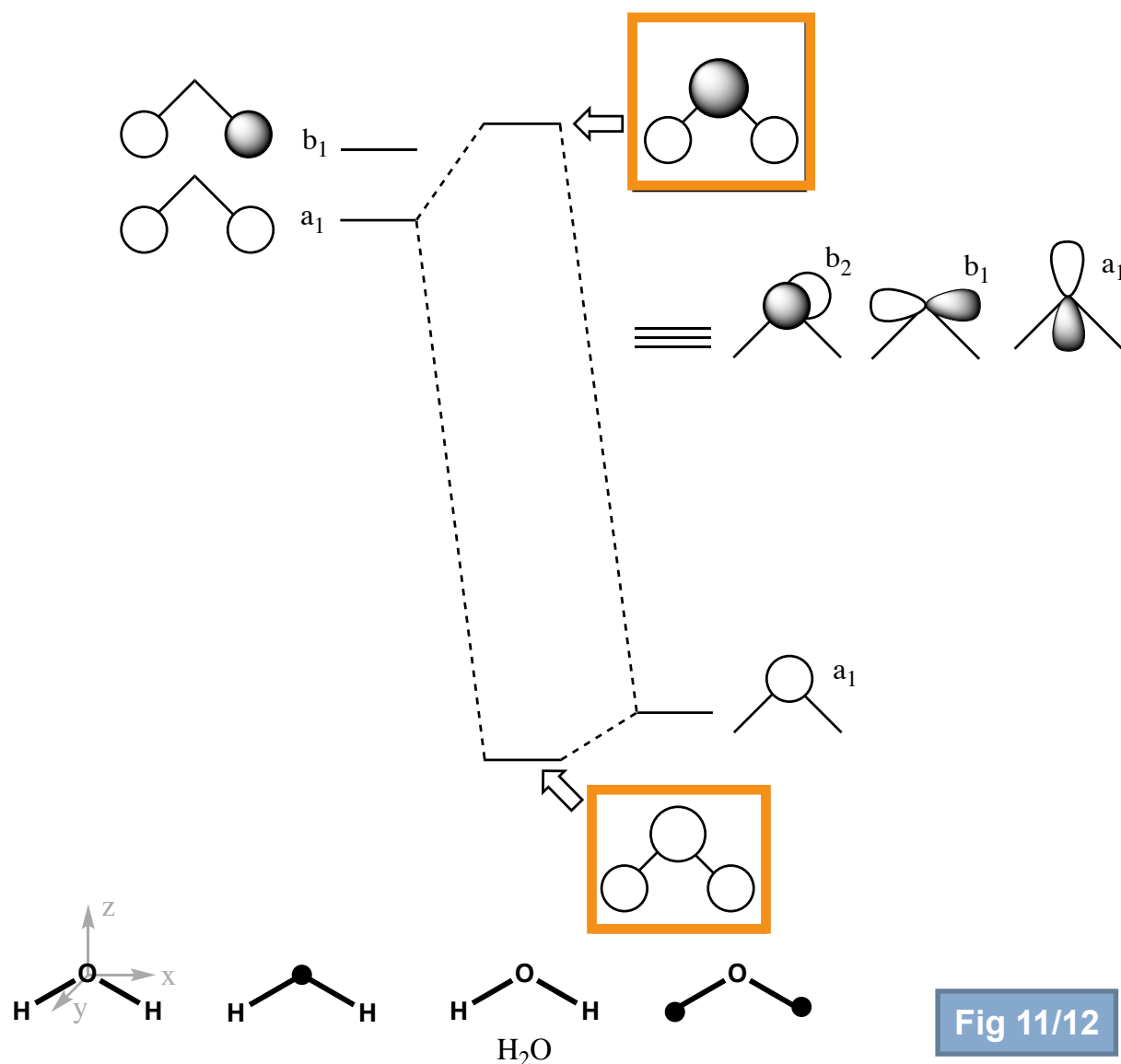


Fig 11/12

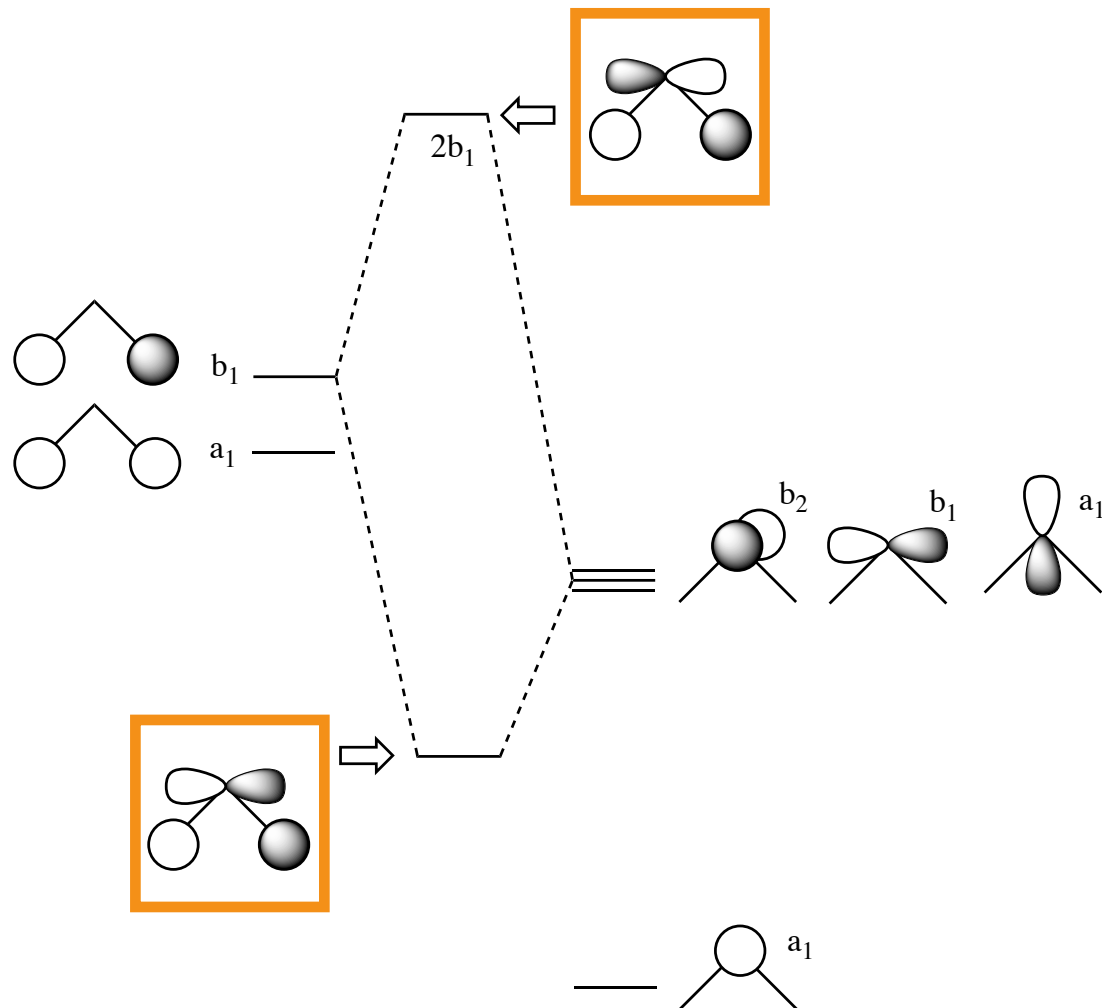
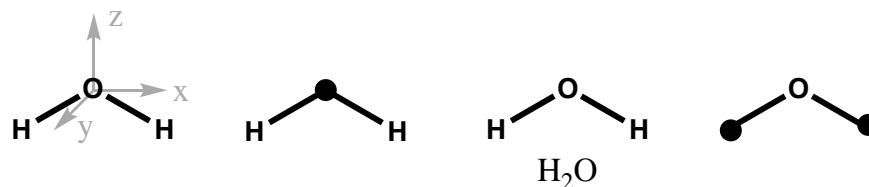
Stage One MO Diagram

Evaluate splitting

- ◆ FOs closer in energy interact more
- ◆ destabilisation is always larger

more on this next
lecture!

THEN MOs on the diagram



Stage One MO Diagram

Label MOs

- ◆ number within symmetry label
- ◆ count the core orbitals only if molecule is small

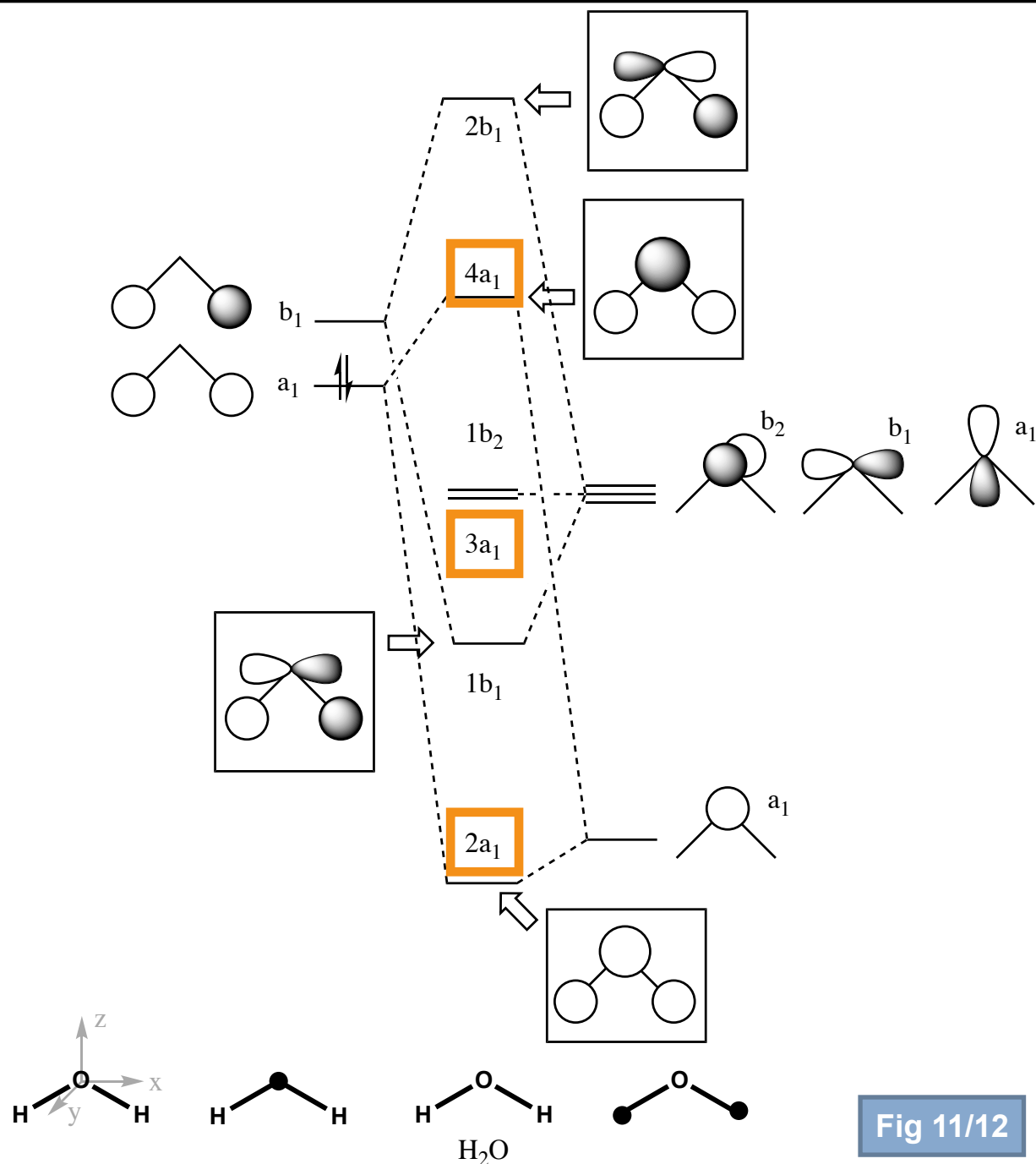


Fig 11/12

Stage One MO Diagram

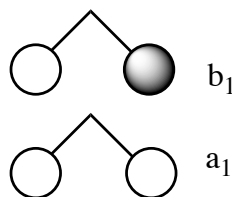
Annotate your diagrams!

Important!

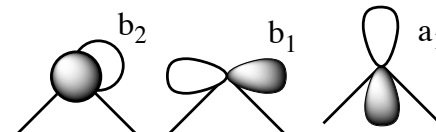
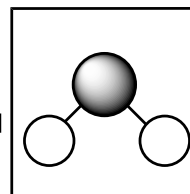
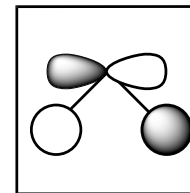


do not repeat information

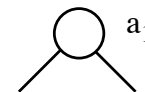
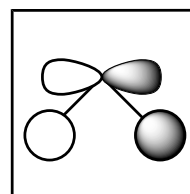
antibonding MO is always destabilised more than the bonding MO is stabilised



a_1 FO left non-bonding in the first stage diagram



FOs are closer in energy and so the interaction between the orbitals is larger for the b_1 MO



$1a_1$ is the O 1sAO which is not shown because this is a valence MO diagram

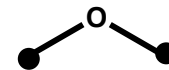
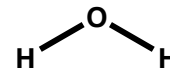
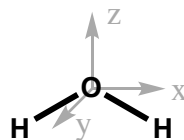
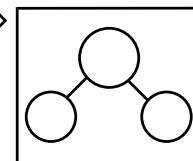


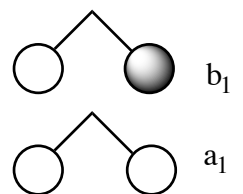
Fig 11/12

Stage One MO Diagram

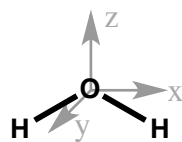
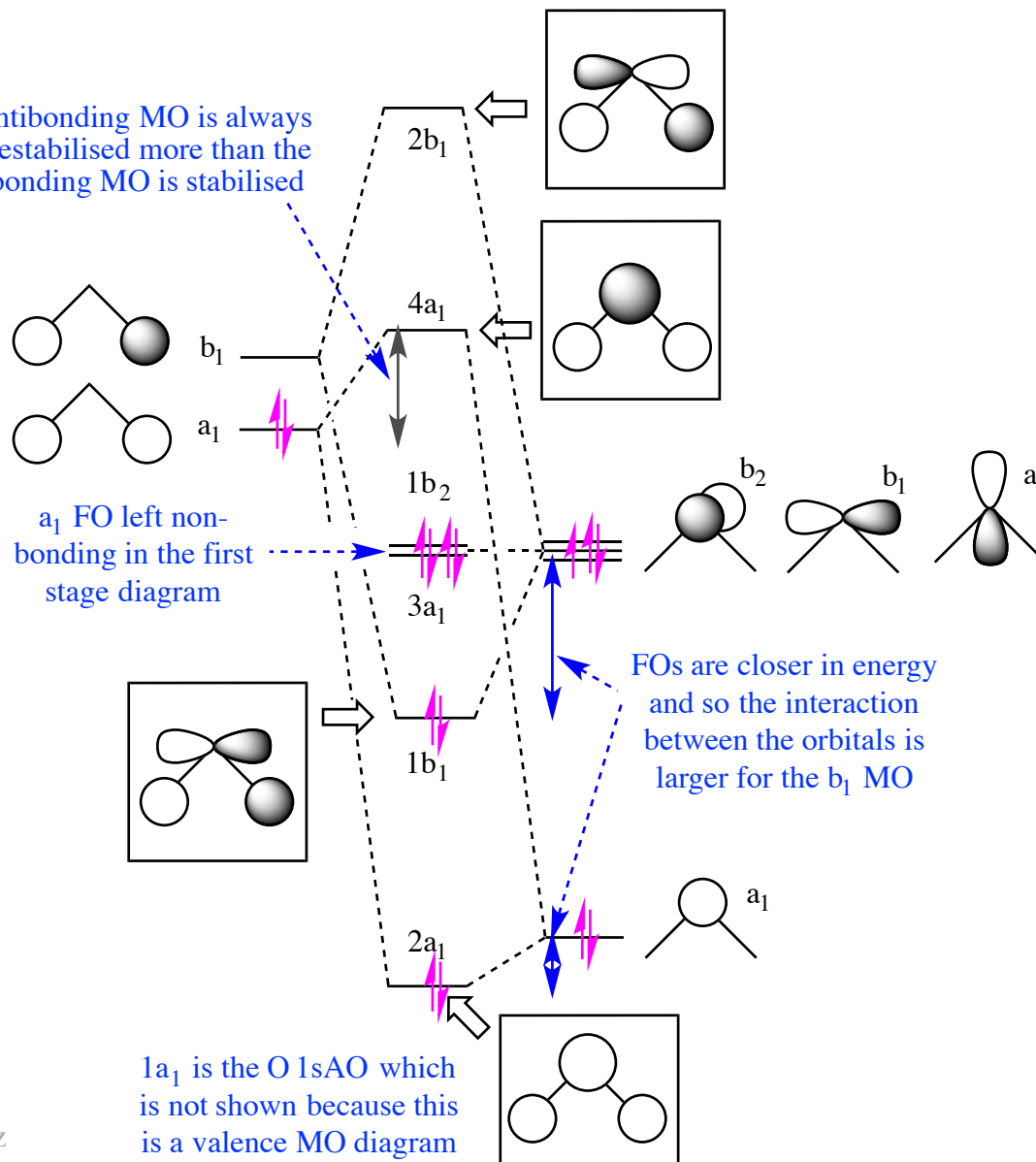
add the electrons!

fill sequentially

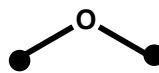
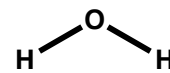
antibonding MO is always destabilised more than the bonding MO is stabilised



a_1 FO left non-bonding in the first stage diagram



2 valence e



6 valence e

Fig 11/12

Stage 2: MO Mixing

● necessary conditions

- ◆ ONLY MOs of the same symmetry can mix
- ◆ to occur mixing MUST stabilise the total energy

● mixing tends to be large when:

- ◆ MOs are close in energy
- ◆ one MO is non-bonding or unoccupied
- ◆ orbitals are in HOMO-LUMO region

Important!

a_1 MO Mixing

mixing orbitals

◆ “add” MOs together “as is”

◆ “add” MOs with ONE MO phase inverted

◆ inspect to determine which is the bonding mixed MO

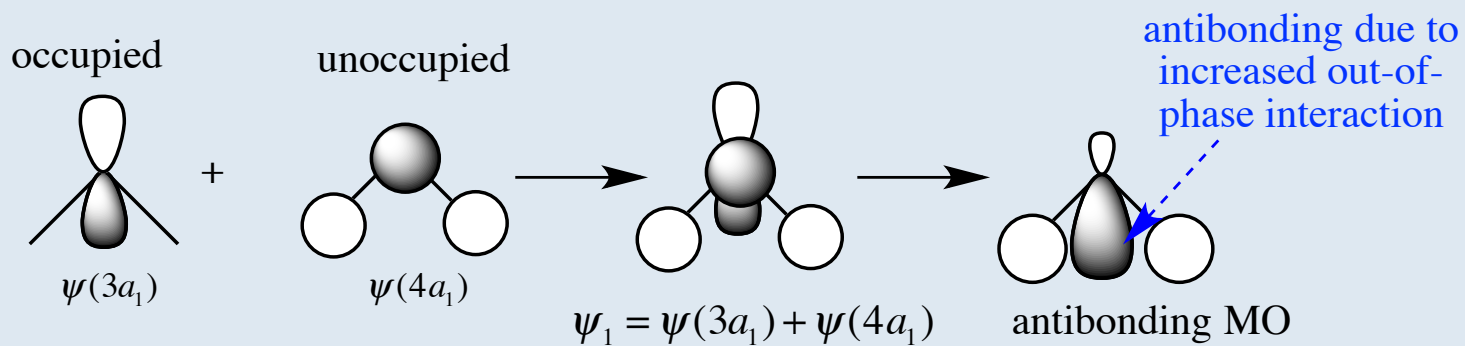


Fig 13

In-Class Activity

● mixing orbitals

- ◆ “add” MOs together “as is”
- ◆ “add” MOs with ONE MO phase inverted
- ◆ inspect to determine which is the bonding mixed MO

form
 $-\psi(3a_1) + \psi(4a_1)$

In-Class Activity

mixing orbitals

- ◆ “add” MOs together “as is”
- ◆ “add” MOs with ONE MO phase inverted
- ◆ inspect to determine which is the bonding mixed MO

form
 $-\psi(3a_1) + \psi(4a_1)$

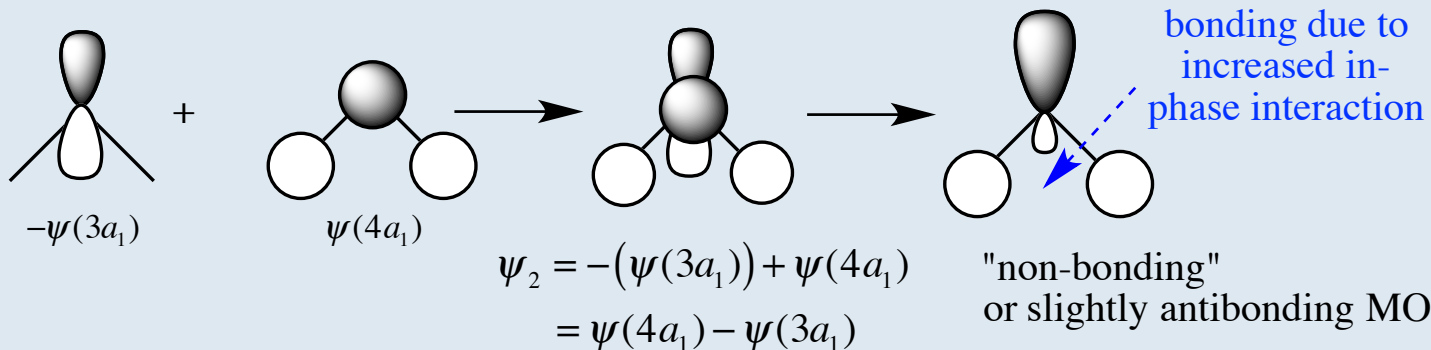


Fig 14

Mixing

strong mixing:

- ◆ $4a_1$ MO unoccupied
- ◆ $3a_1$ MO non-bonding
- ◆ in HOMO/LUMO region
- ◆ close in energy
- ◆ occupied MO is stabilised

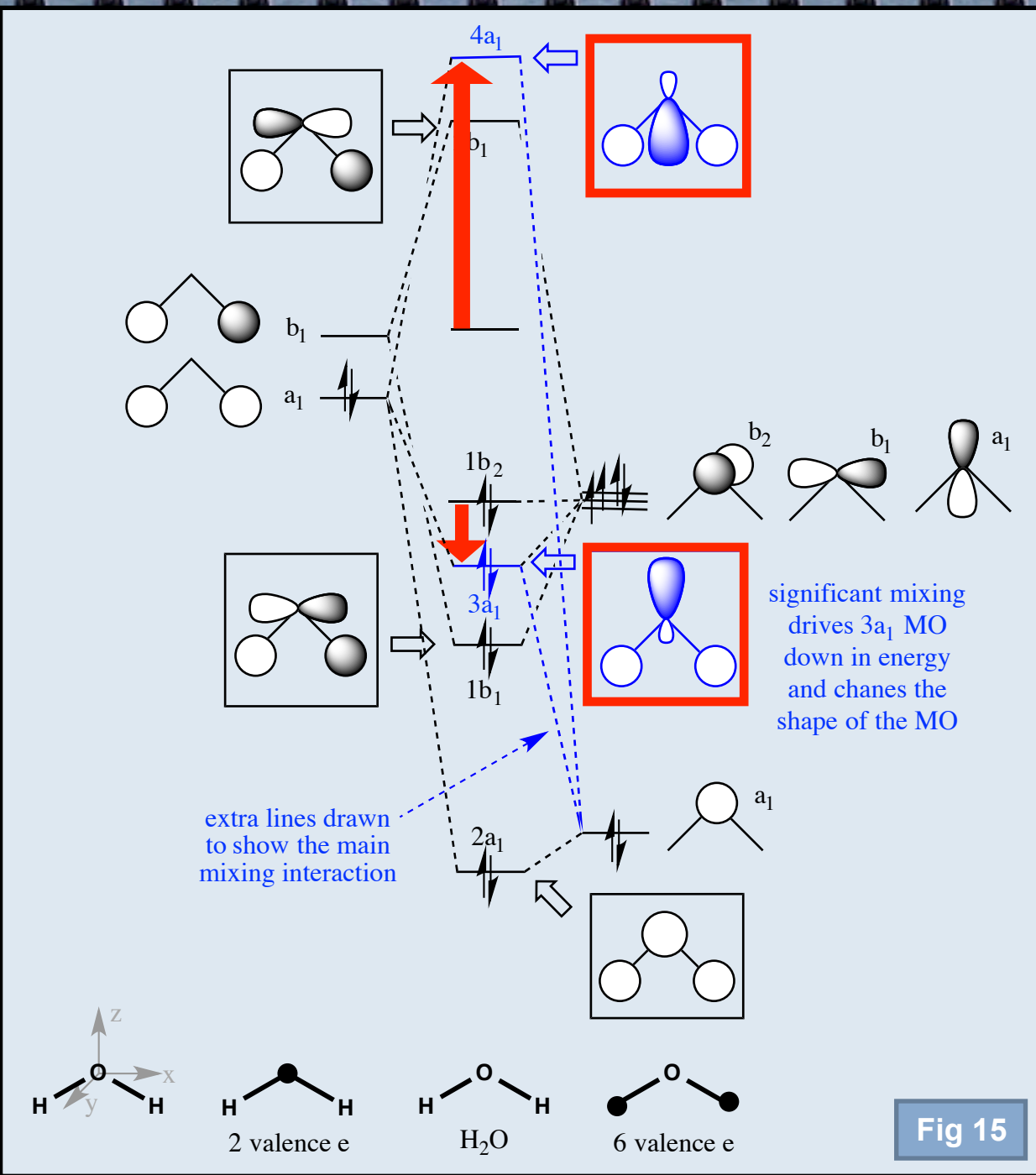


Fig 15

Final MO Diagram of H₂O

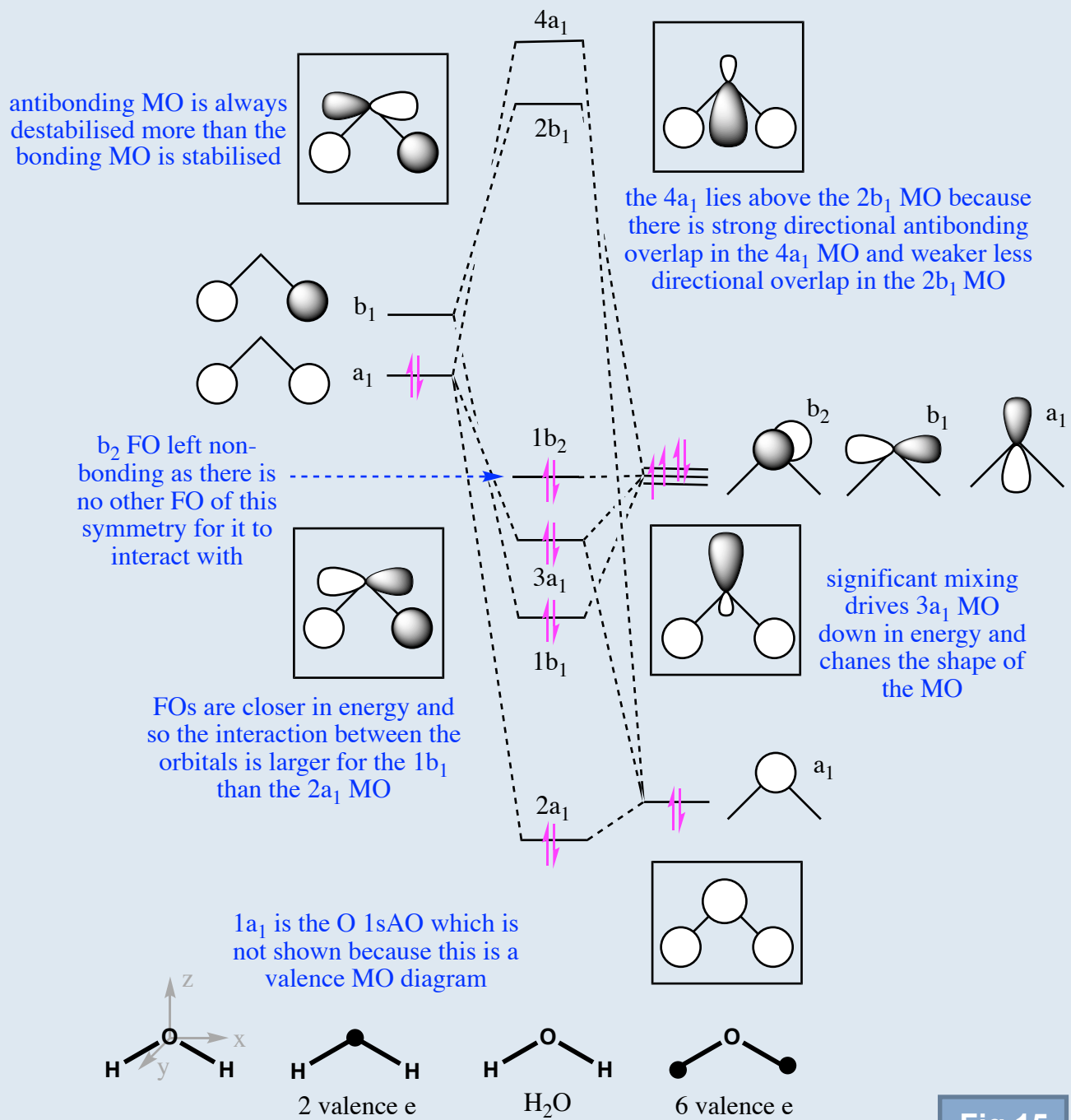


Fig 15

"Real" MOs

computed
molecular
orbitals

we have
"solved" the
Schrödinger
equation!!!

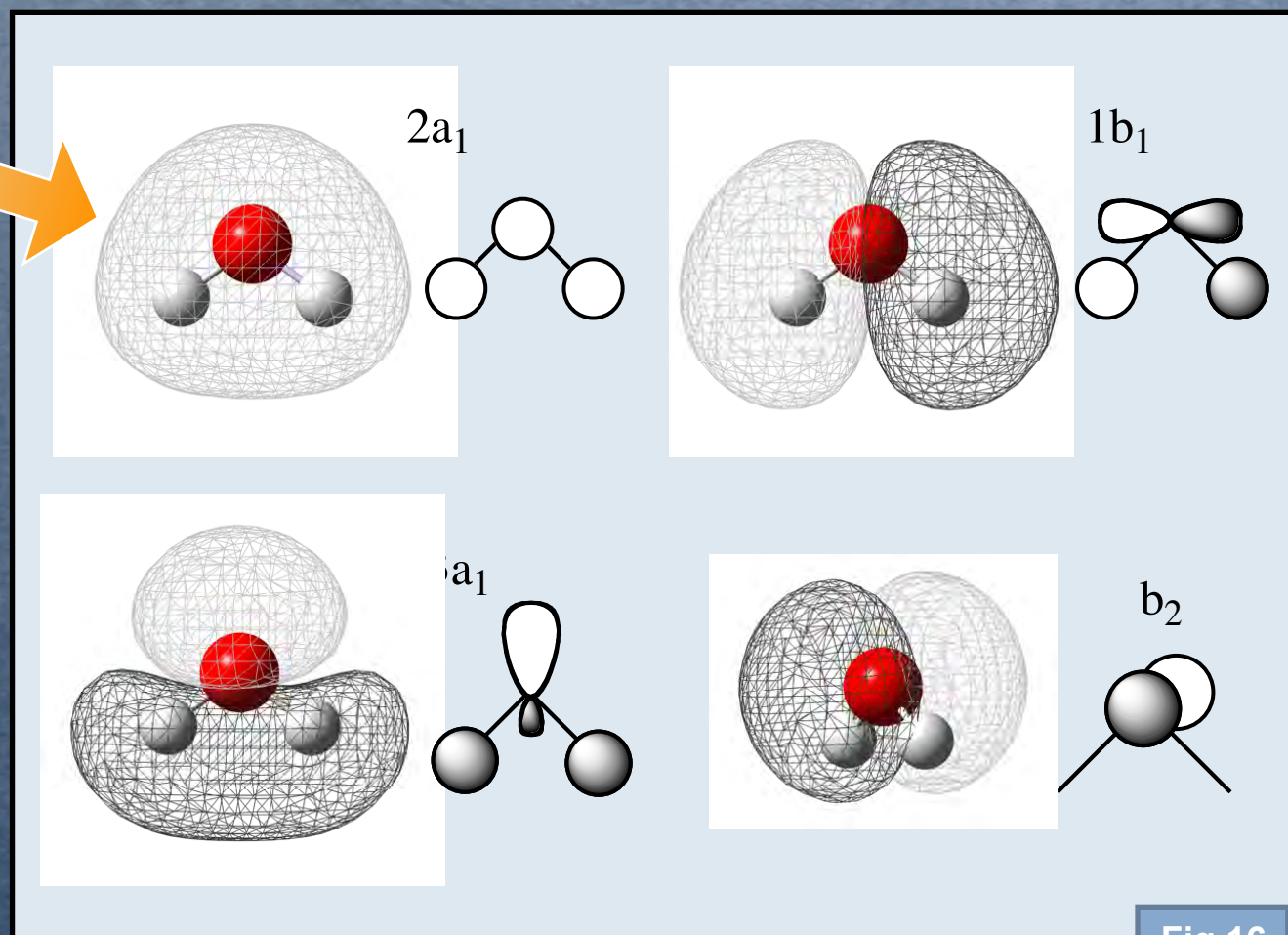


Fig 16

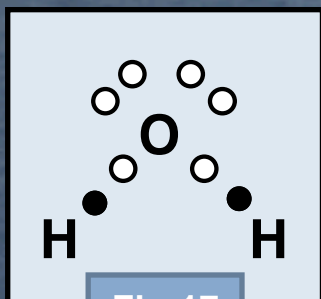
Experimental Evidence

Photoelectron spectrum

- ✦ energy required to eject an electron from its orbital

“traditional” theory:

- ✦ expect 2 equivalent bonds and 2 equivalent lone pairs for water = 2 lines in photo-electron spectrum



BUT

- ✦ have 3 lines in photo-electron spectrum which relate to delocalised $1b_1$, $3a_1$ and $1b_2$ MOs

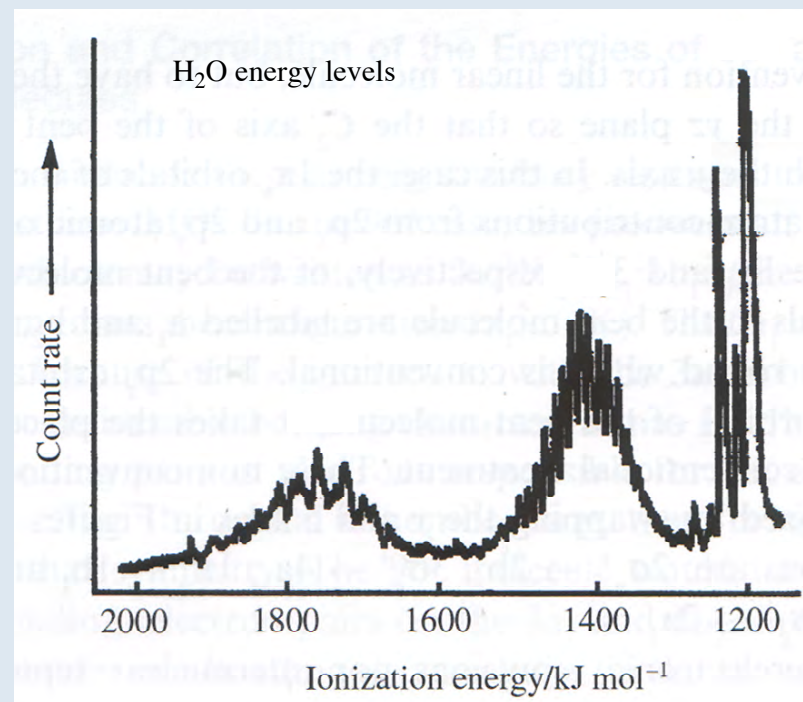
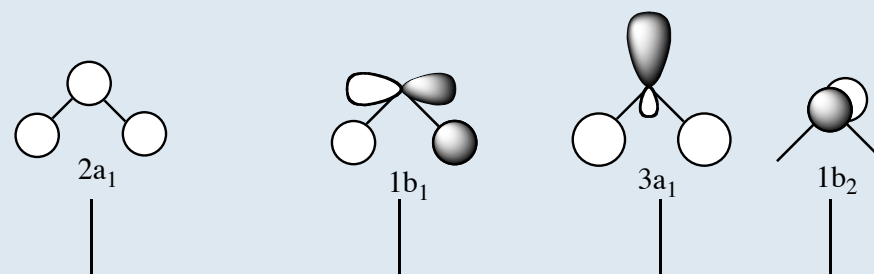


Fig 5.13
from
“Structure
and
Bonding” by
J. Barrett

Fig 18

Delocalisation

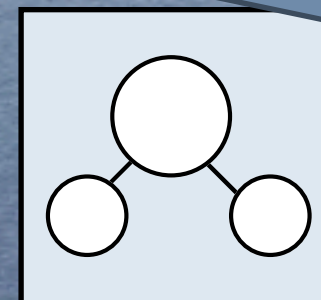
● MOs are delocalised

- ◆ not 2 center 2 electron
- ◆ most of MOs extend over ALL atoms in molecule
- ◆ there are no “bonds”

● Bonds represent a build up of the TOTAL electron density

● We keep ideas of hybridisation and 2c-2e bonds because they are USEFUL

where have the bonds gone???



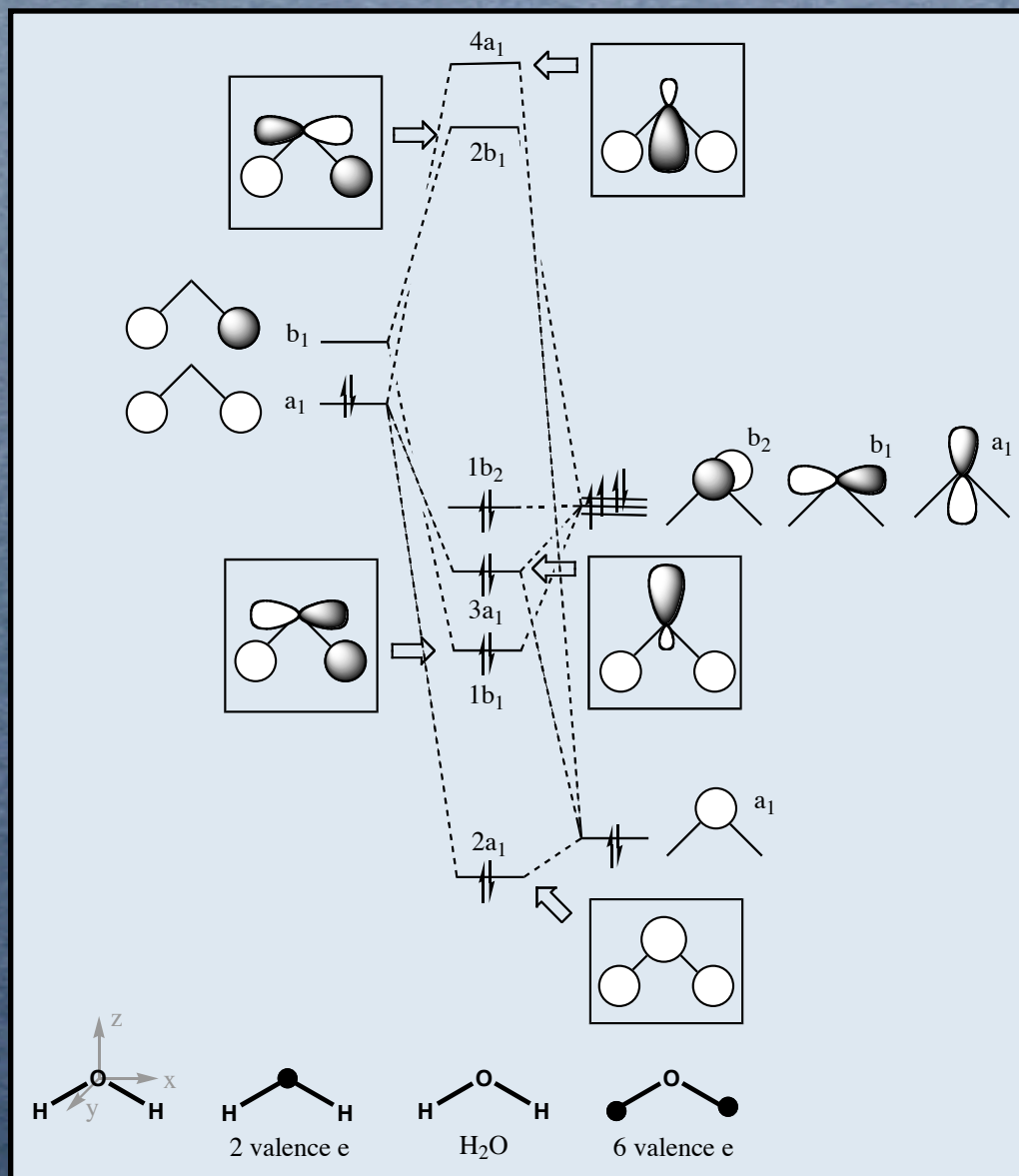
Analysis

MO diagrams are transferable

- ◆ one diagram is good for many molecules or fragments!
- ◆ molecules BeH_2 (homework), H_2S
- ◆ fragments CH_2 (lecture 4), NH_2
- ◆ we can even treat metal fragments: MH_2

general formula AH_2

- ◆ A=main group element, M=metal
- ◆ slight modifications:
- ◆ different numbers of electrons
- ◆ slightly different position of the fragment orbitals



Correlation Diagram

Walsh diagram: change one geometric parameter and examine changes in MOs and energies

- ✦ normally a bond distance or angle
- ✦ link the MOs for two extreme geometries

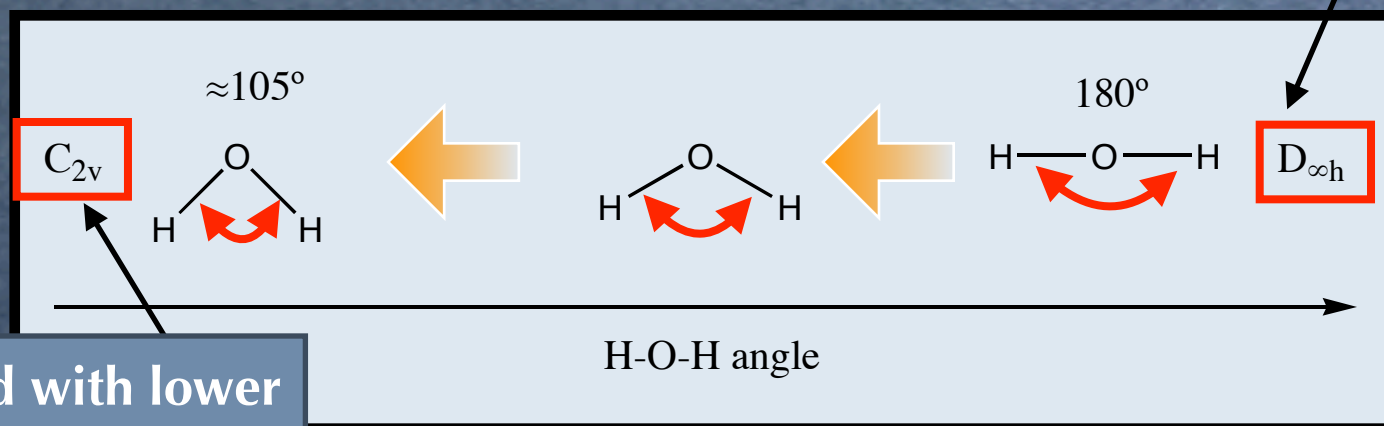
example: Why is H₂O bent?

start with high symmetry



Fig 21

Prof. A.D Walsh
University of Dundee
from: <http://www.dundee.ac.uk/museum/scientists.htm>

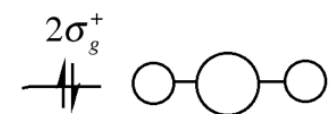
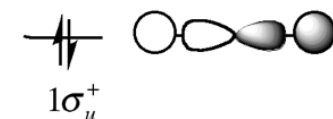
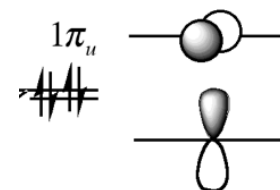
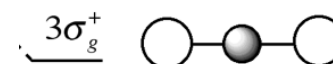
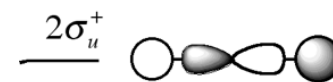


end with lower symmetry

Walsh Diagram

typically start from the highest symmetry

✦ I've constructed the MO diagram for linear H₂O for you (Self-study for you to reproduce)



≈105°

H-O-H angle

180°

H₂O

Walsh Diagram

then examine how MOs change under geometric distortion

Qualitative
not
Quantitative!

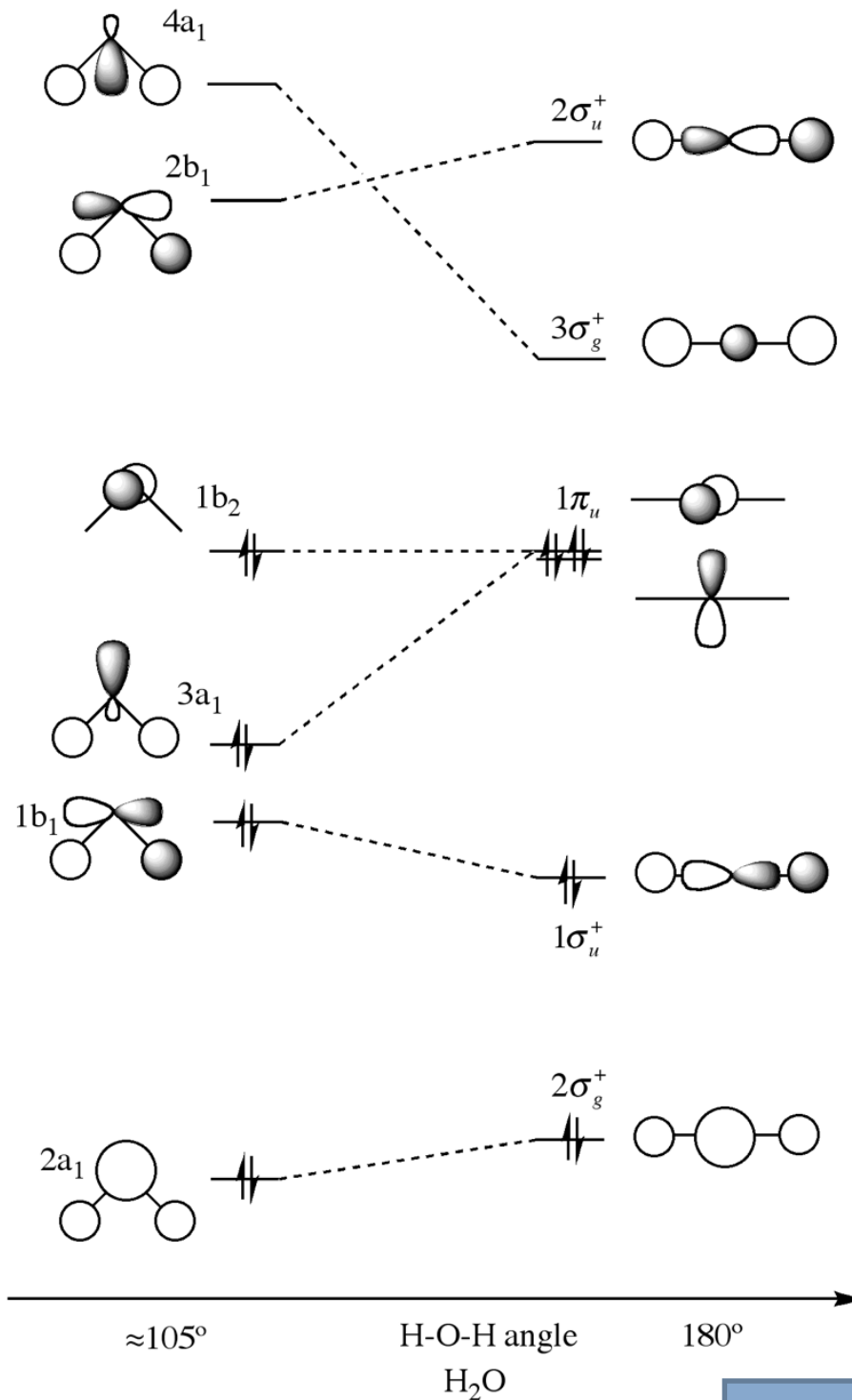


Fig 21

Energy of MOs

then examine how MOs change under geometric distortion

$2\sigma_g^+$ ($2a_1$) stabilised

- ◆ BONDED overlap dominates
- ◆ directed O & H overlap is stronger in linear structure
- ◆ on bending ↓ O-H bonding overlap
- ◆ ALSO ↑ H...H through space bonding overlap
- ◆ net result small stabilisation

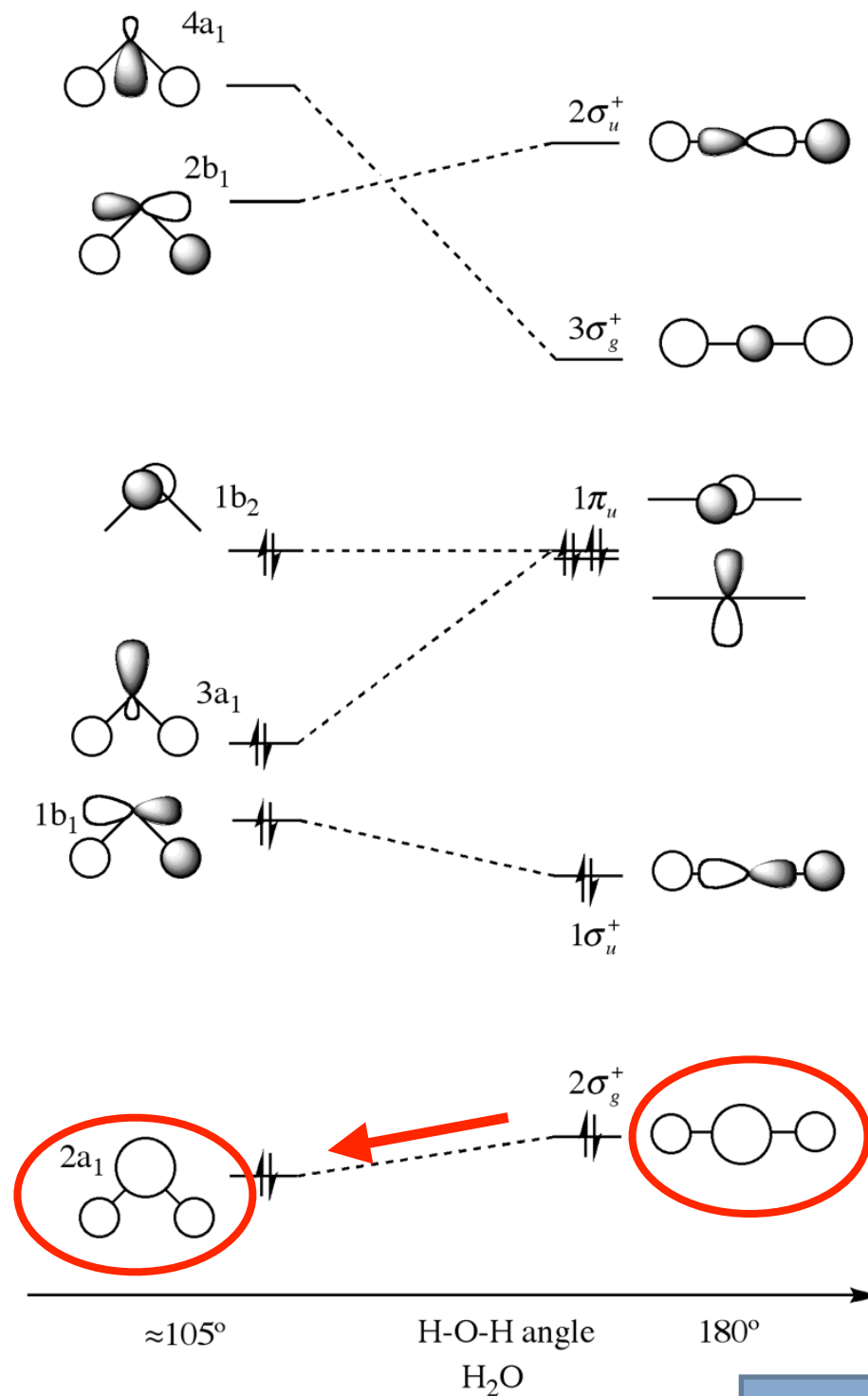


Fig 21

Energy of MOs

then examine how MOs change under geometric distortion

$1\sigma_u^+$ ($1b_1$) destabilised

- ◆ \downarrow O-H bonding overlap
- ◆ ALSO \uparrow H...H through space antibonding
- ◆ net result destabilisation

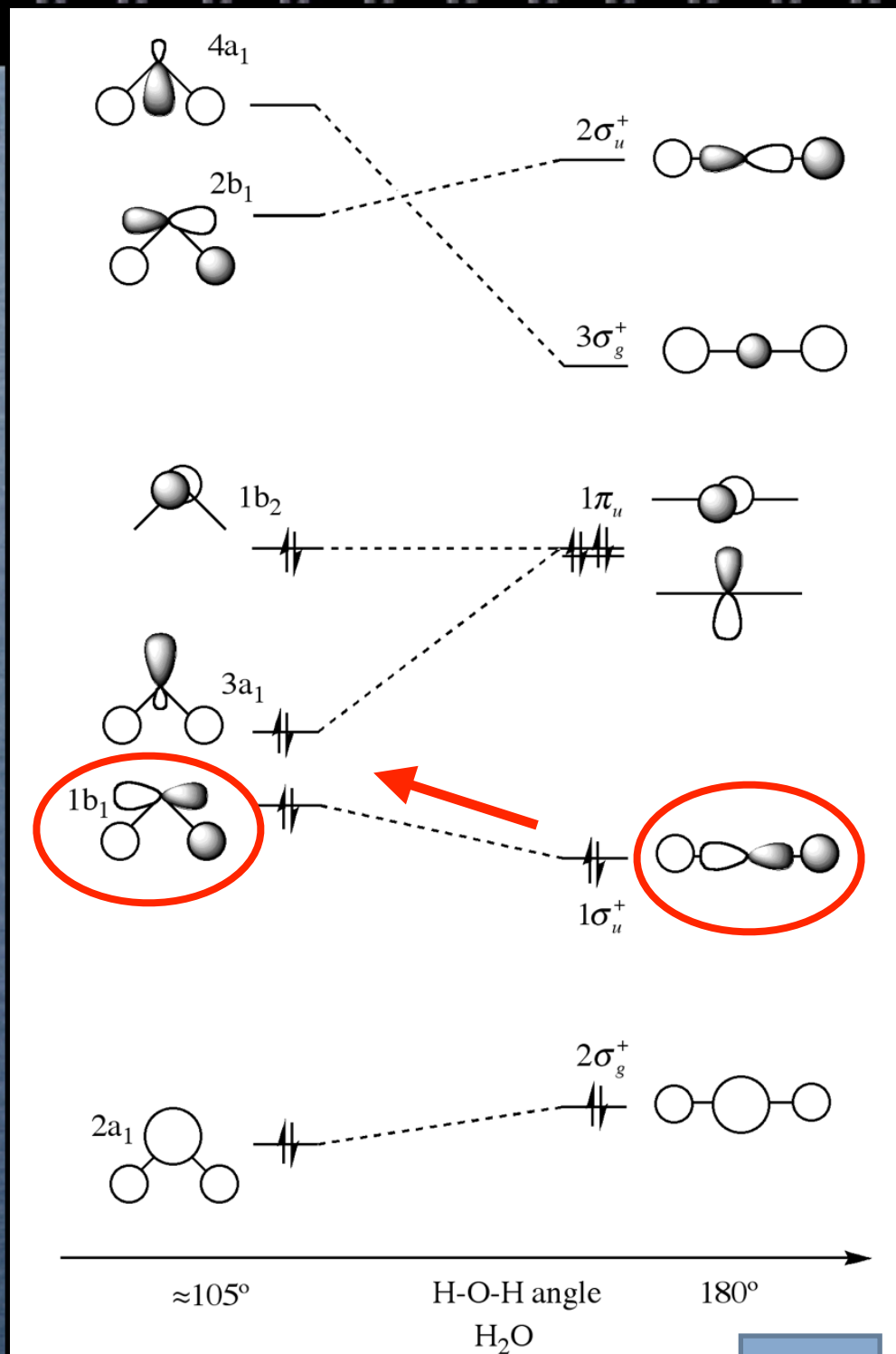


Fig 21

Energy of MOs

then examine how MOs change under geometric distortion

$1\pi_u$ ($1b_2$) no change

◆ non-bonding orbital

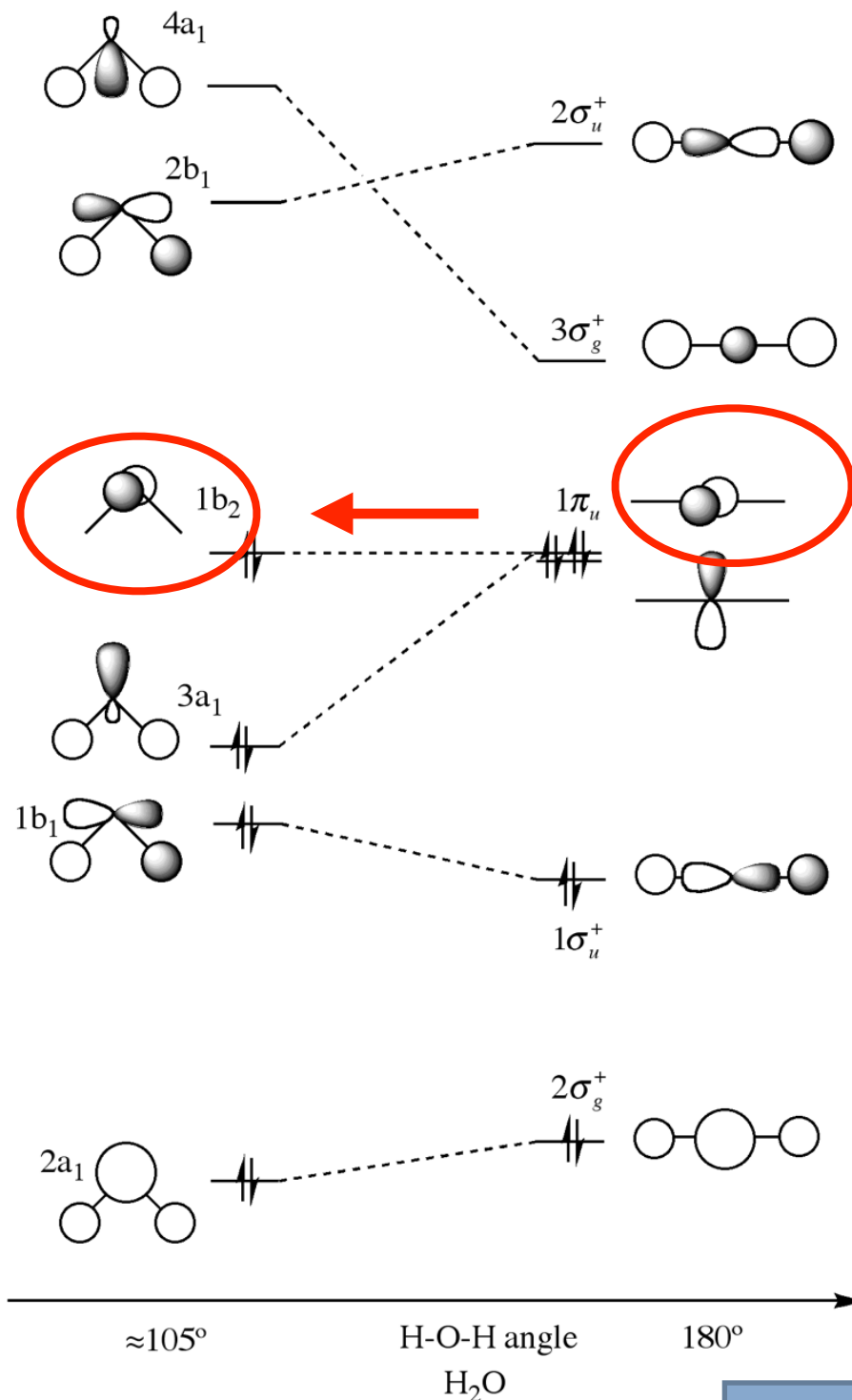


Fig 21

Energy of MOs

then examine how MOs change under geometric distortion

$2\sigma_u^+$ ($2b_1$) stabilised

socratic quiz!

WHZ9KBWC3

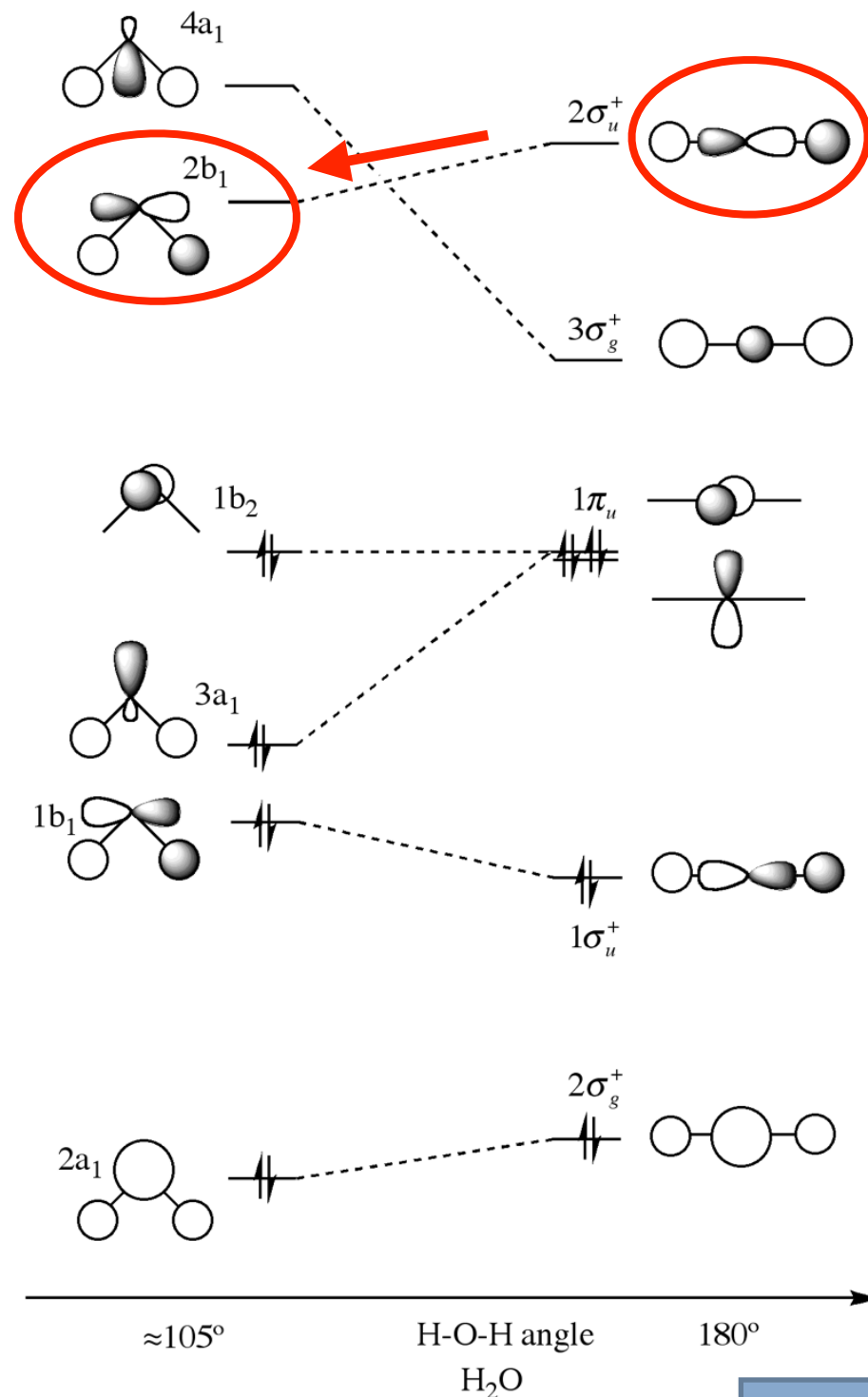


Fig 21

Energy of MOs

then examine how MOs change under geometric distortion

$2\sigma_u^+(2b_1)$ stabilised

- ◆ \downarrow O-H antibonding overlap \Rightarrow stabilize
- ◆ also \uparrow H...H through space antibonding
- ◆ \Rightarrow destabilize
- ◆ shorter distance overlap dominates
- ◆ \Rightarrow net result stabilisation

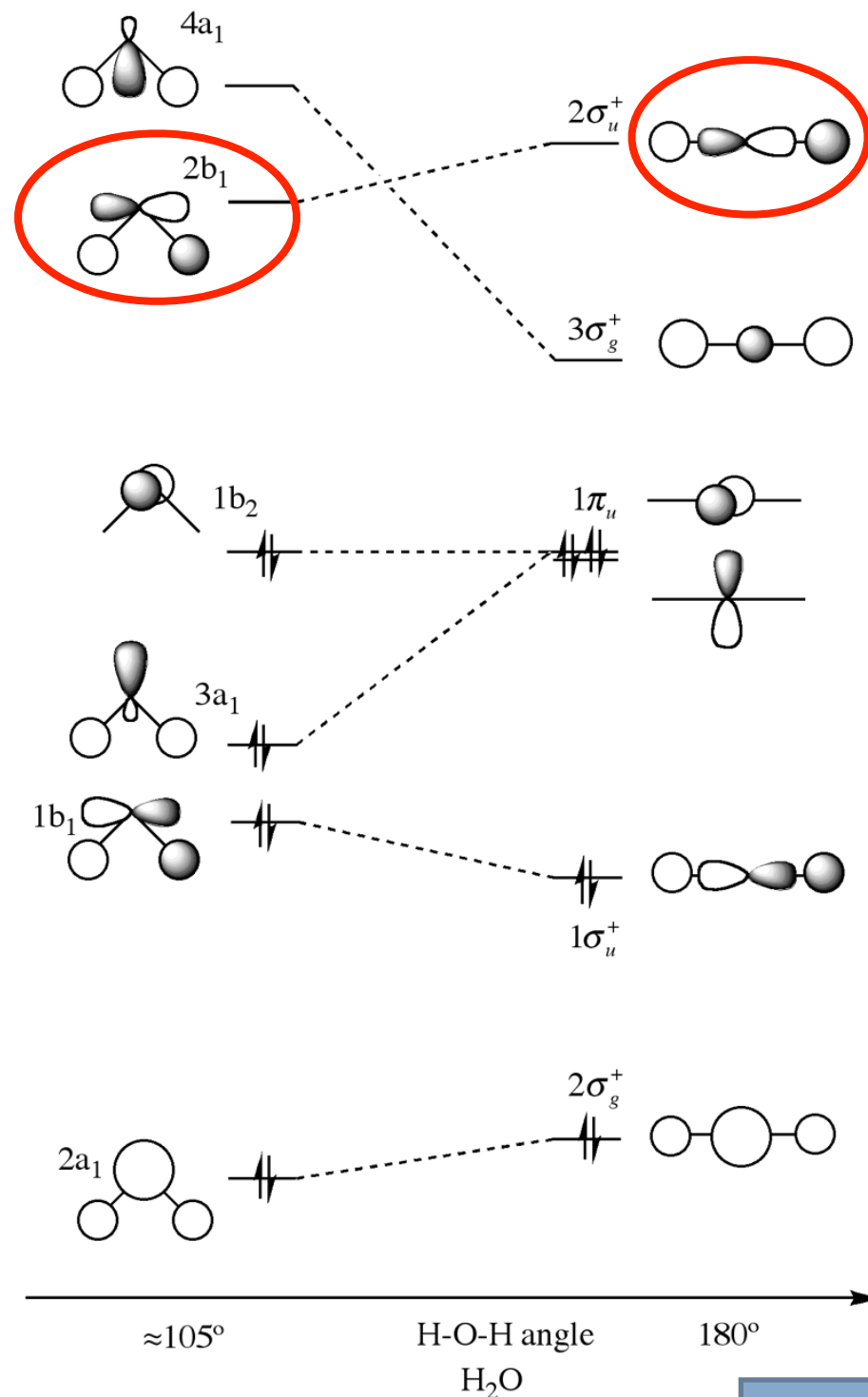


Fig 21

Energy of MOs

then examine how MOs change under geometric distortion

$1\pi_u / 3\sigma_g^+$ or $3a_1 / 4a_1$ special

- as planar molecule $1\pi_u$ and $3\sigma_g^+$ cannot mix (not same symmetry)
- when molecule distorts they become the same symmetry: mixing occurs
- $1\pi_u$ goes to $3a_1$
- $3\sigma_g^+$ goes to $4a_1$
- on mixing the $1\pi_u$ ($3a_1$) is stabilised

Important!

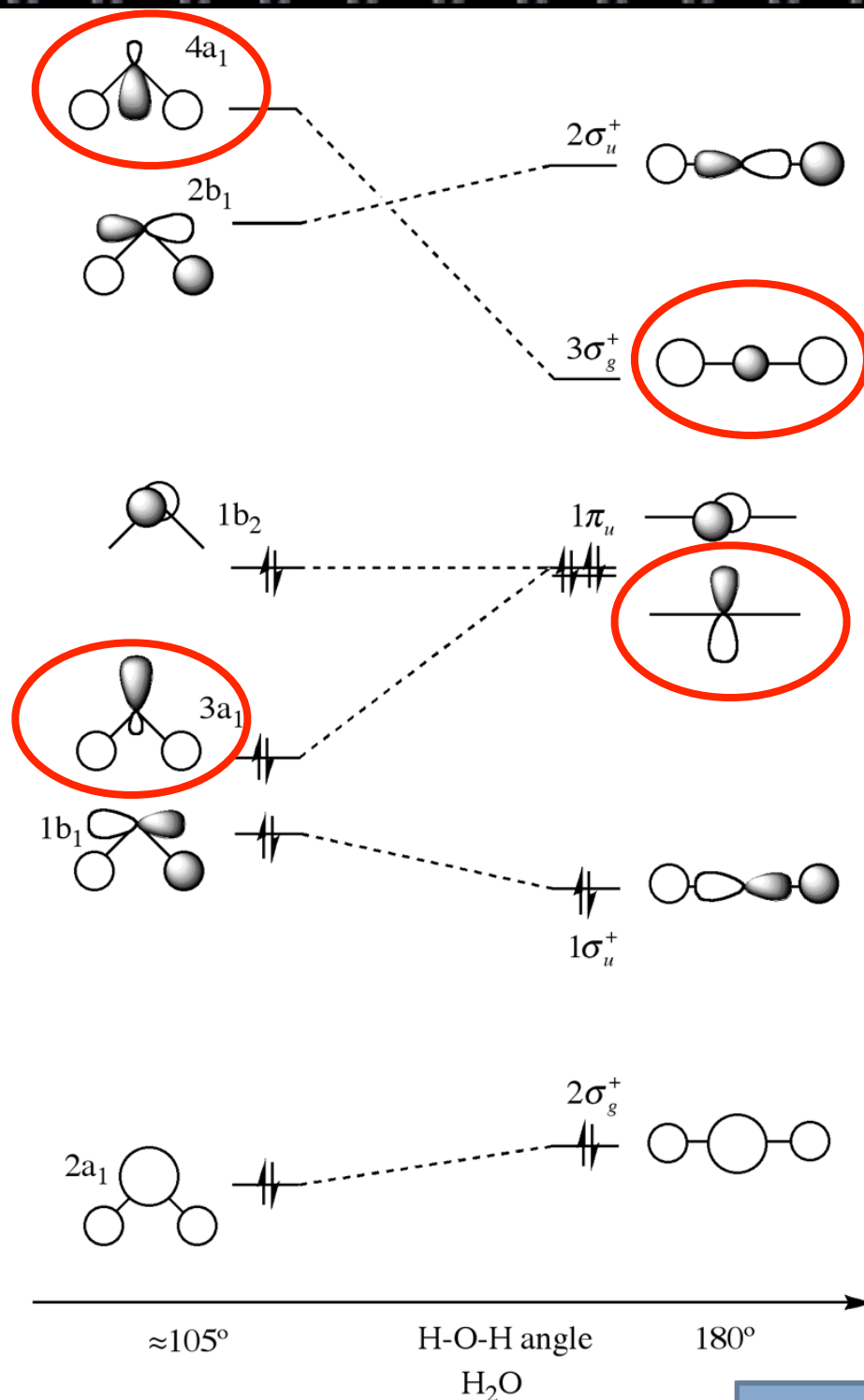


Fig 21

Change of Axes

When the symmetry point group changes the axial definition changes!

- ◆ z-axis reorientated
- ◆ orbital remains the same
- ◆ only labels change
- ◆ then follow with mixing

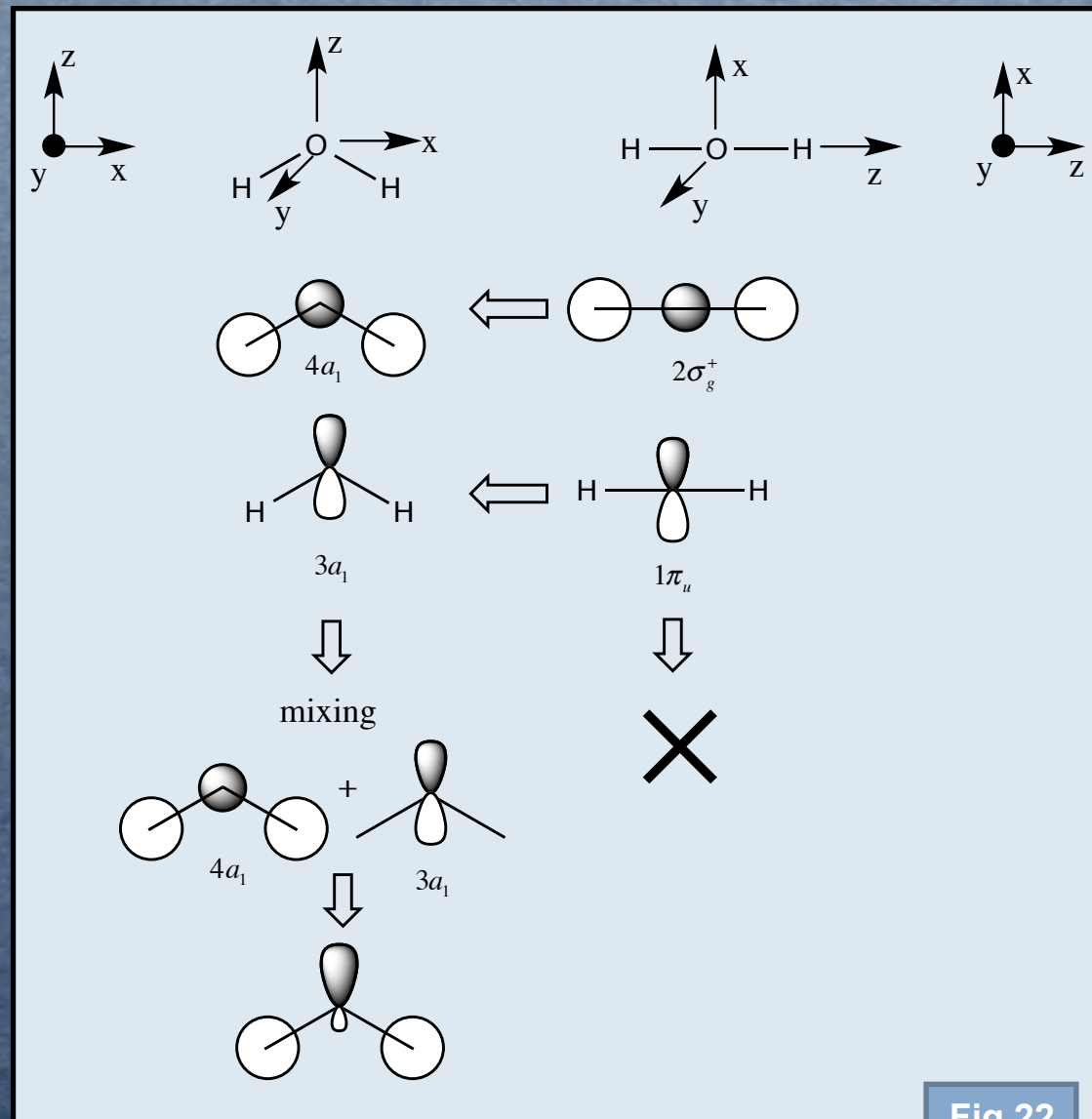


Fig 22

Walsh Diagram

Orbital changes

- ◆ AOs move with the atoms
- ◆ form or shape of AOs remains constant
- ◆ !! except for MOs which undergo mixing

Molecular stability

- ◆ examine how occupied MOs change under geometric distortion
- ◆ look for occupied MOs which show a large change in energy
- ◆ these orbitals drive the change in shape

self-study
questions

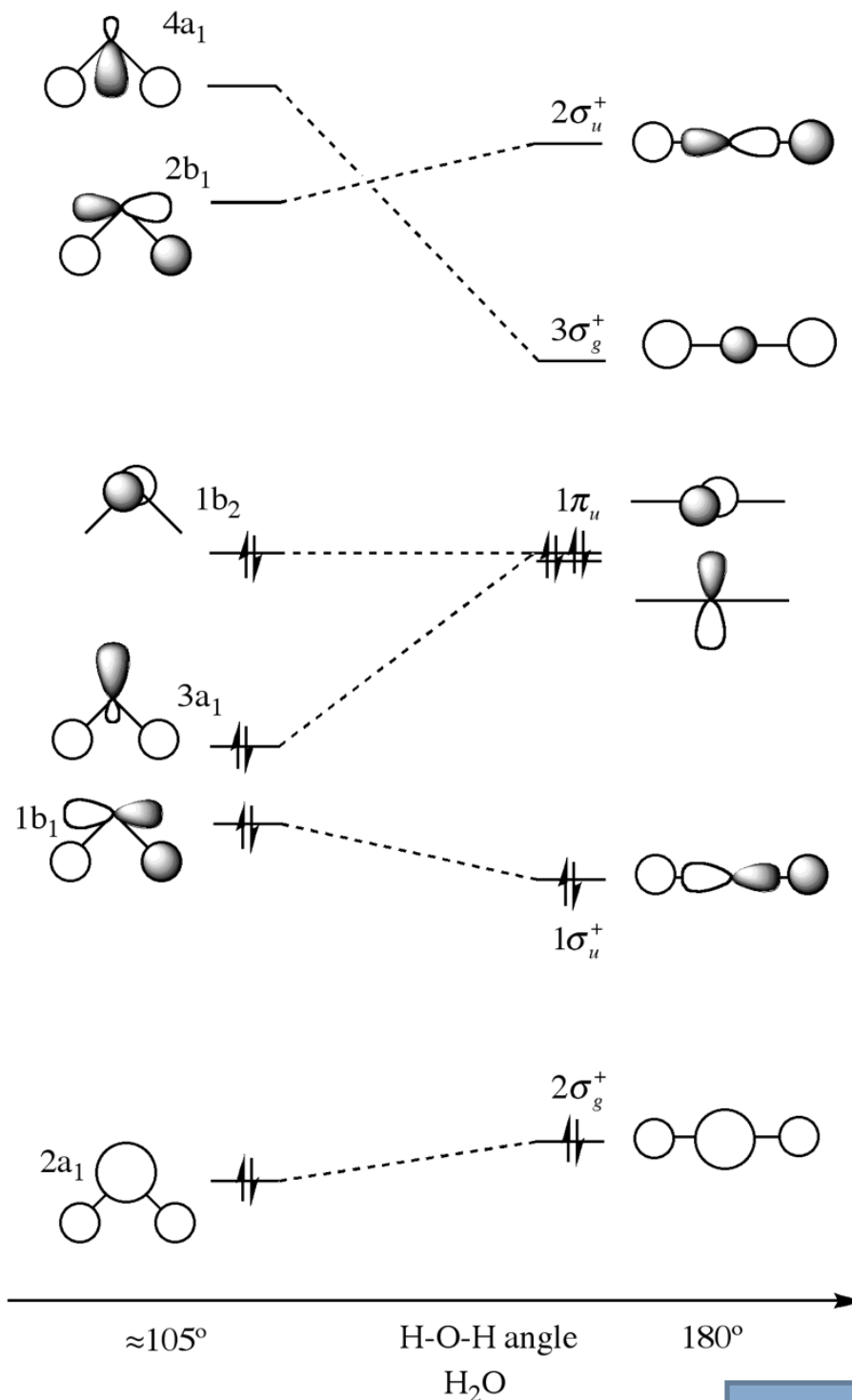
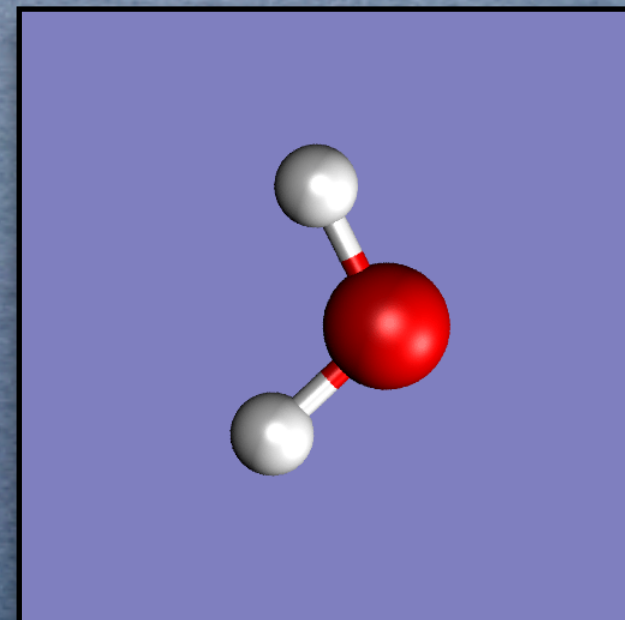


Fig 22

Symmetry Breaking

- **But how does the drop in symmetry start?**
- **nuclear vibrations provide infinitesimal distortion required for MO mixing**
- **vibronic coupling = coupling of electronic and nuclear motions**
- **breakdown of the Born-Oppenheimer approximation!**
 - ◆ collapse of a VERY fundamental approximation
 - ◆ more common than you think!
 - ◆ of which Jahn-Teller theorem is a special case



Symmetry Breaking

- symmetry & symmetry breaking underlies many theories in physics and chemistry

Noether's Theorem

Shows that a conservation law can be derived from any continuous symmetry.

- invariance with respect to translation gives the law of conservation of linear momentum
- invariance with respect to time translation gives the law of conservation of energy

magnetism

superconductivity

Serious Stuff!

general relativity

standard model of particle physics

existence of Higgs particle

Heisenberg Uncertainty Principle

field theory



Emmy Noether

source: <http://en.wikipedia.org/wiki/Image:Noether.jpg> accessed 17/08/07

MO checklist

Steps to construct a MO diagram

- ◆ determine the molecular shape and identify the point group
- ◆ define the axial system and all of the symmetry operations
- ◆ identify the chemical fragments, put them on the bottom of the diagram
- ◆ determine the energy levels and symmetry labels of the fragment orbitals (use H1s as a reference)
- ◆ 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!)
- ◆ determine the number of electrons in each fragment and hence the central MO region, add them to the diagram
- ◆ identify if any MO mixing occurs, determine the mixed orbitals and redraw the MO diagram with shifted energy levels and the mixed MOs
- ◆ annotate your diagram
- ◆ use the MO diagram to understand the structure, bonding and chemistry of the molecule

steps we have used today to form a MO diagram

VERY Important!

Key Points

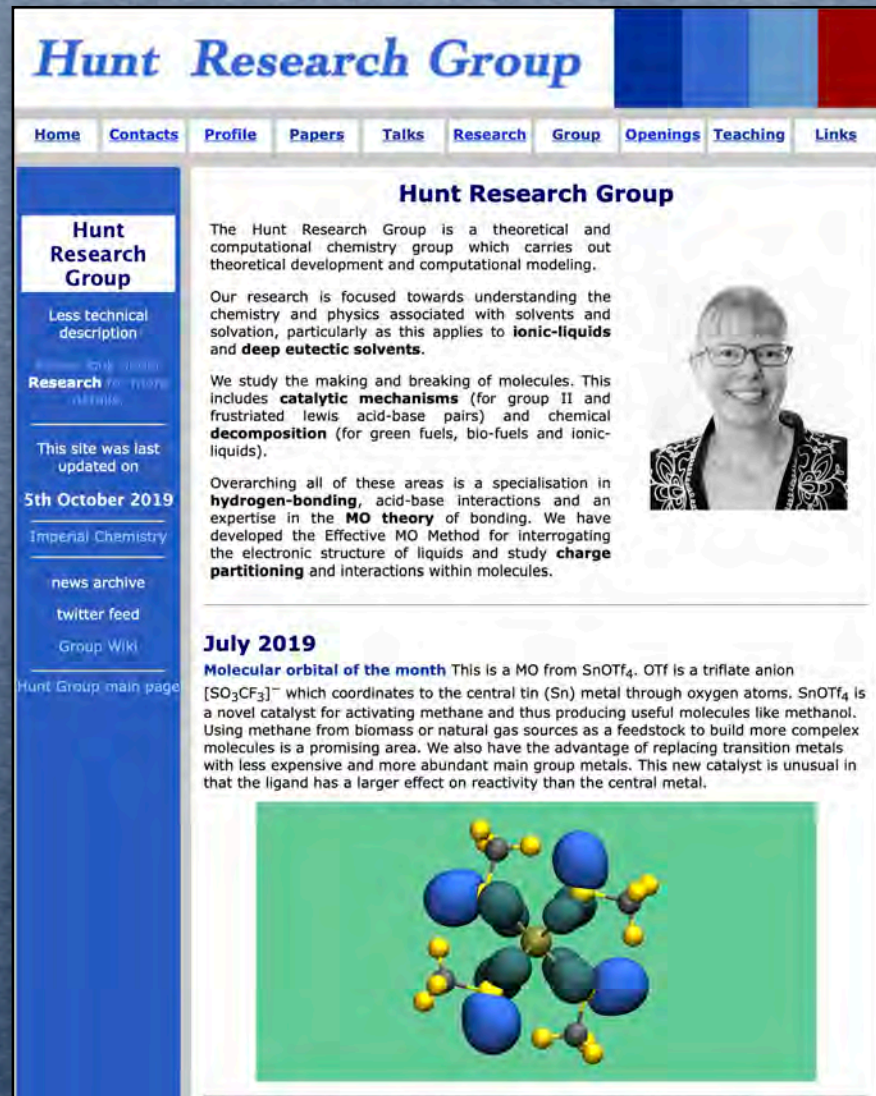
- be able to form MO diagrams for molecules with the general formula AH_2 and AH_3 (tutorial) where A= main group element or a metal
- be able to explain and illustrate MO mixing
- be able to critically evaluate VSEPR theory, localised 2c-2e bonding and the delocalised MO picture of bonding
- be able to describe how a PES is formed and be able to relate a spectrum to the MOs, and MO diagram of 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 the MOs
- be able to discuss symmetry breaking and vibronic coupling
- be able to describe the process of forming a MO diagram (the MO checklist)

Finally

<http://www.huntresearchgroup.org.uk/>

See my web-site

- ◆ notes AND slides
- ◆ link to panopto when it becomes available
- ◆ optional background support for beginners
- ◆ optional material to take you a little further
- ◆ links to interesting people and web-sites
- ◆ links to relevant research papers on MOs
- ◆ model answers!!



The screenshot shows the homepage of the Hunt Research Group website. The header features the group's name in a blue serif font. Below the header is a navigation menu with links for Home, Contacts, Profile, Papers, Talks, Research, Group, Openings, Teaching, and Links. The main content area is divided into two columns. The left column contains a sidebar with a 'Hunt Research Group' logo, a 'Less technical description' link, a 'Research for more details' link, a date stamp '5th October 2019', and links to 'Imperial Chemistry', 'news archive', 'twitter feed', and 'Group Wiki'. The right column features a 'Hunt Research Group' title, a paragraph describing the group's focus on theoretical and computational chemistry, a portrait of a woman with glasses, and a 'July 2019' section titled 'Molecular orbital of the month' which discusses a catalyst for methane activation. At the bottom of the right column is a 3D ball-and-stick model of a molecular orbital.

Hunt Research Group

The Hunt Research Group is a theoretical and computational chemistry group which carries out theoretical development and computational modeling.

Our research is focused towards understanding the chemistry and physics associated with solvents and solvation, particularly as this applies to **ionic-liquids** and **deep eutectic solvents**.

We study the making and breaking of molecules. This includes **catalytic mechanisms** (for group II and frustrated Lewis acid-base pairs) and chemical **decomposition** (for green fuels, bio-fuels and ionic-liquids).

Overarching all of these areas is a specialisation in **hydrogen-bonding**, acid-base interactions and an expertise in the **MO theory** of bonding. We have developed the Effective MO Method for interrogating the electronic structure of liquids and study **charge partitioning** and interactions within molecules.

July 2019

Molecular orbital of the month This is a MO from SnOTf_4 . OTf is a triflate anion $[\text{SO}_3\text{CF}_3]^-$ which coordinates to the central tin (Sn) metal through oxygen atoms. SnOTf_4 is a novel catalyst for activating methane and thus producing useful molecules like methanol. Using methane from biomass or natural gas sources as a feedstock to build more complex molecules is a promising area. We also have the advantage of replacing transition metals with less expensive and more abundant main group metals. This new catalyst is unusual in that the ligand has a larger effect on reactivity than the central metal.

