Molecular Orbitals in Inorganic Chemistry

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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

We will cover all of these

pure metals
solids
semi-conductors

not covered

Lecture 2 Outline

L2 build a MO diagram to show you the process

- quick revision
- stage 1: basic MO diagram for H_2O
- 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

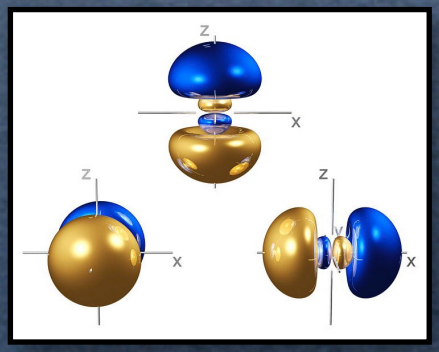
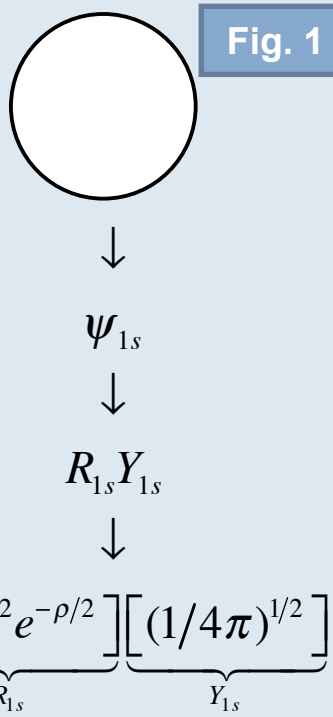


Fig. 1



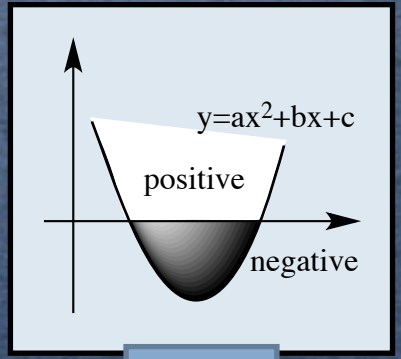


Fig. 2

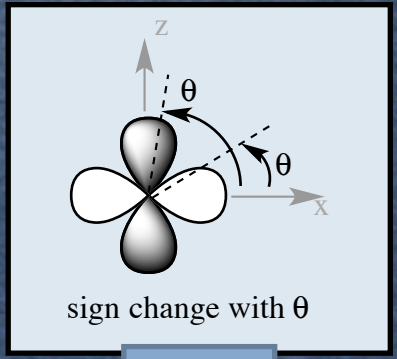


Fig. 3

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

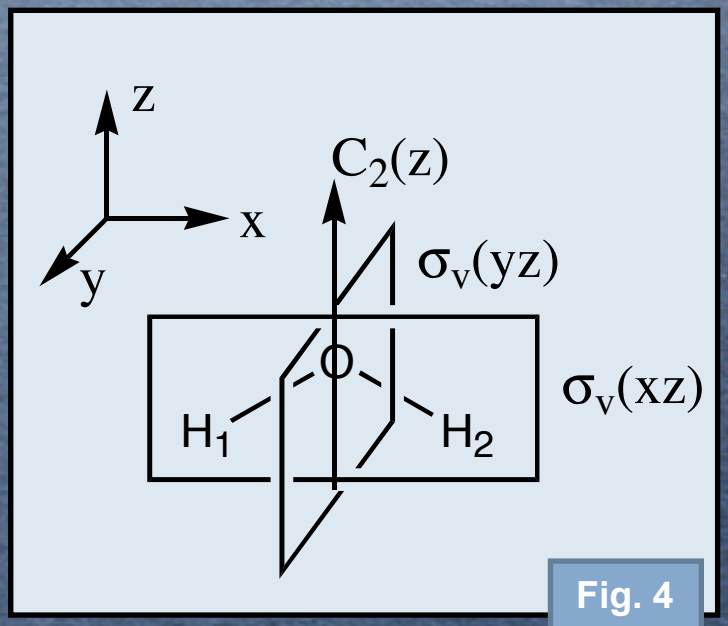


Fig. 4

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!

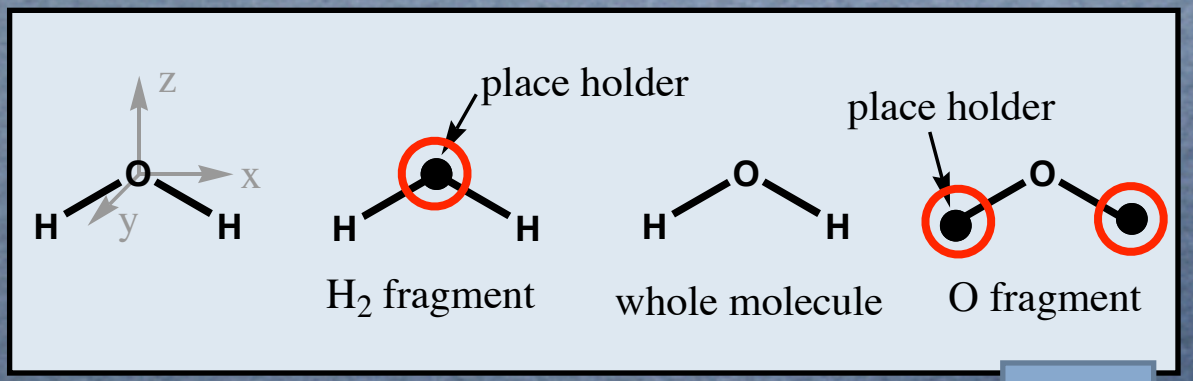
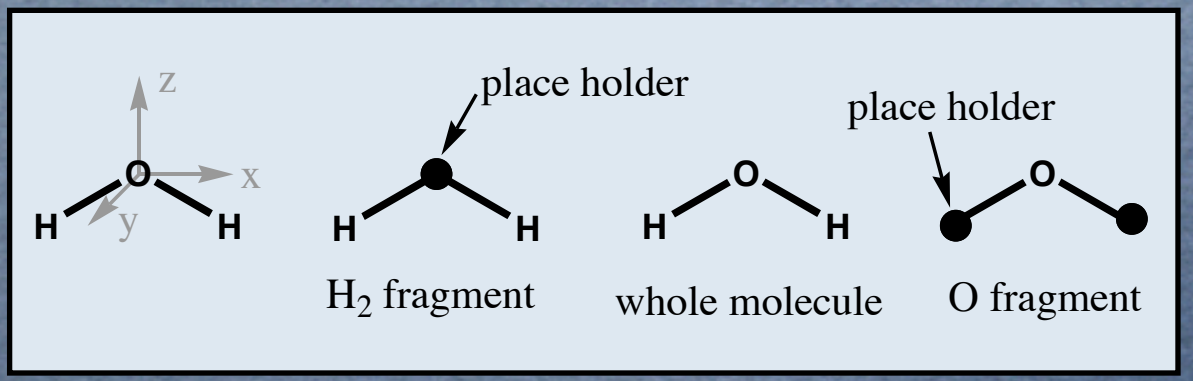


Fig. 5

Fragments

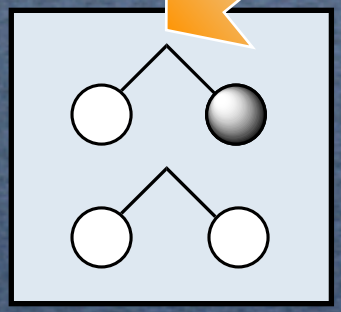
- **map onto each other under the symmetry operations**
  - H atoms map onto each other
  - O atom maps onto its self
  - H_2 and O atom are the fragments

use place holders!

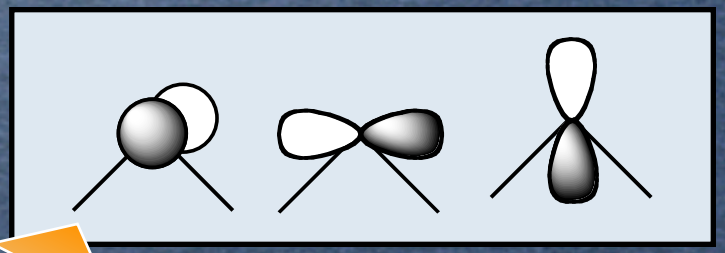


reproduce the whole of the molecular structure in the MO

- **fragment orbitals**
  - H_2 orbitals
  - O atom orbitals



H_2 orbitals



O (s and p) orbitals

Fig. 6

Set Up MO Diagram

- **vertical axis: Energy**
  - ✦ add H 1s reference level

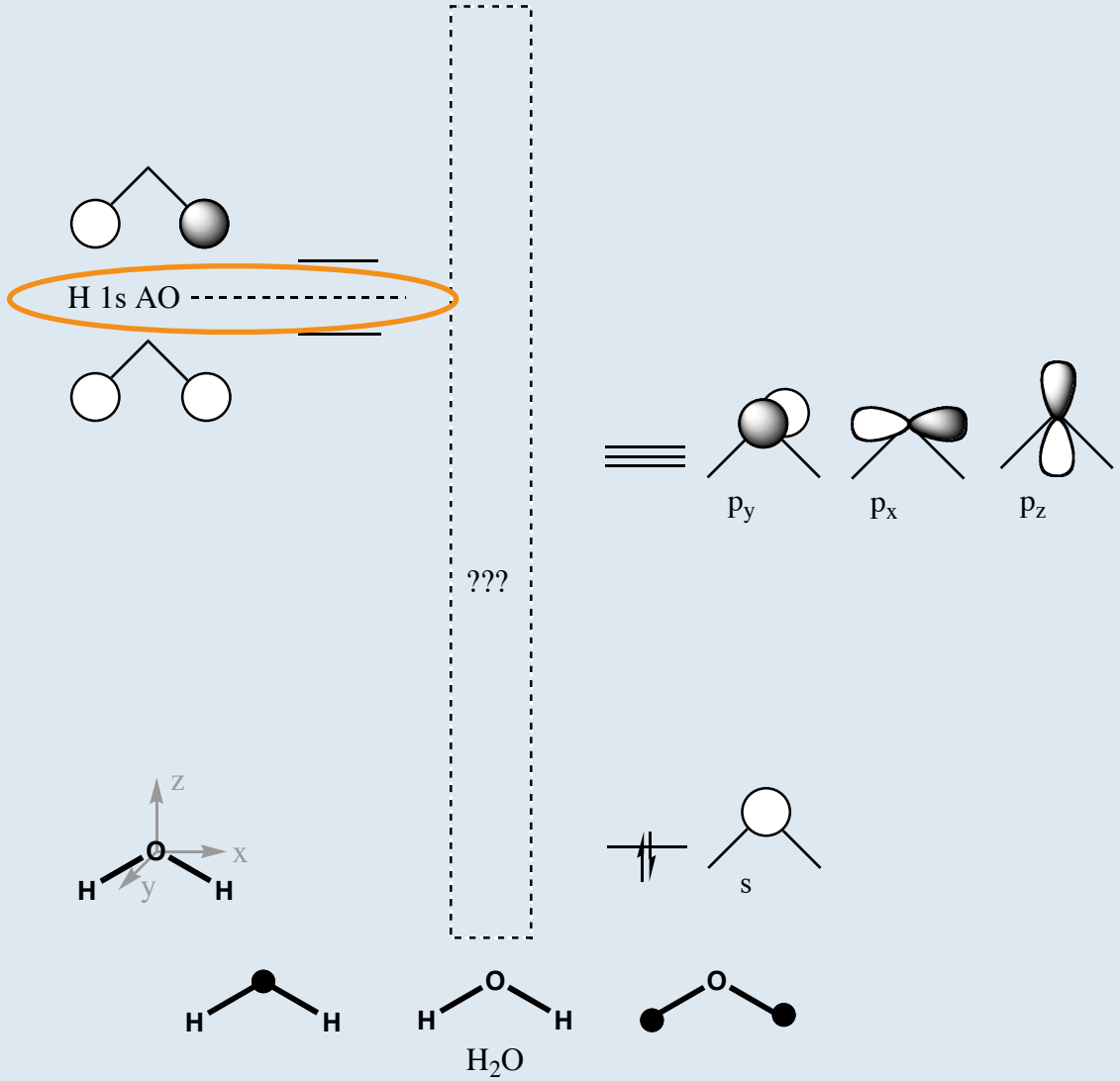


Fig. 6

Set Up MO Diagram

- vertical axis: Energy
- position AOs
  - ✦ O more electronegative => so valence orbitals lie below H 1s reference orbital

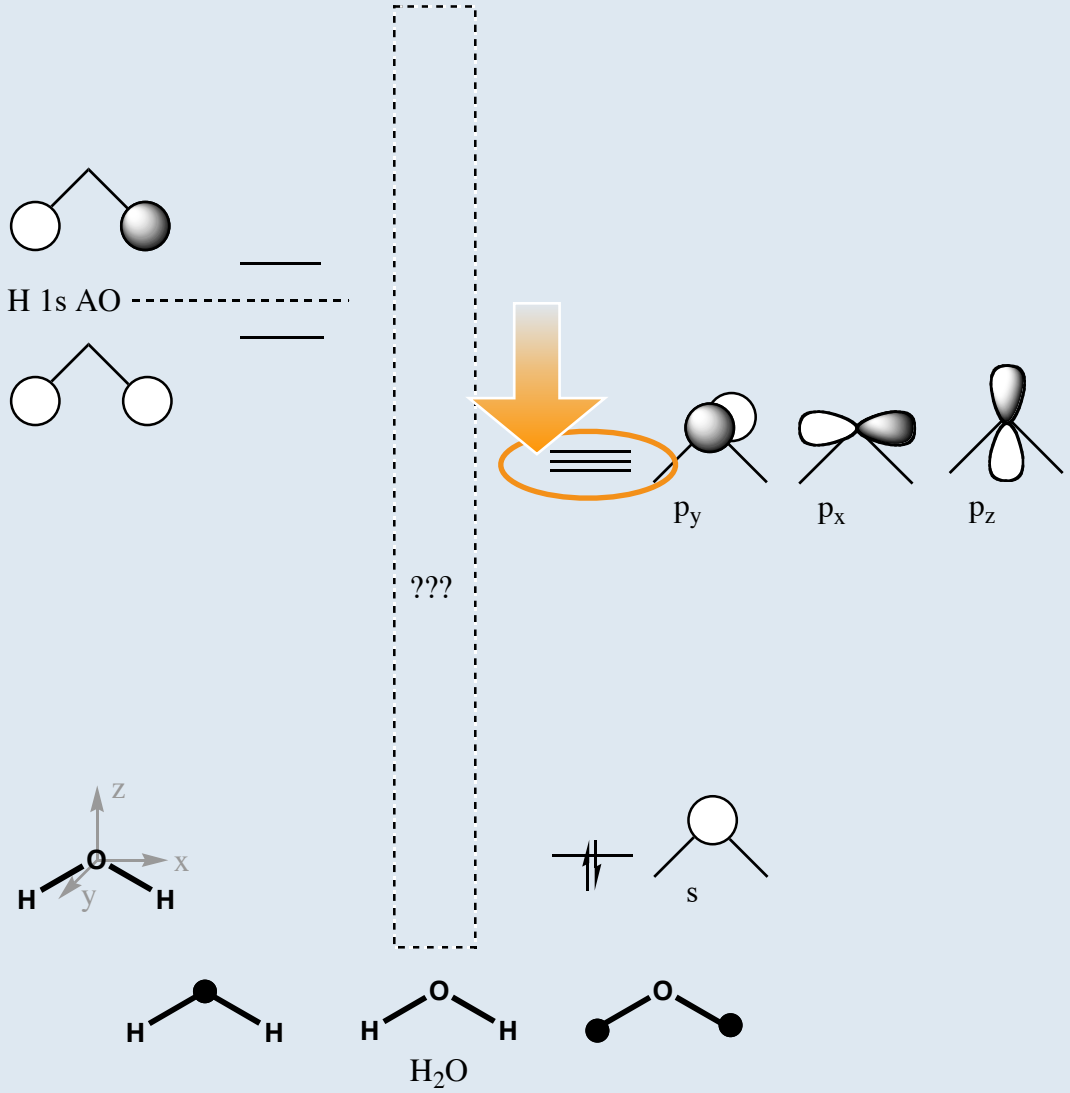


Fig. 6

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 H_2 =>stabilisation and destabilisation are less ie splitting energy is less

more on this next lecture!

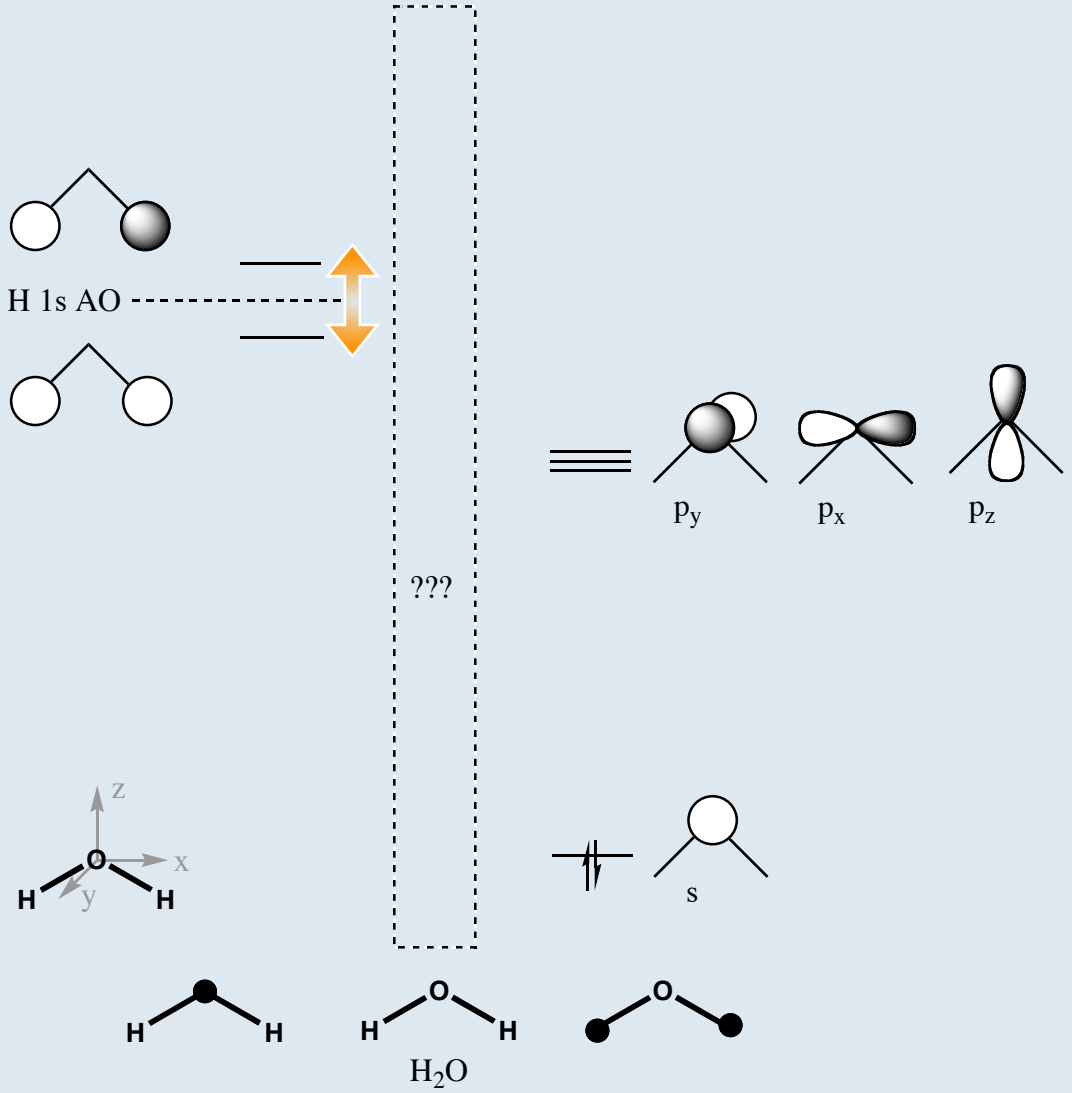
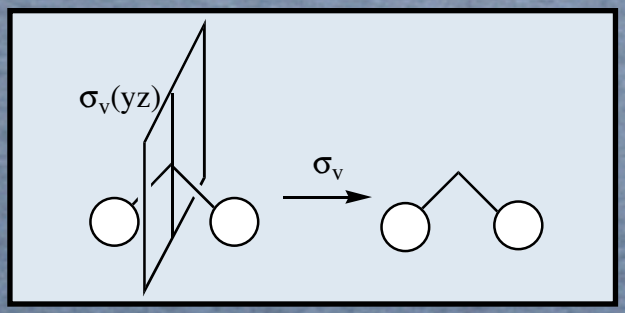


Fig. 6

Fragment Orbital Symmetry

- **How does each orbital transform under the symmetry operations of the group?**
  - ✦ orbital is unchanged => character = 1
  - ✦ a sign change => character = -1
  - ✦ check against the character table



Lecture 1

No change under σ_v ⇒ $\chi = 1$

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
Γ { }	1	1	1	1

⇒ a_1

Fig. 7

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

Short-Cut!

Important!

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	$\sigma_v(xz)$	$\sigma_v'(yz)$		
Γ { }	1	-1	-1	1	T_y	b_2
Γ { }	1	-1	1	-1	T_x	b_1
Γ { }	1	1	1	1	T_z	a_1

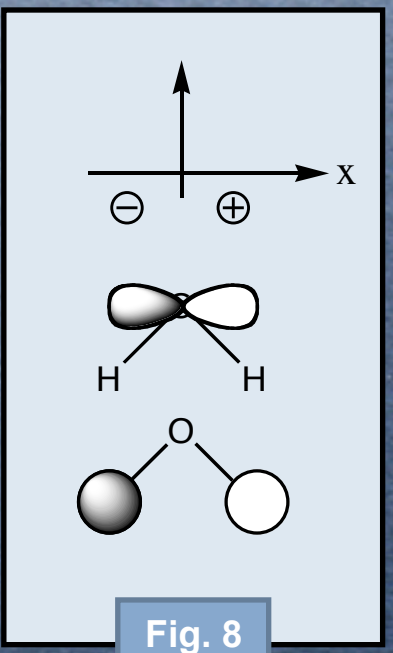


Fig. 8

H_2

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
Γ { }	1	1	1	1		a_1
Γ { }	1	-1	1	-1		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

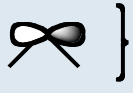
C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$			
Γ { }	1	-1	-1	1	p_y	⇨	b_2
Γ {  }	1	-1	1	-1	p_x	⇨	b_1
Γ { }	1	1	1	1	p_z	⇨	a_1

Fig. 7

Add symmetry labels to MO diagram

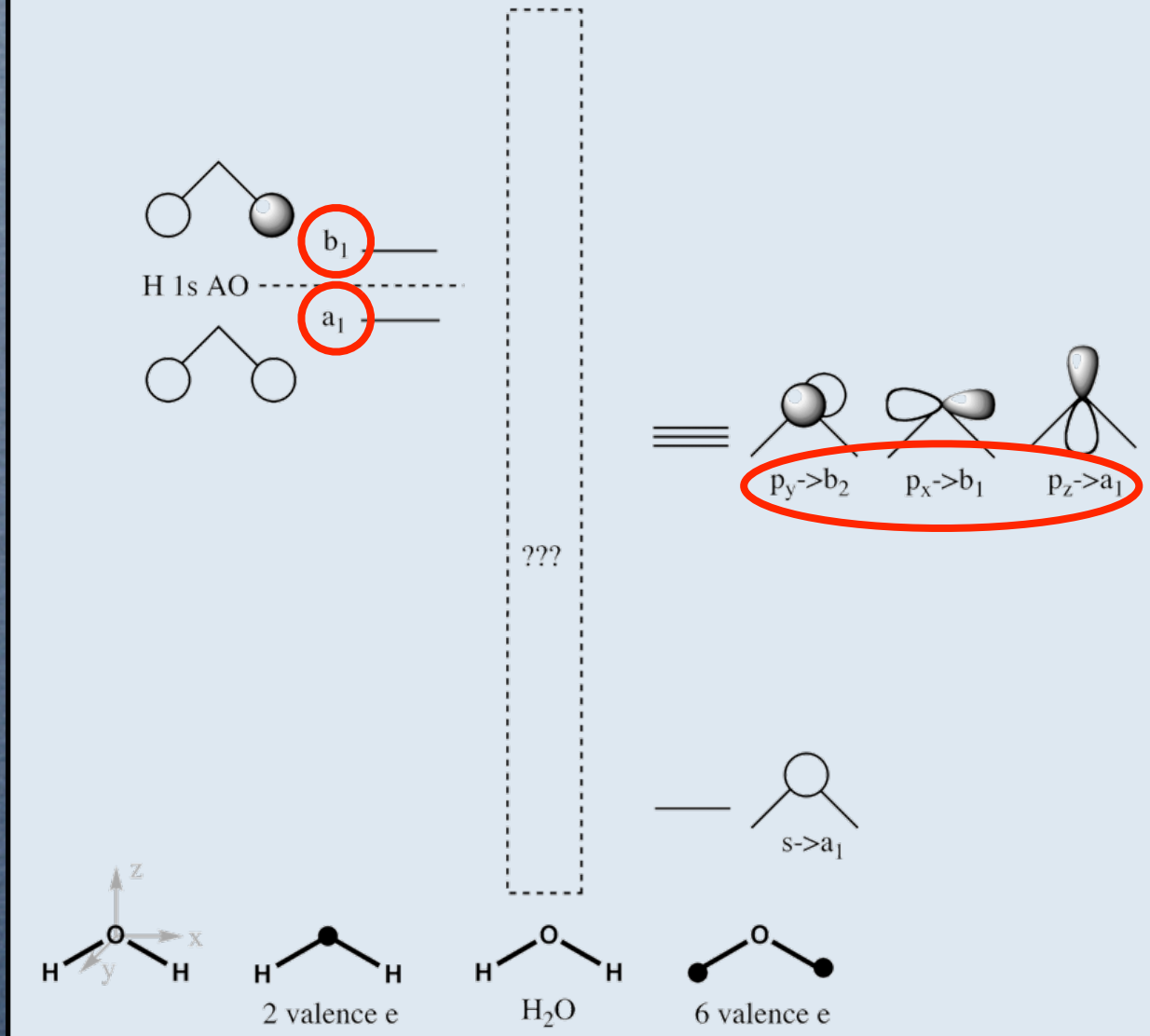


Fig. 9

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

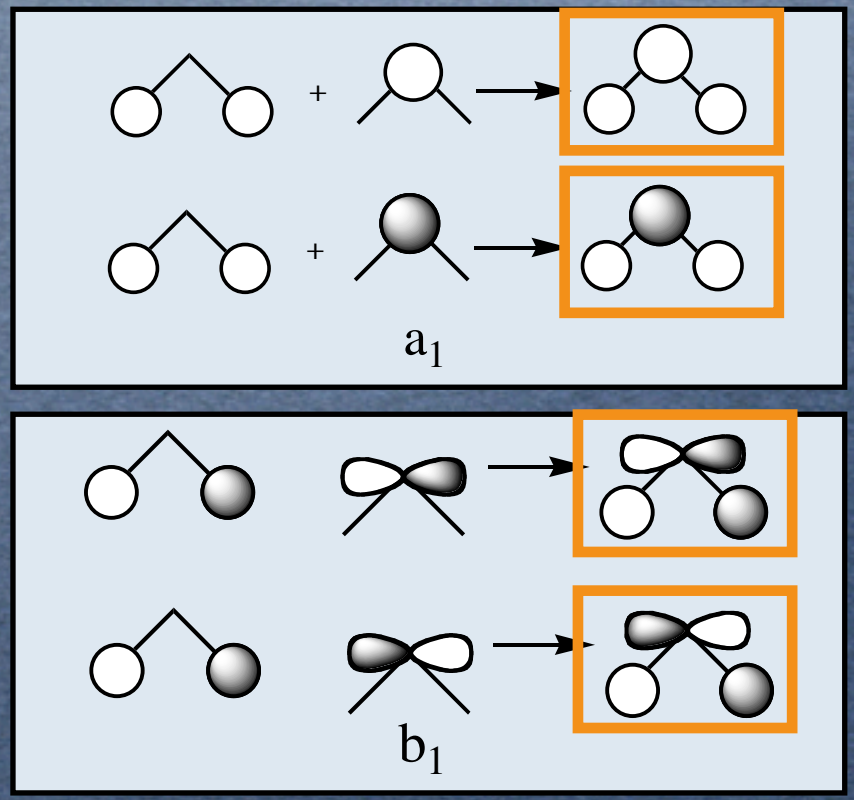


Fig 10

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**

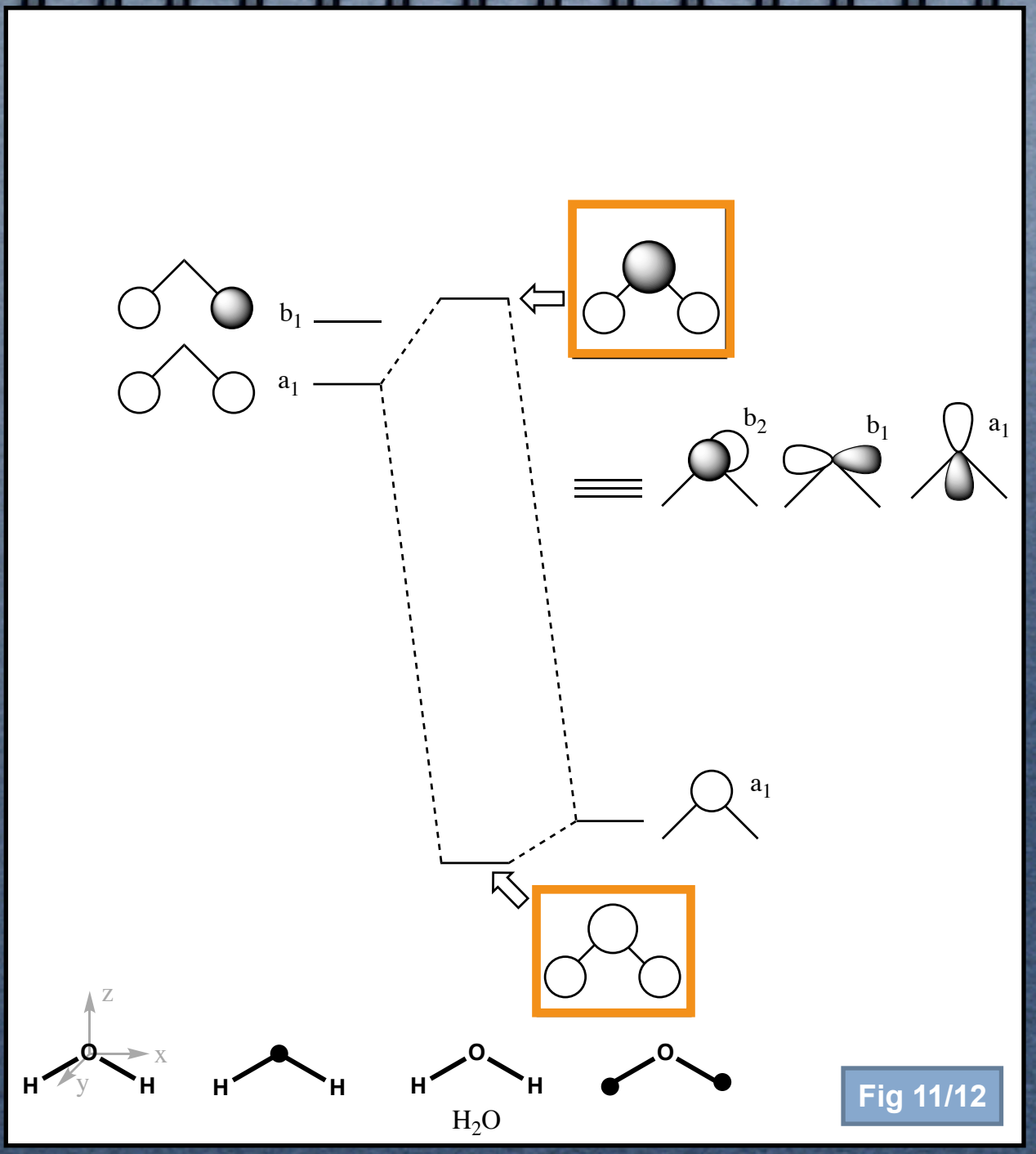


Fig 11/12

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**

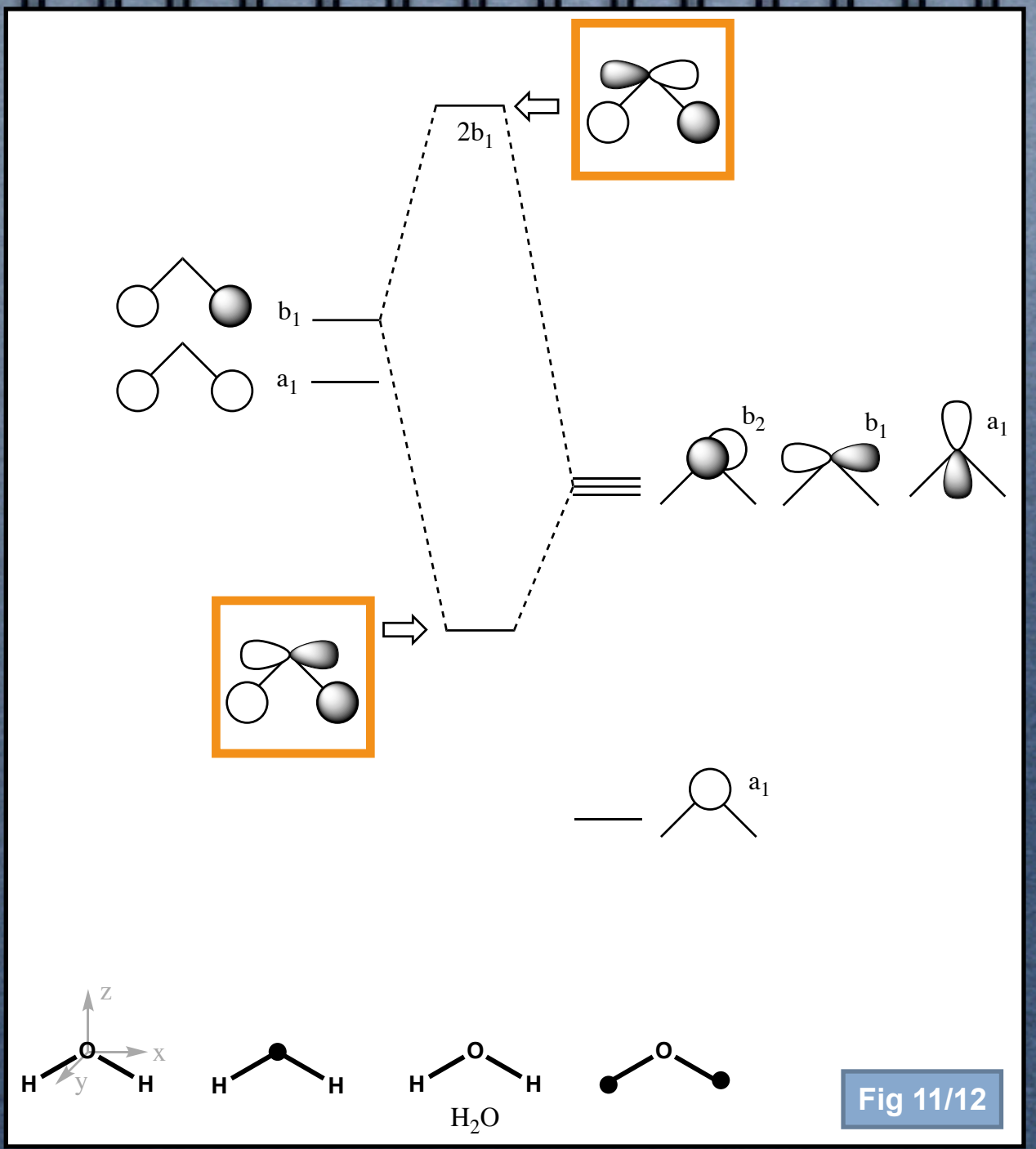


Fig 11/12

Stage One MO Diagram

- **Label MOs**
  - ✦ number within symmetry label
  - ✦ count the core orbitals only if molecule is small

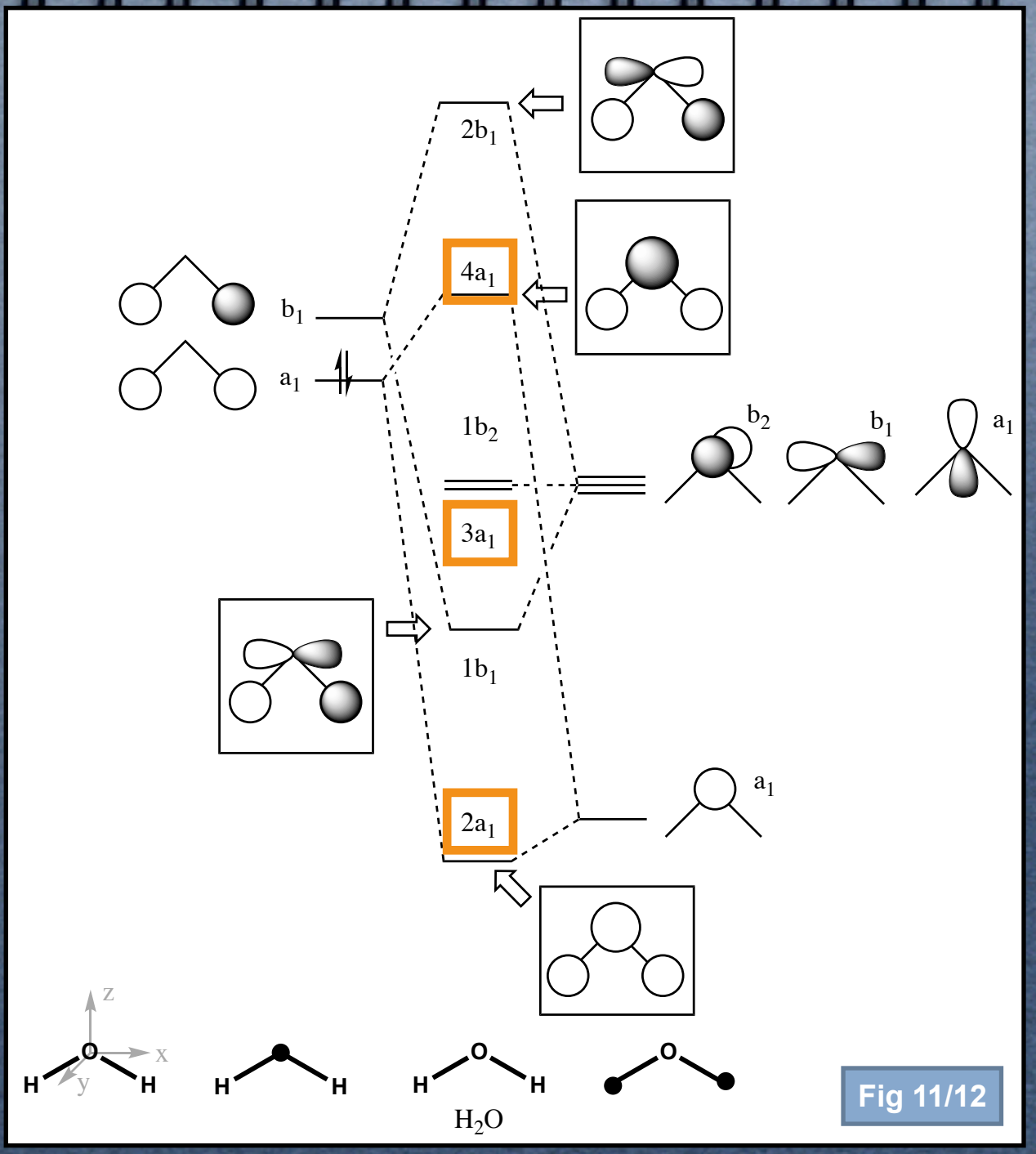


Fig 11/12

Stage One MO Diagram

Annotate your diagrams!

Important!

do not repeat information

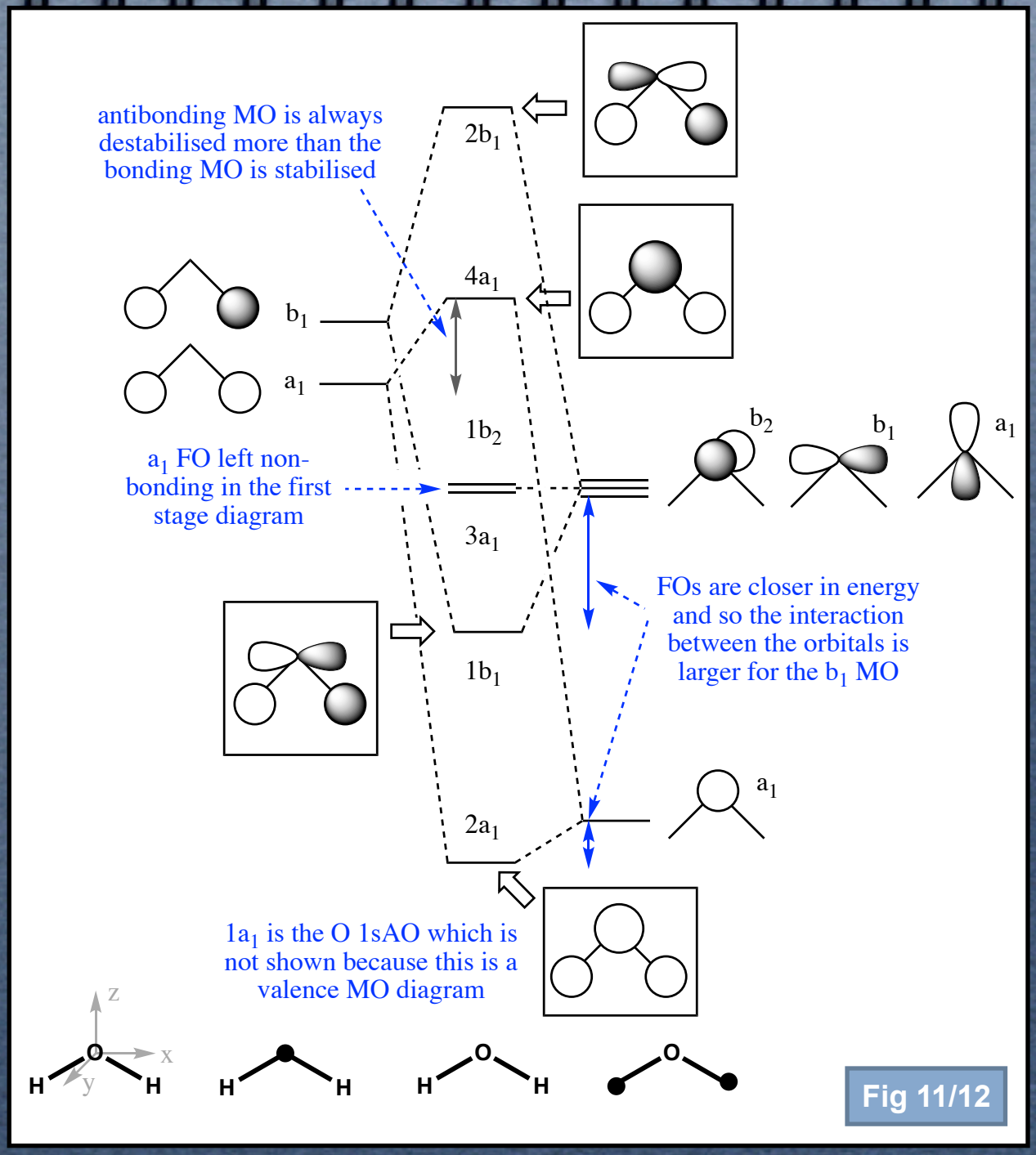


Fig 11/12

Stage One MO Diagram

- **add the electrons!**
  - ✦ **fill sequentially**

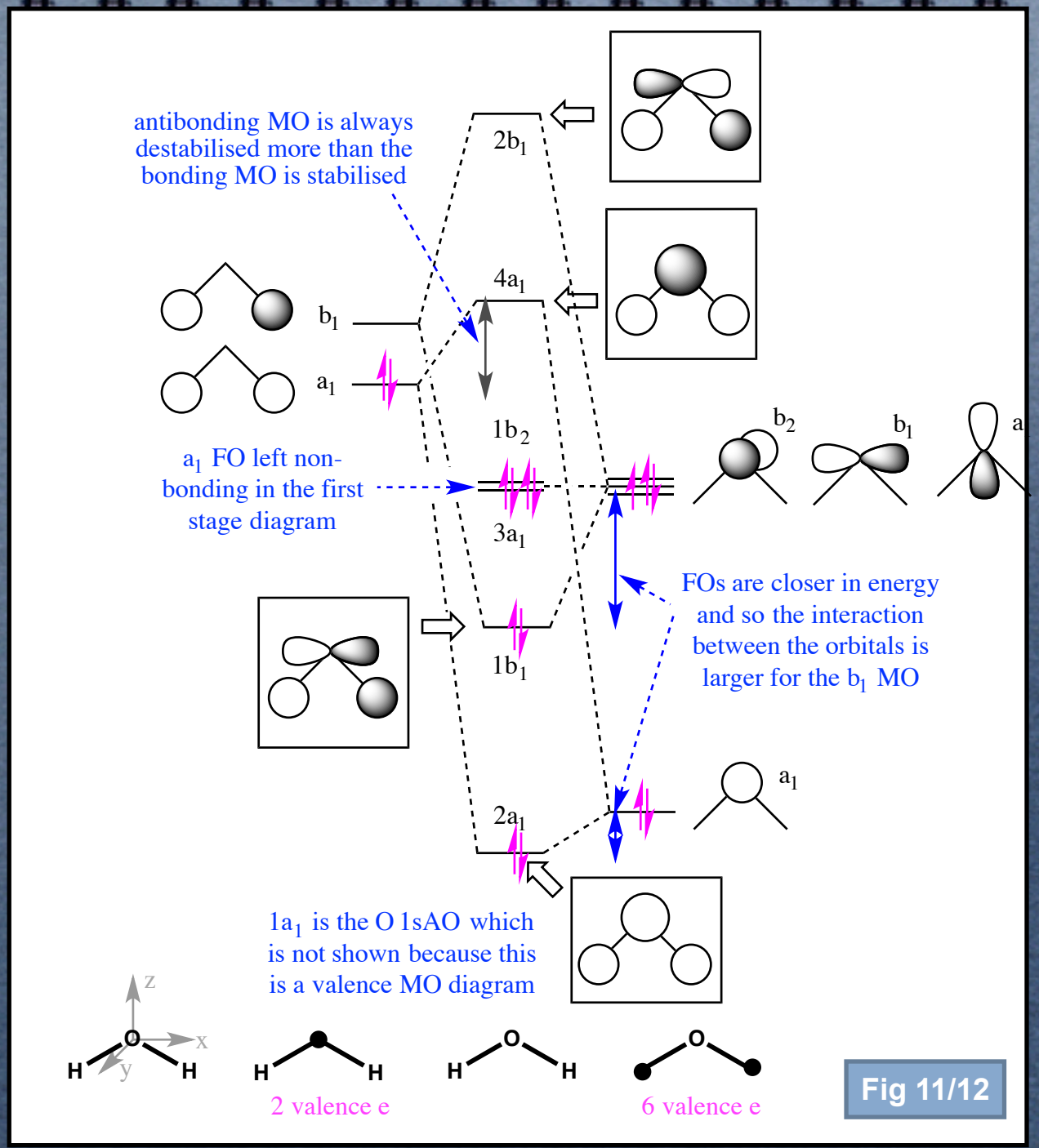


Fig 11/12

Stage One MO Diagram

- **add the electrons!**
  - ✦ fill sequentially

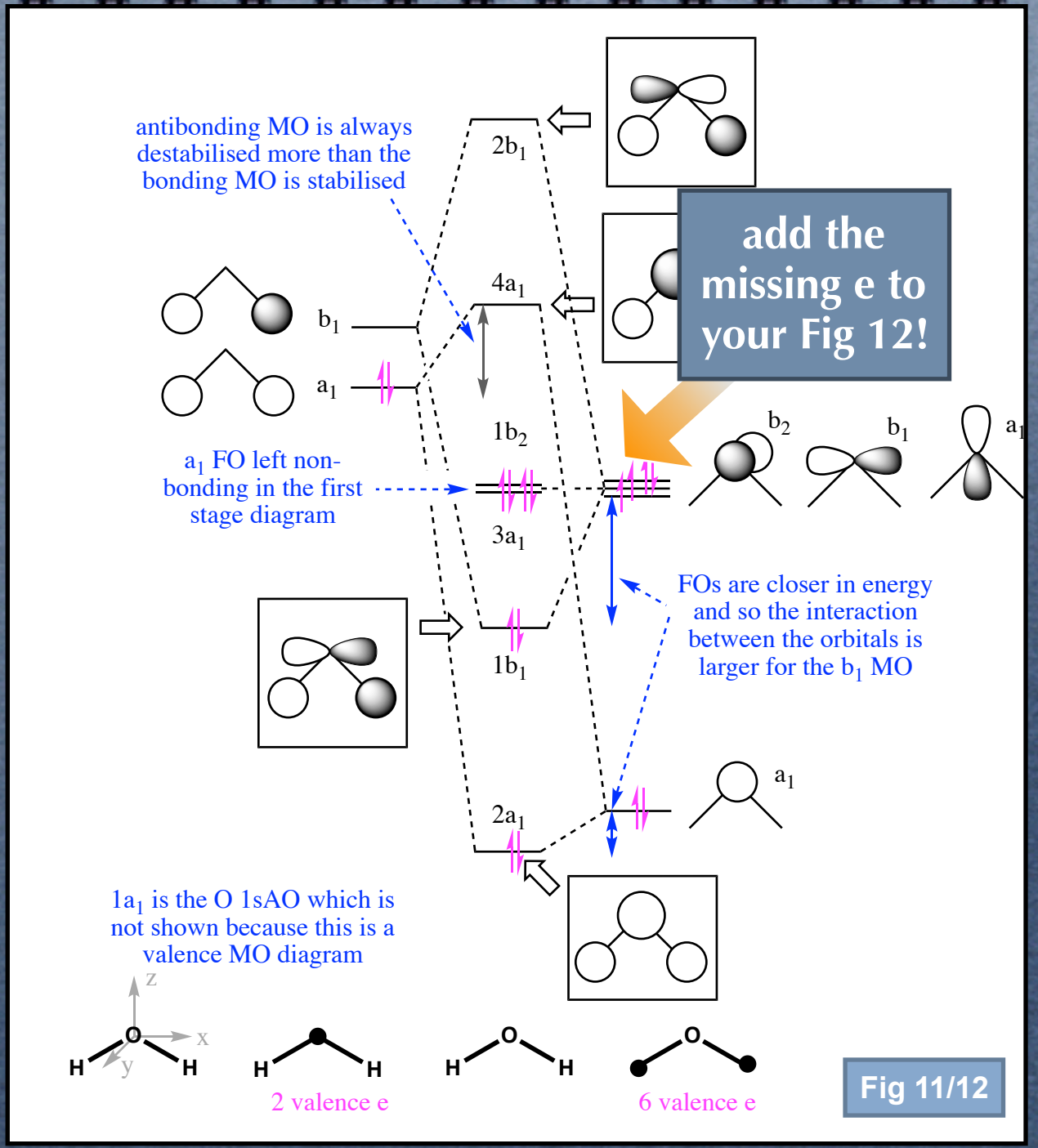


Fig 11/12

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

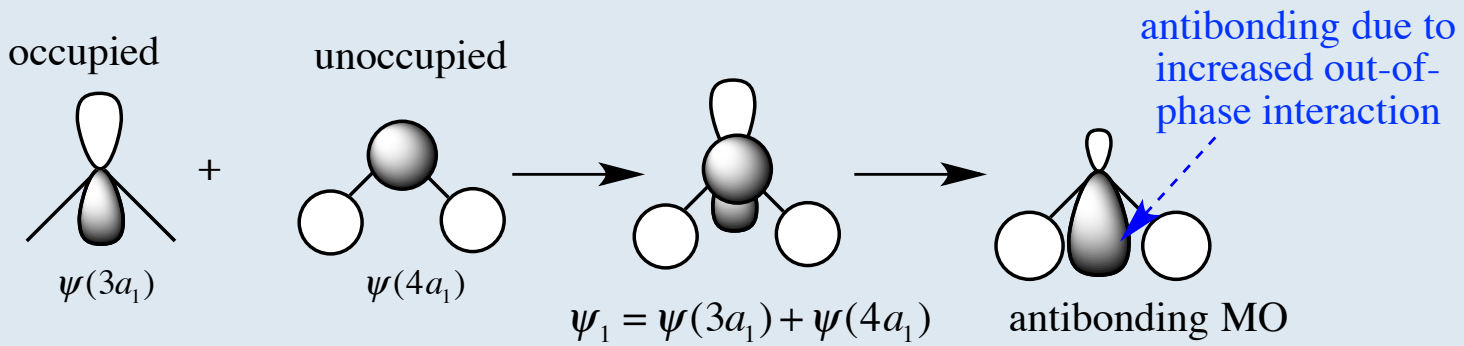


Fig 13

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

Fig 14

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

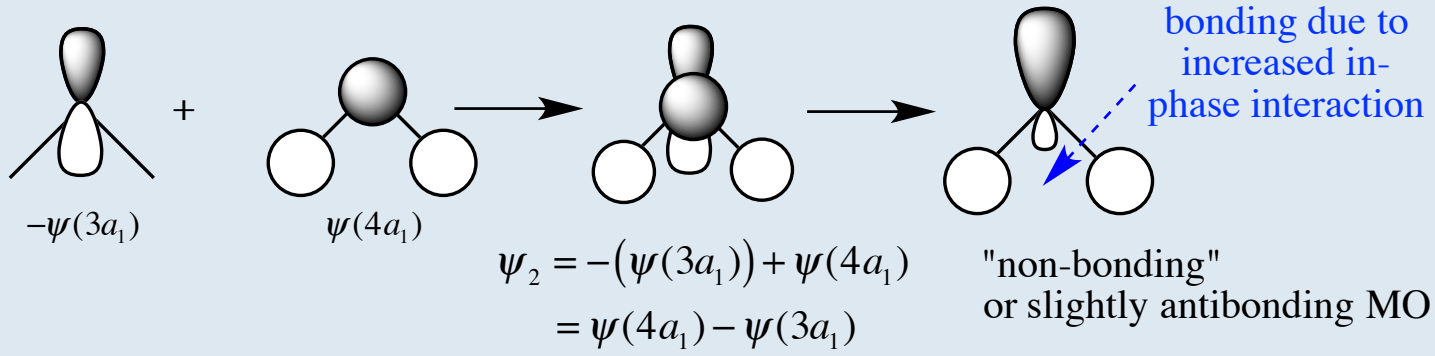
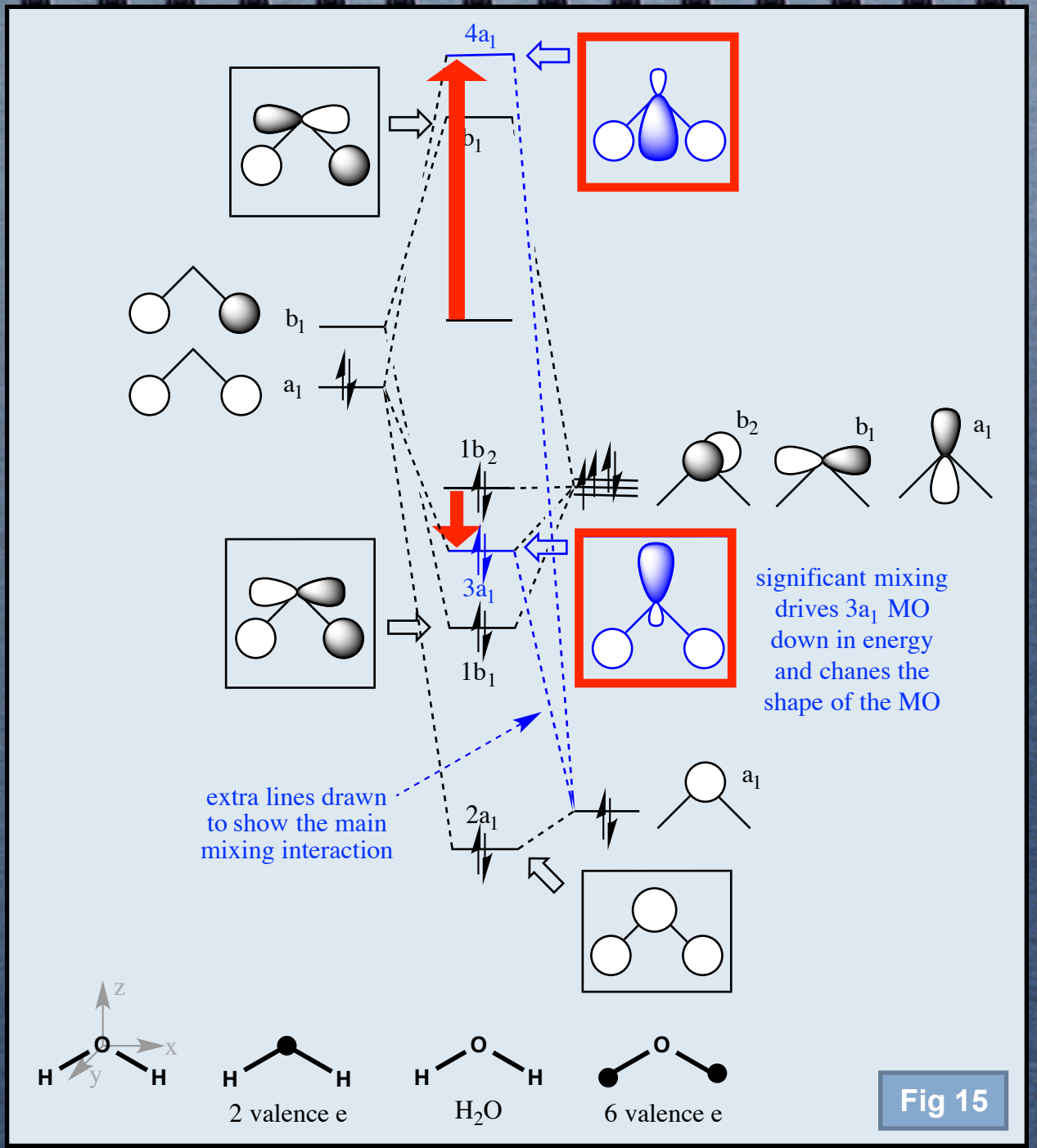


Fig 14

Mixing

- **strong mixing:**
  - ✦ $4a_1$ MO unoccupied
  - ✦ $3a_1$ MO non-bonding
  - ✦ in HOMO/LUMO region
  - ✦ close in energy
  - ✦ occupied MO is stabilised



Final MO Diagram of H_2O

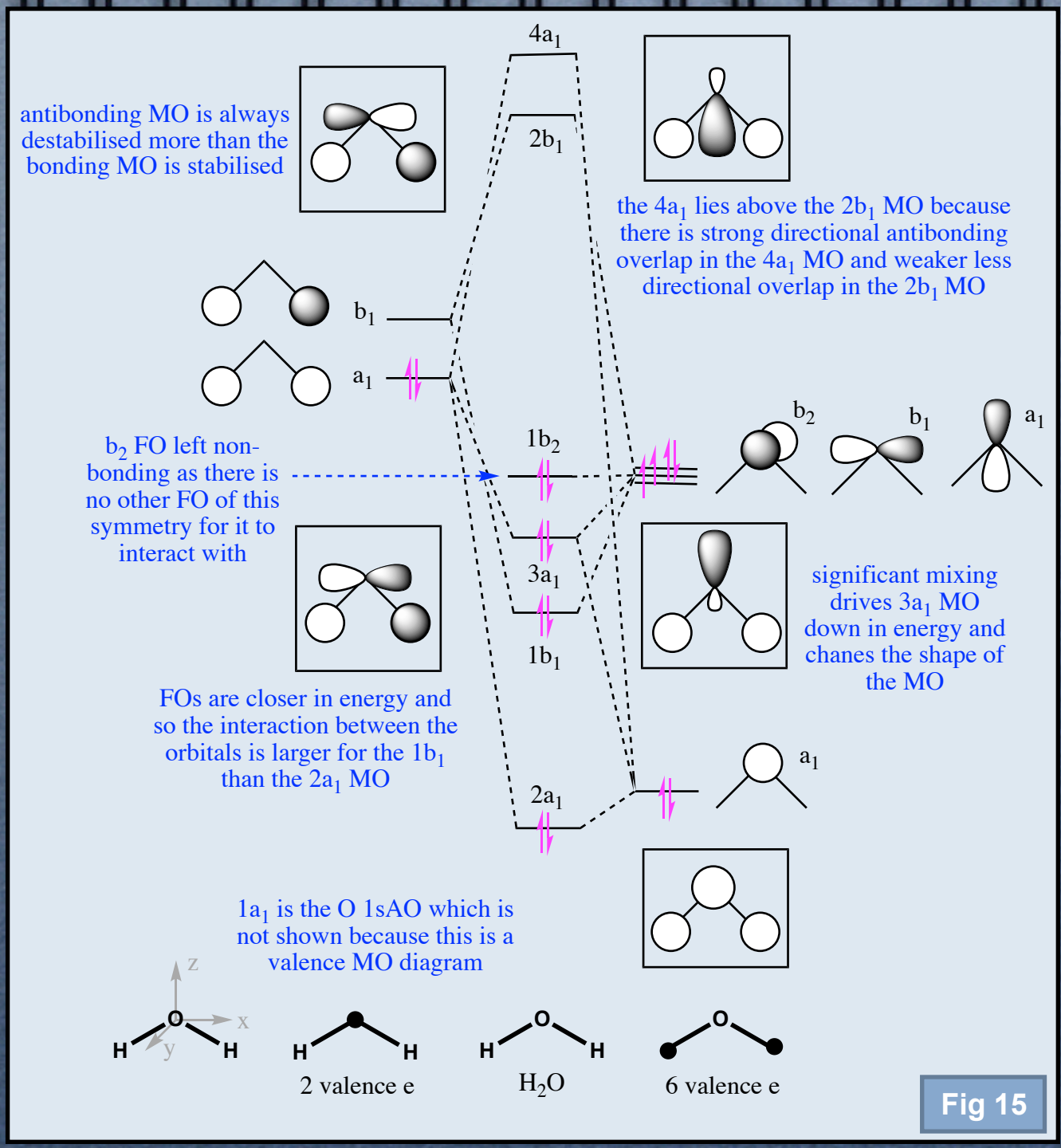
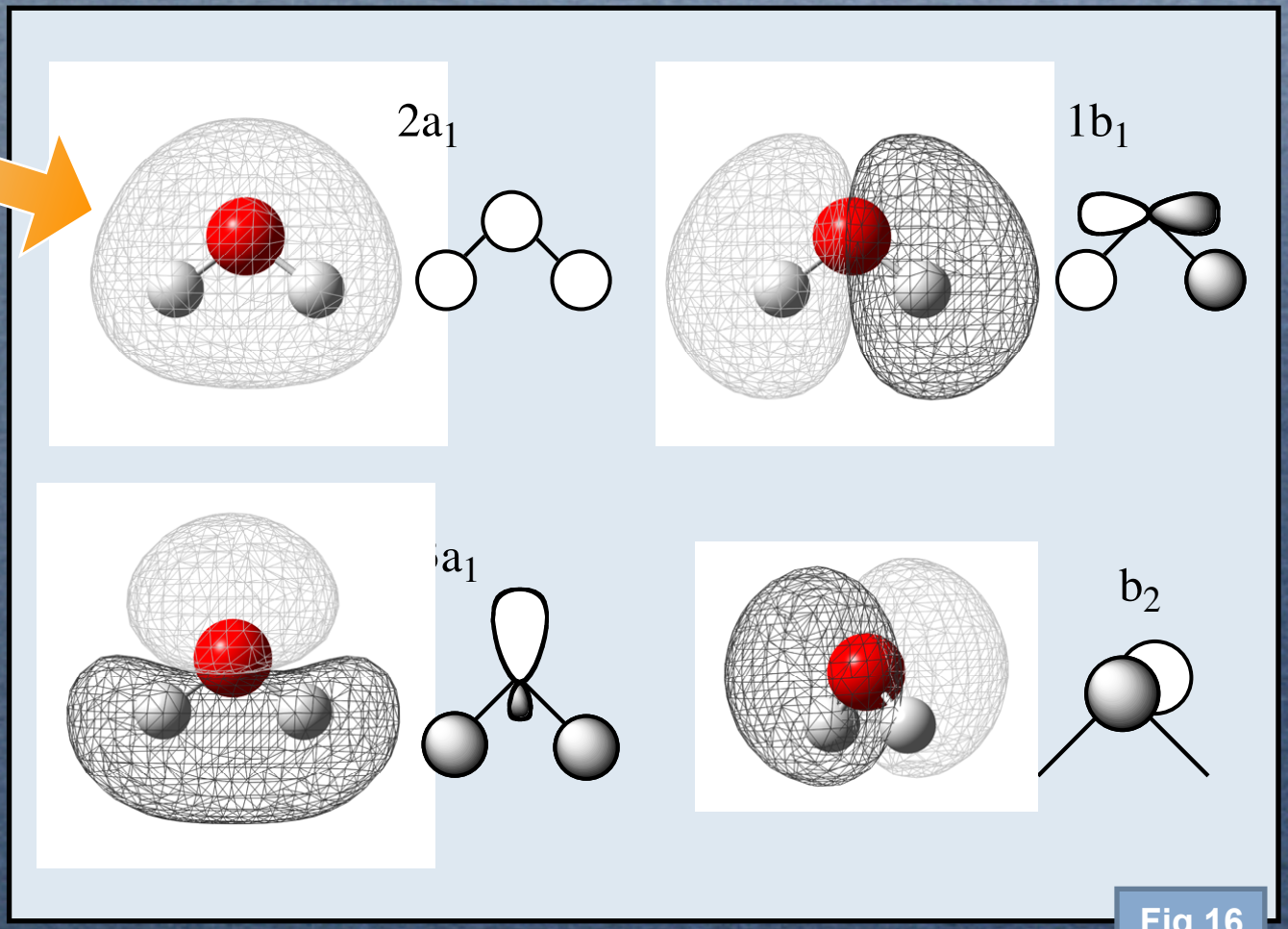


Fig 15

"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

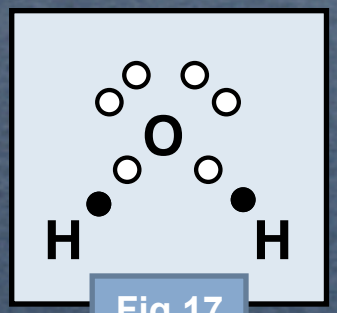
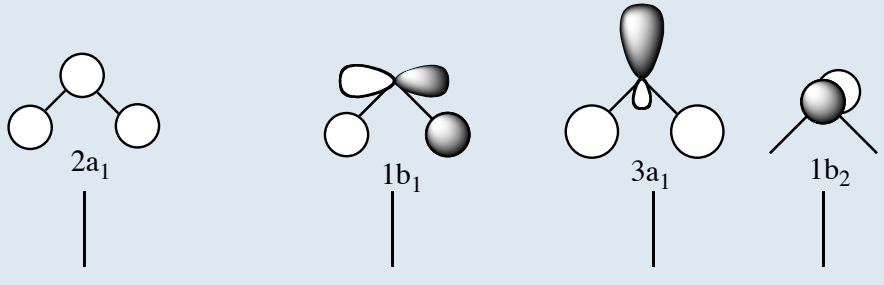


Fig 17

BUT

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



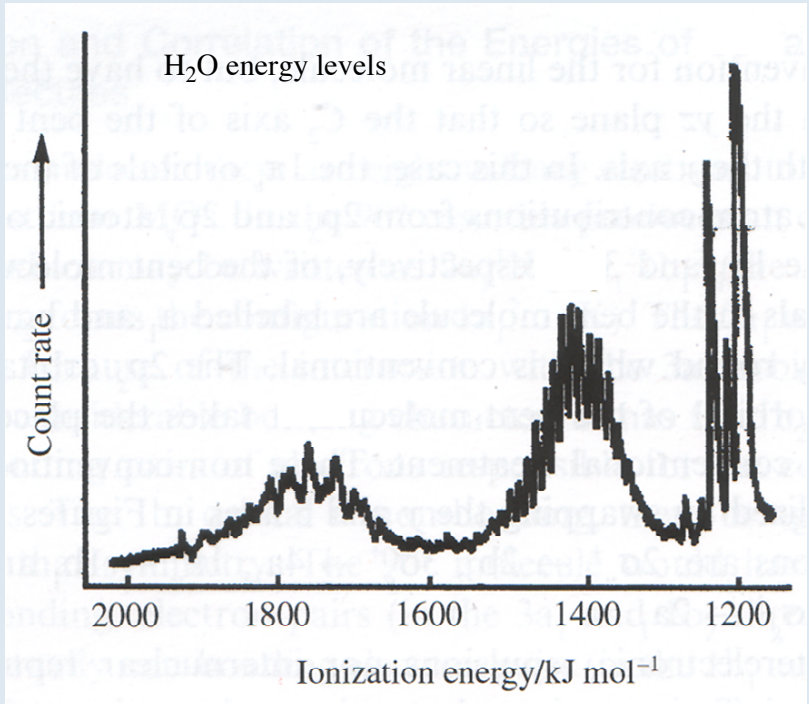


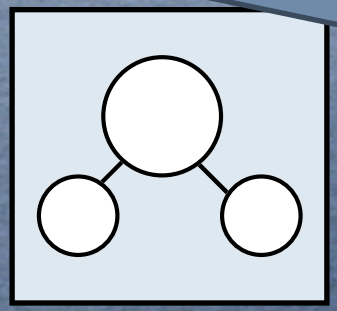
Fig 5.13 from "Structure and Bonding" by J. Barrett

Fig 18

Delocalisation

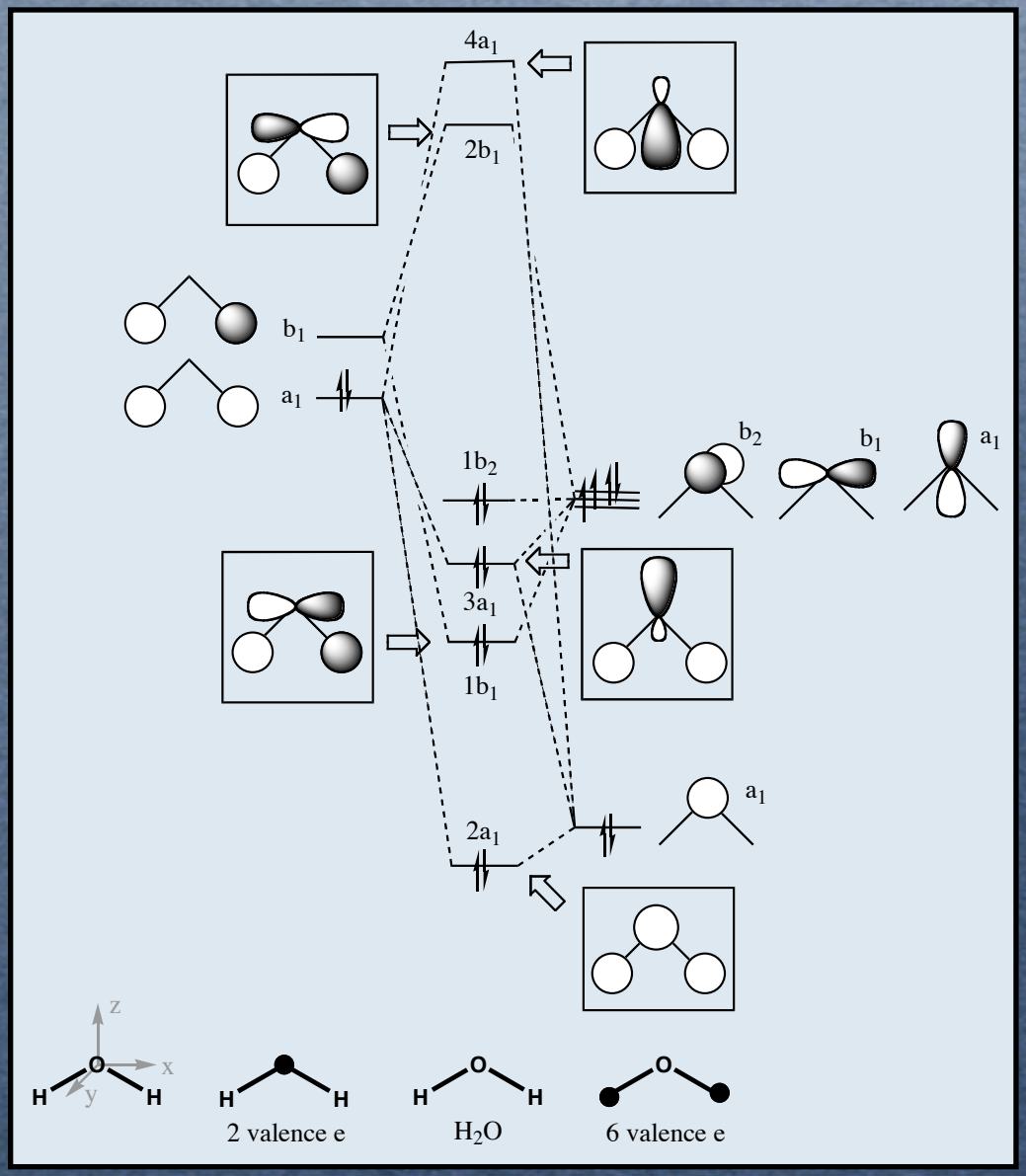
- **MOs are delocalised**
  - ✦ not 2 center 2 electron
  - ✦ most of MOs extend over ALL atoms in molecule
  - ✦ there are no “bonds”
- **Bonds represent a build up of the TOTAL electron density**
- **We keep ideas of hybridisation and 2c-2e bonds because they are USEFUL**

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

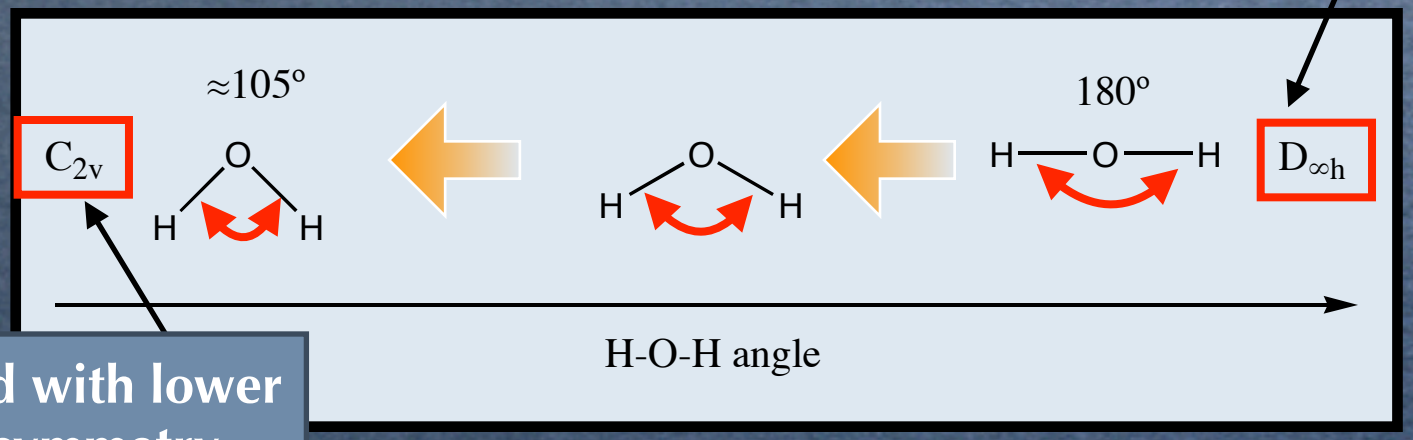


Correlation Diagram

- **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 H_2O bent?**

Fig 21

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



Walsh Diagram

- typically start from the highest symmetry
  - I've constructed the MO diagram for linear H_2O for you (Self-study for you to reproduce)

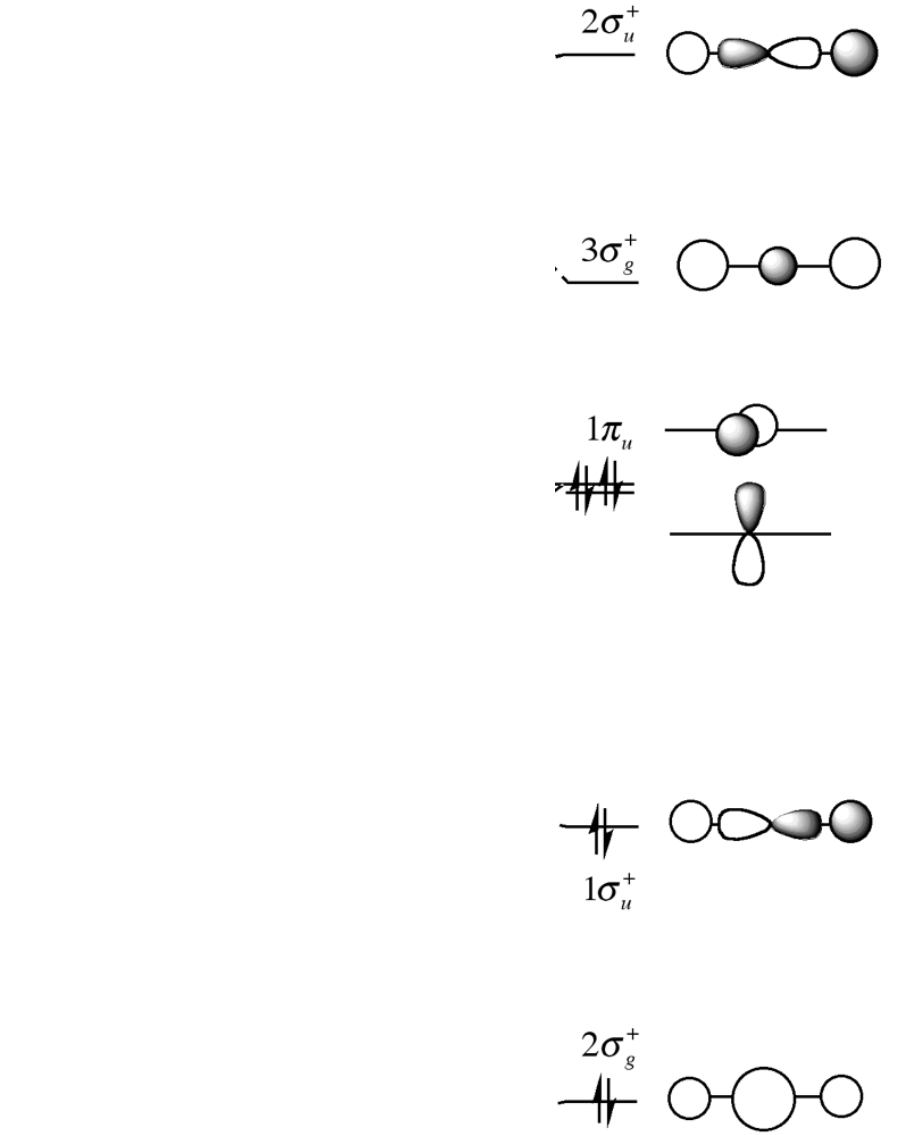


Fig 21

Walsh Diagram

- then examine how MOs change under geometric distortion

Qualitative not Quantitative!

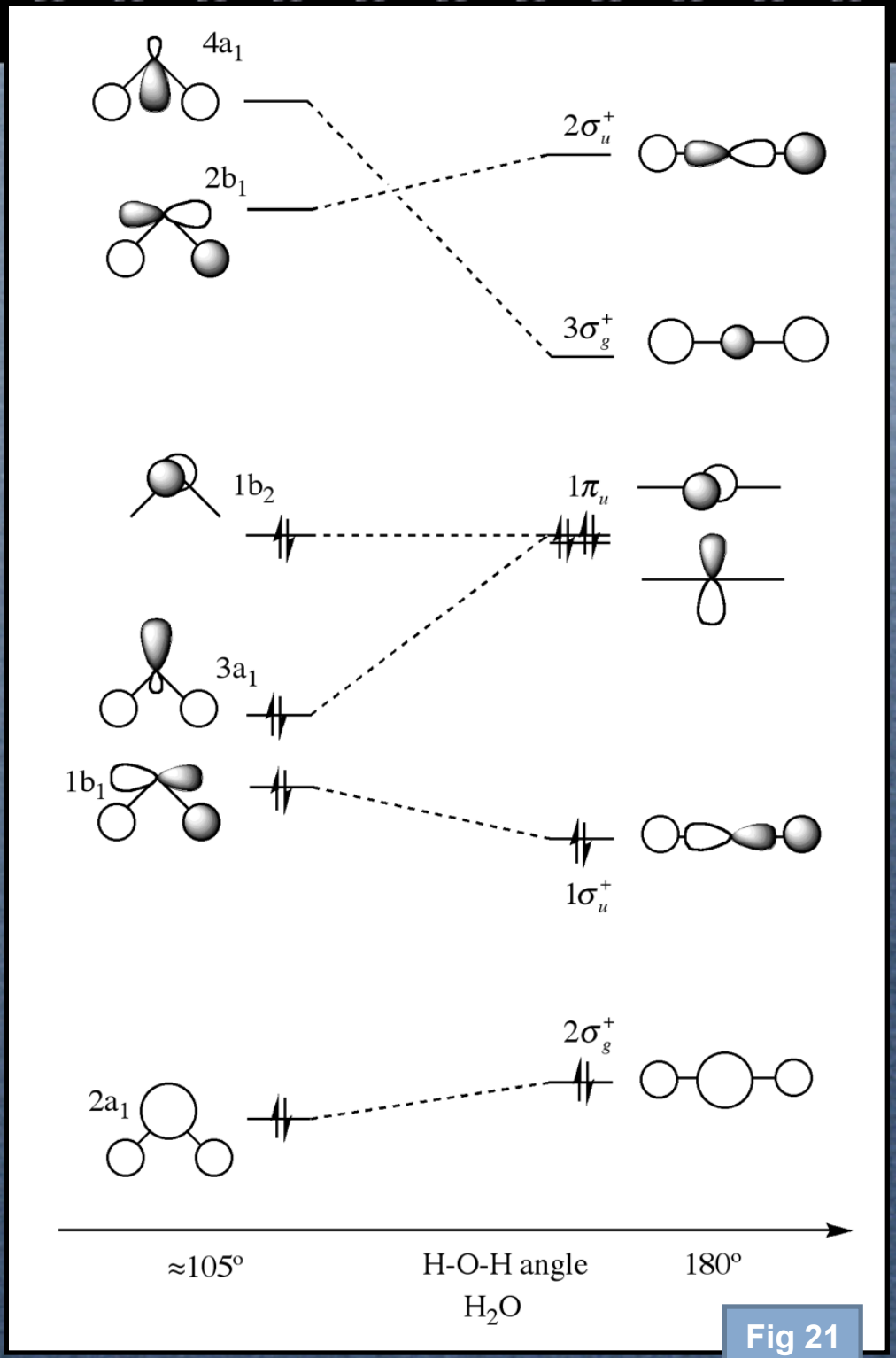


Fig 21

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

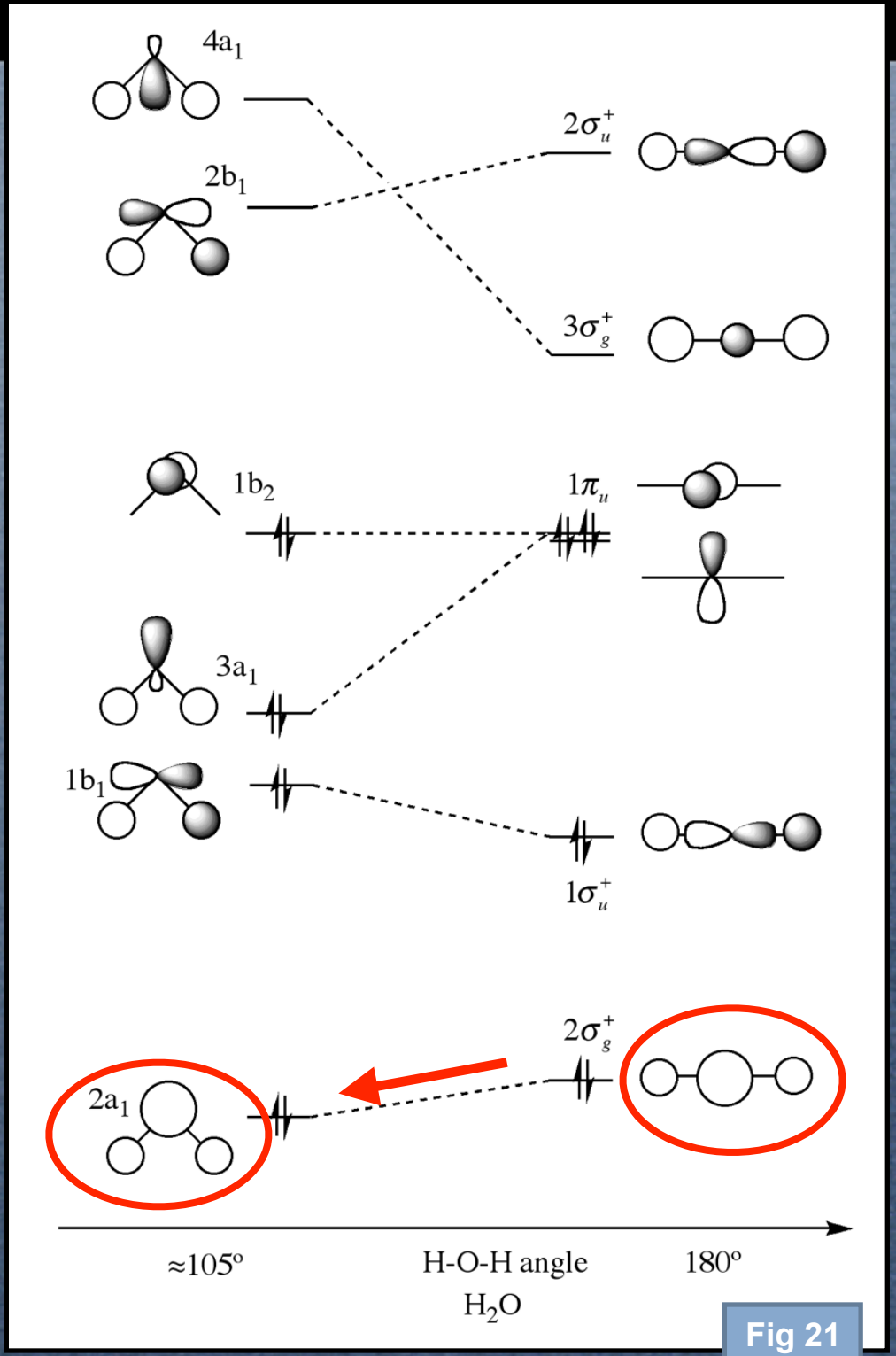


Fig 21

Energy of MOs

- then examine how MOs change under geometric distortion

- $1\sigma_u^+$ ($1b_1$) destabilised
  - ↓ O-H bonding overlap
  - ALSO ↑ H···H through space antibonding
  - net result destabilisation

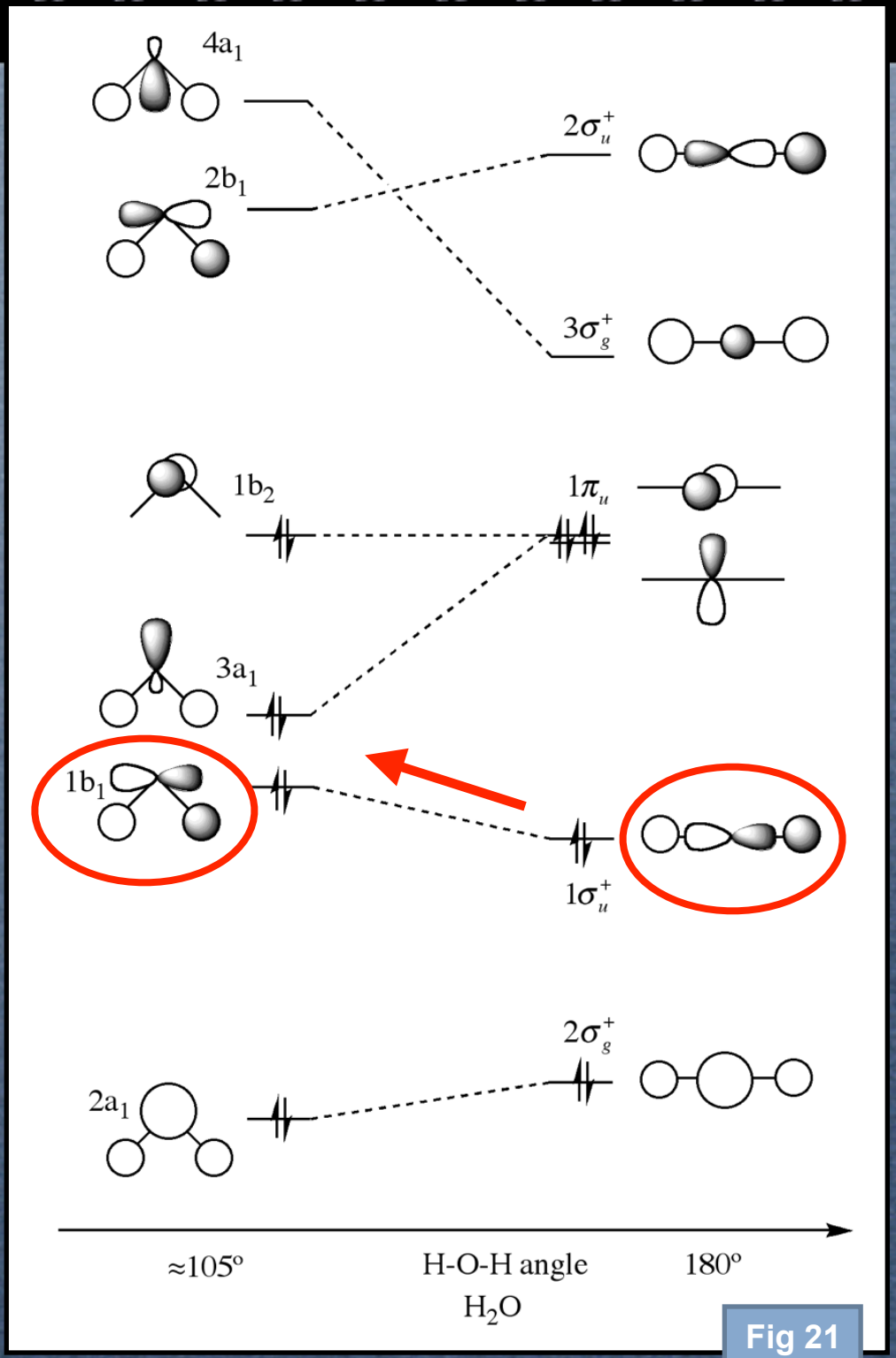


Fig 21

Energy of MOs

- then examine how MOs change under geometric distortion

- $1\pi_u$ (**1b₂**) no change
  - ✦ non-bonding orbital

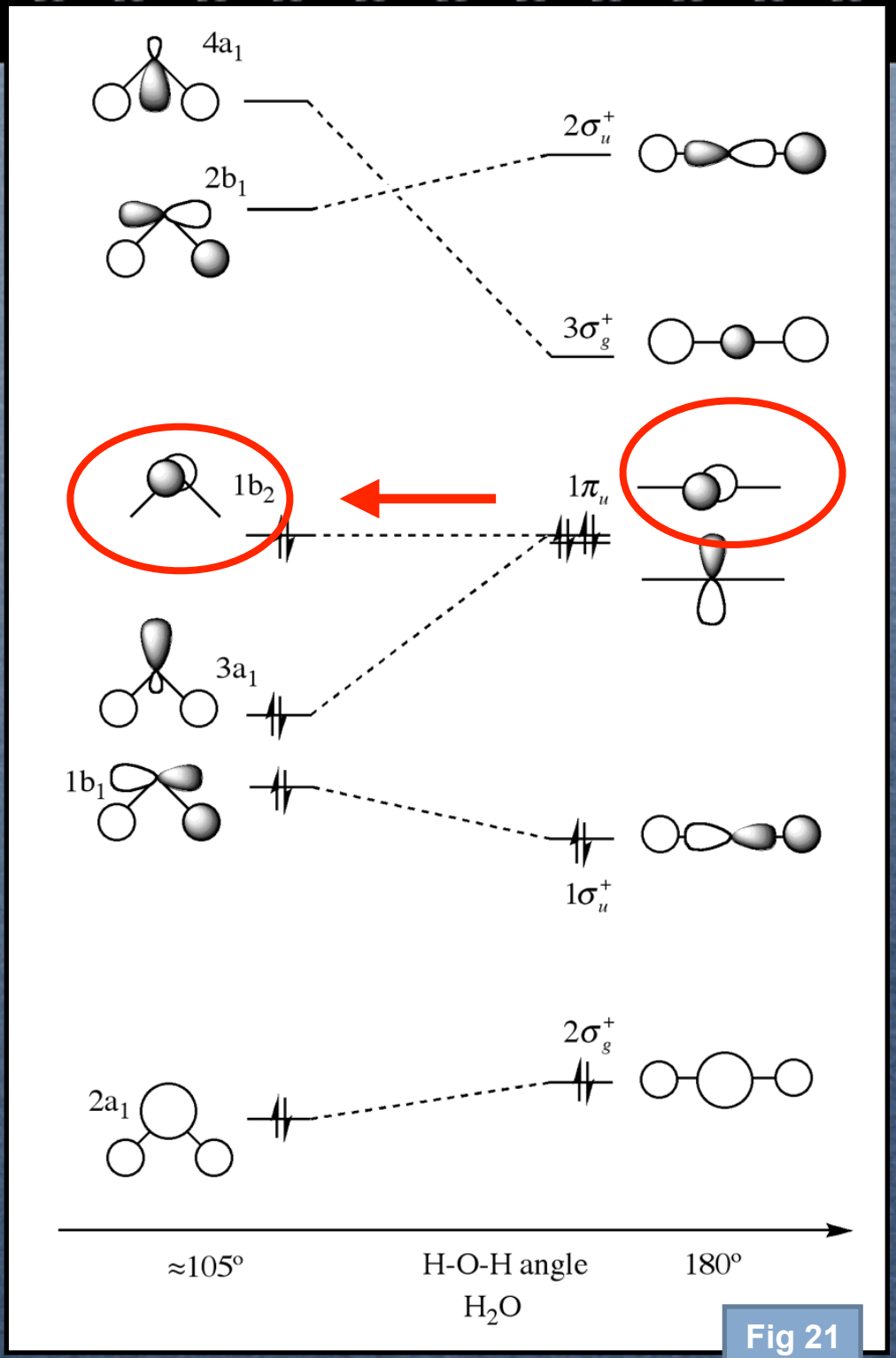


Fig 21

Energy of MOs

- then examine how MOs change under geometric distortion

- $2\sigma_u^+$(2b₁) stabilised

socrative quiz!

WHZ9KBWC3

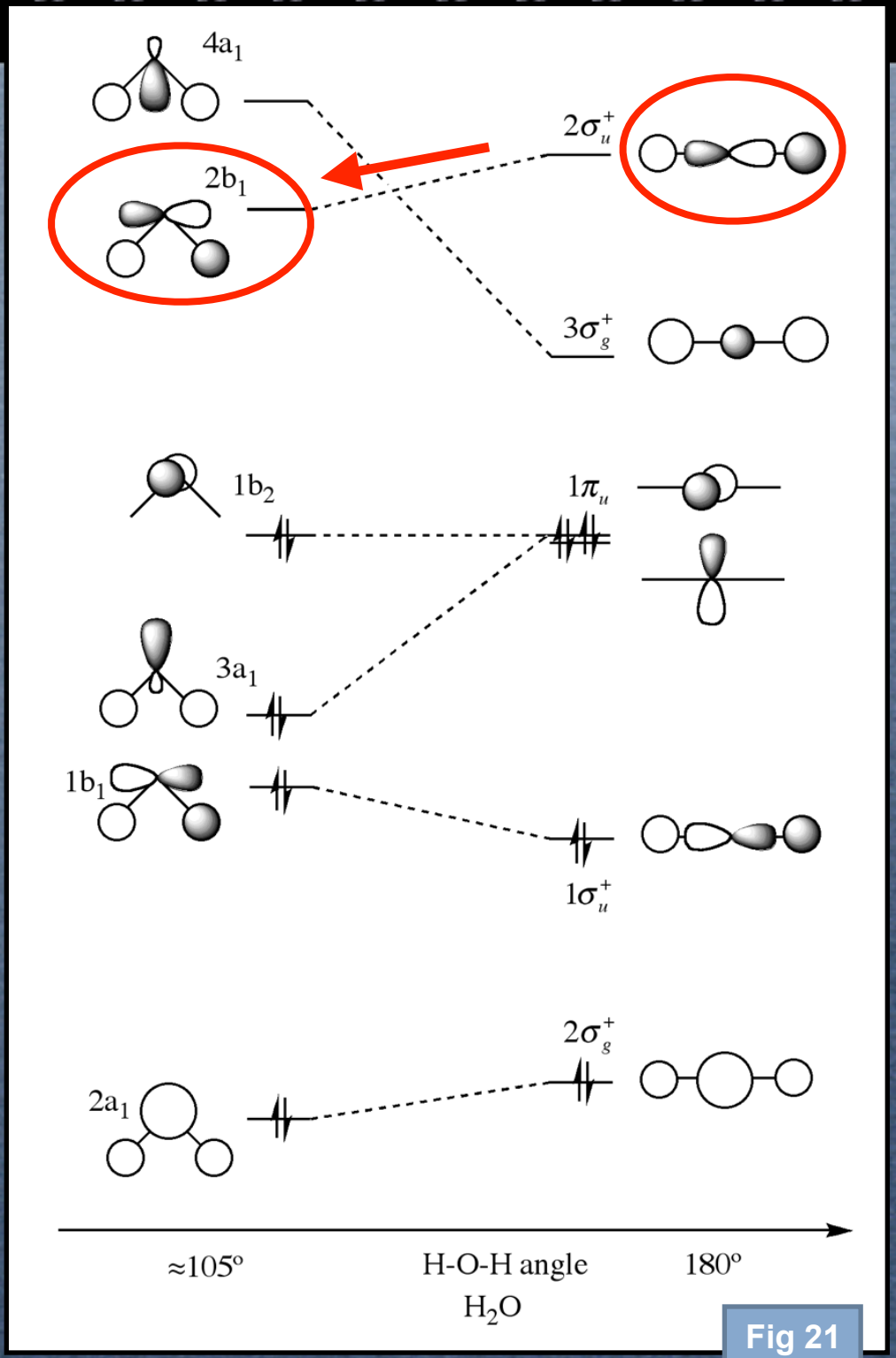


Fig 21

Energy of MOs

- then examine how MOs change under geometric distortion

- $2\sigma_u^+(2b_1)$ stabilised
  - ↓ O-H antibonding overlap =>stabilize
  - also ↑ H···H through space antibonding
  - =>destabilize
  - shorter distance overlap dominates
  - =>net result stabilisation

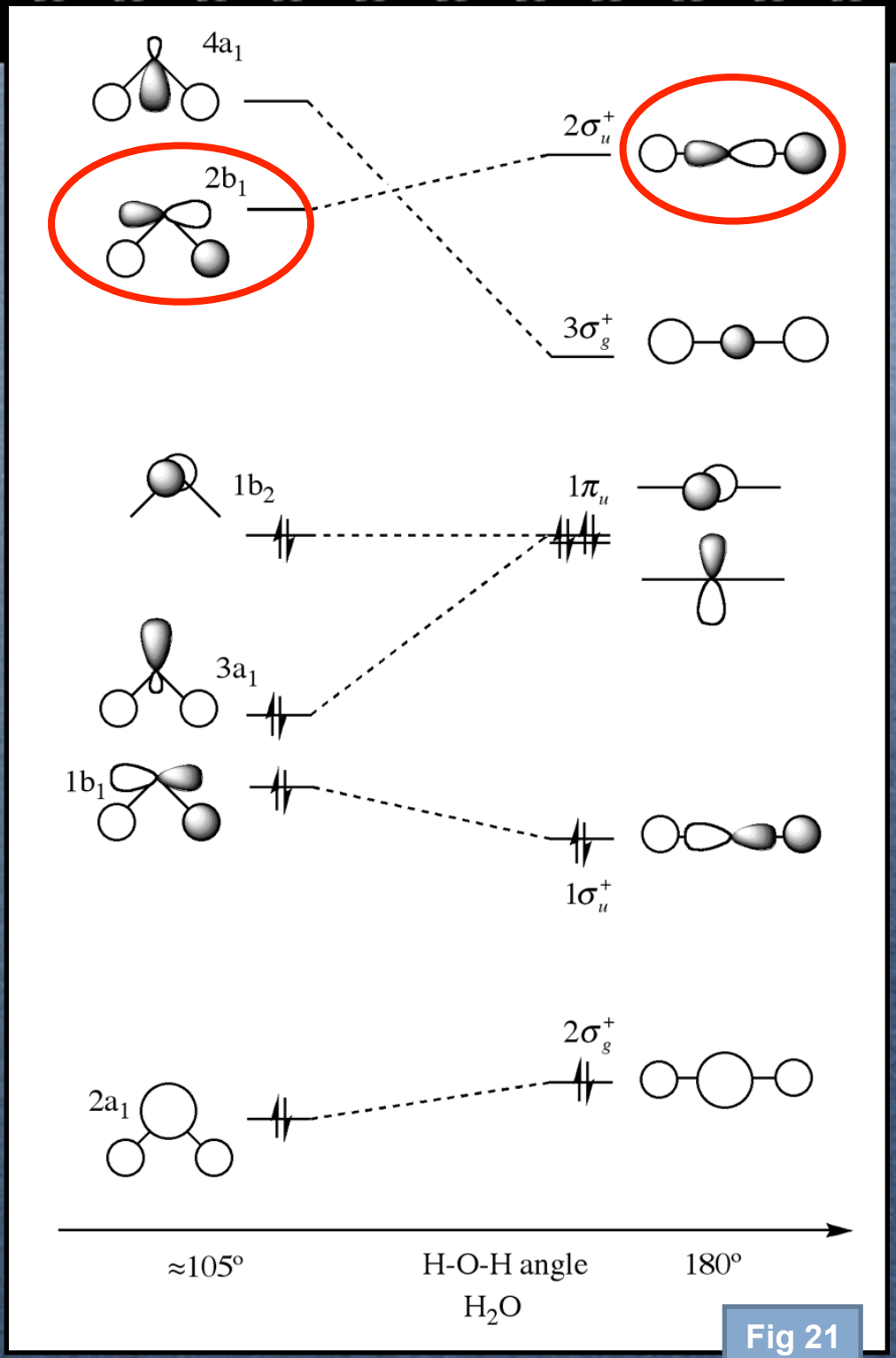


Fig 21

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!

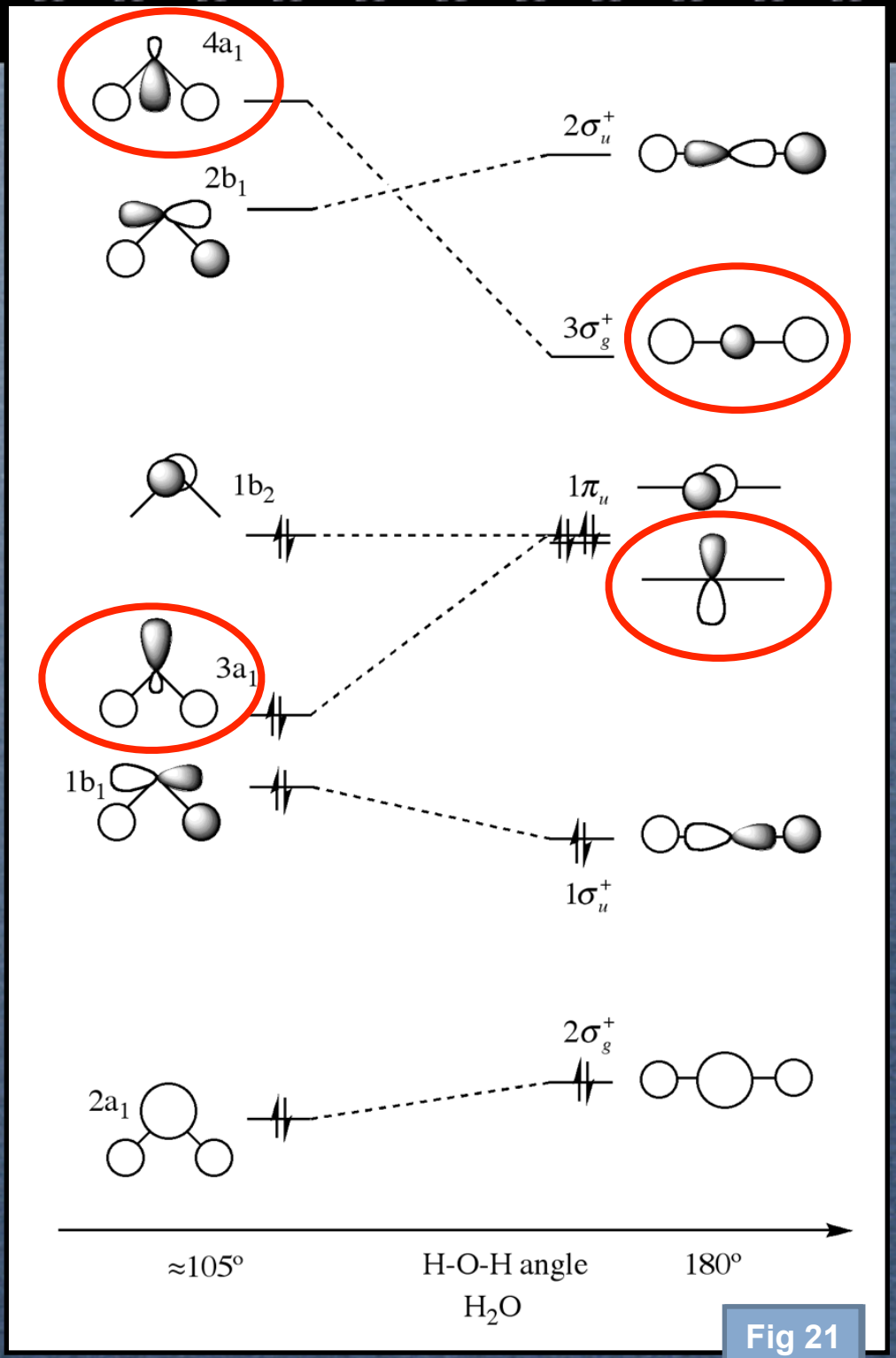


Fig 21

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

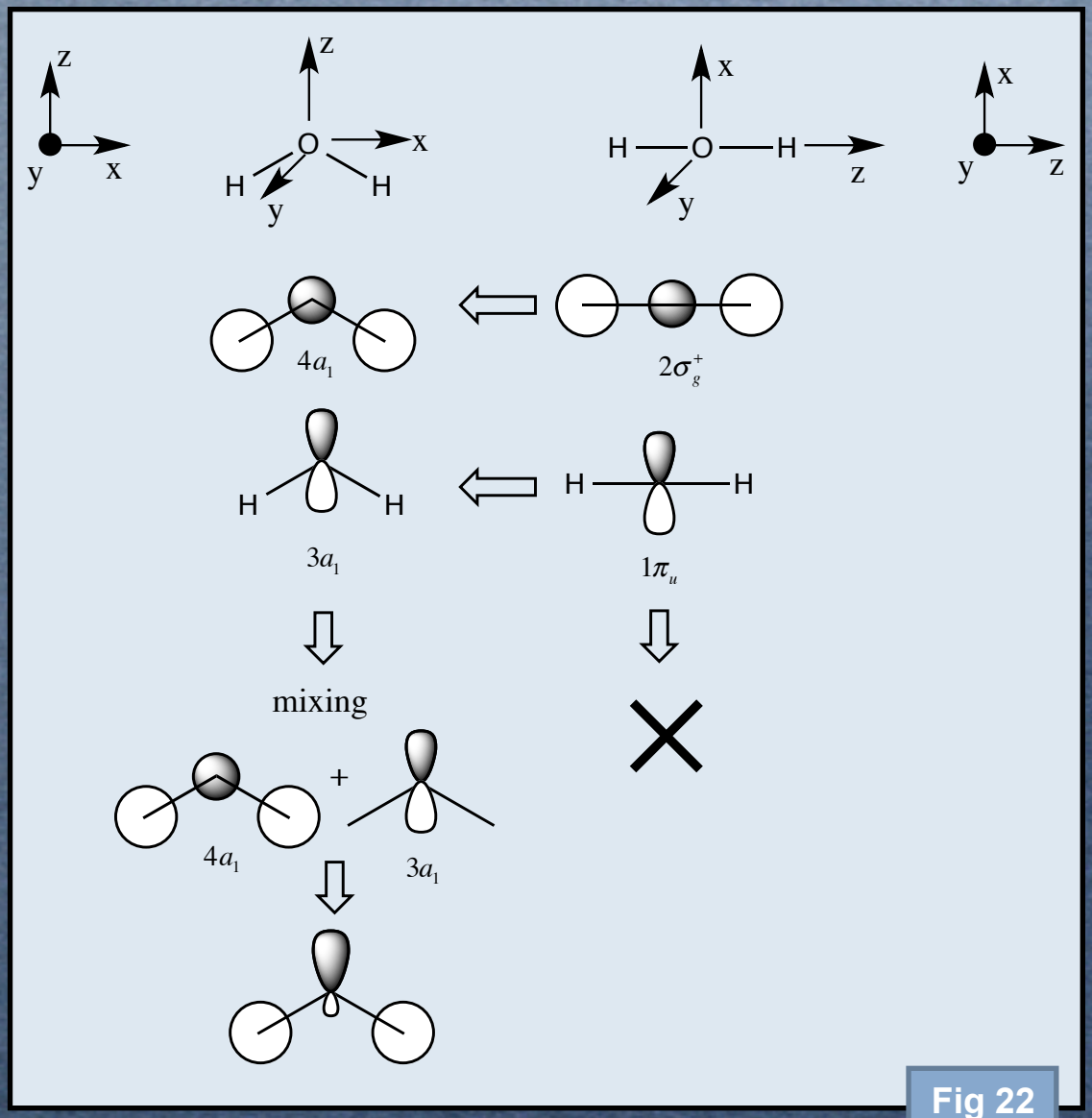


Fig 22

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

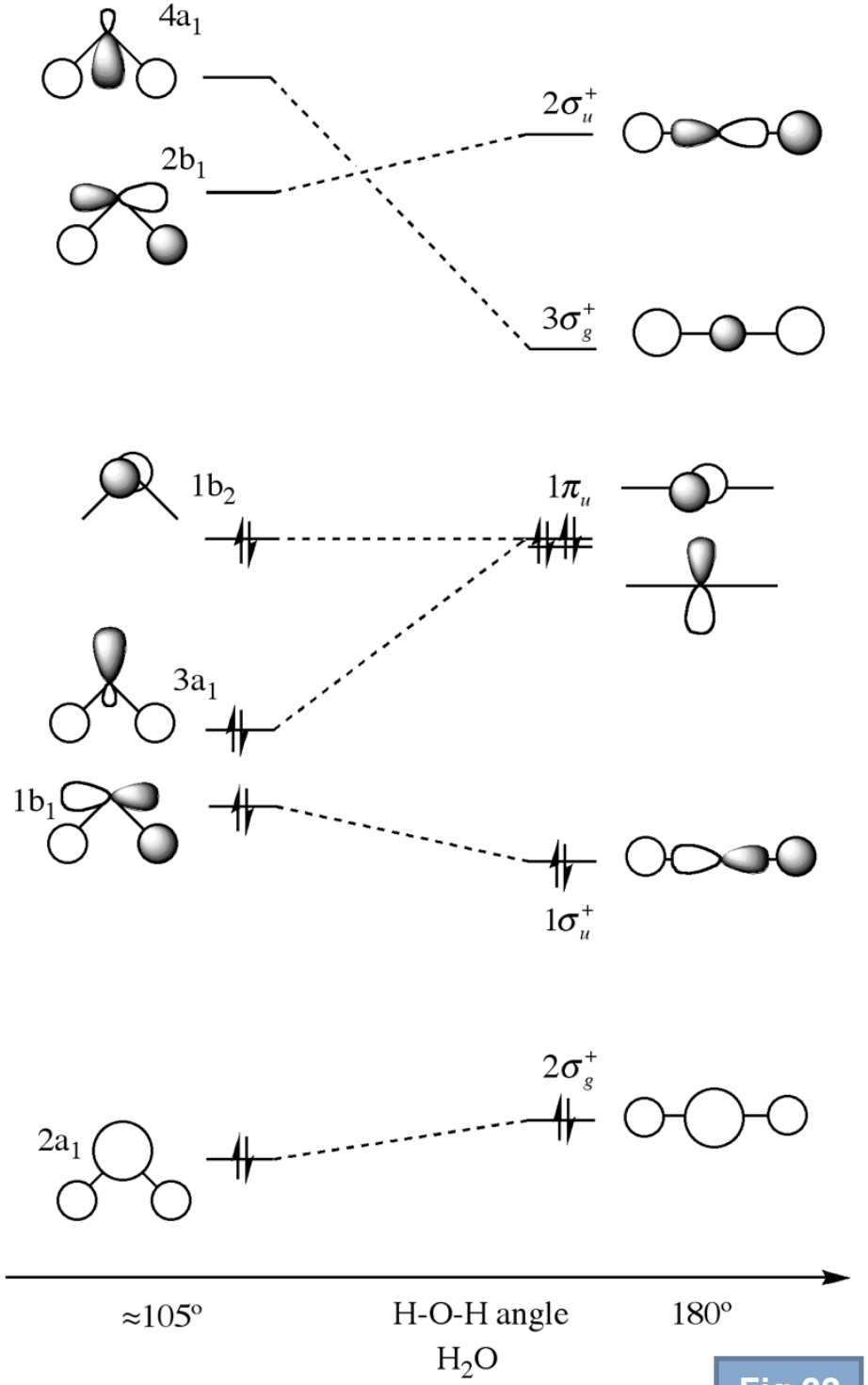
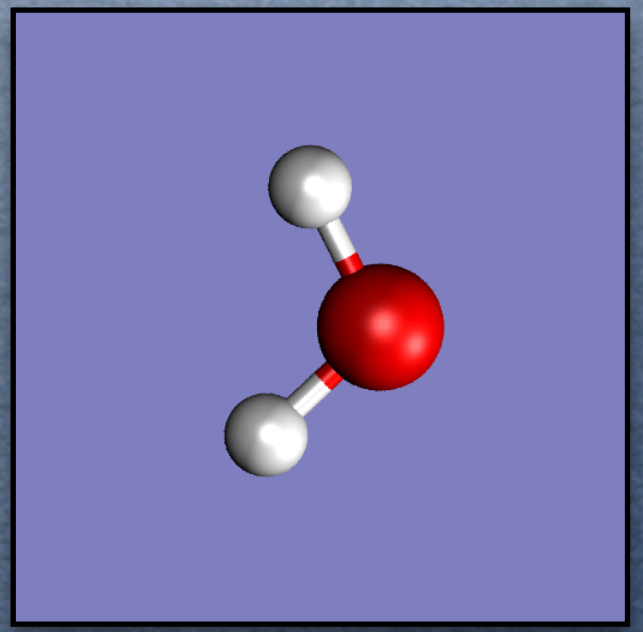


Fig 22

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

general relativity

Serious Stuff!

Heisenberg Uncertainty Principle

standard model of particle physics

existence of Higgs particle

field theory

Emmy Noether

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

MO checklist

steps we have used today to form a MO diagram

VERY Important!

Steps to construct a MO diagram

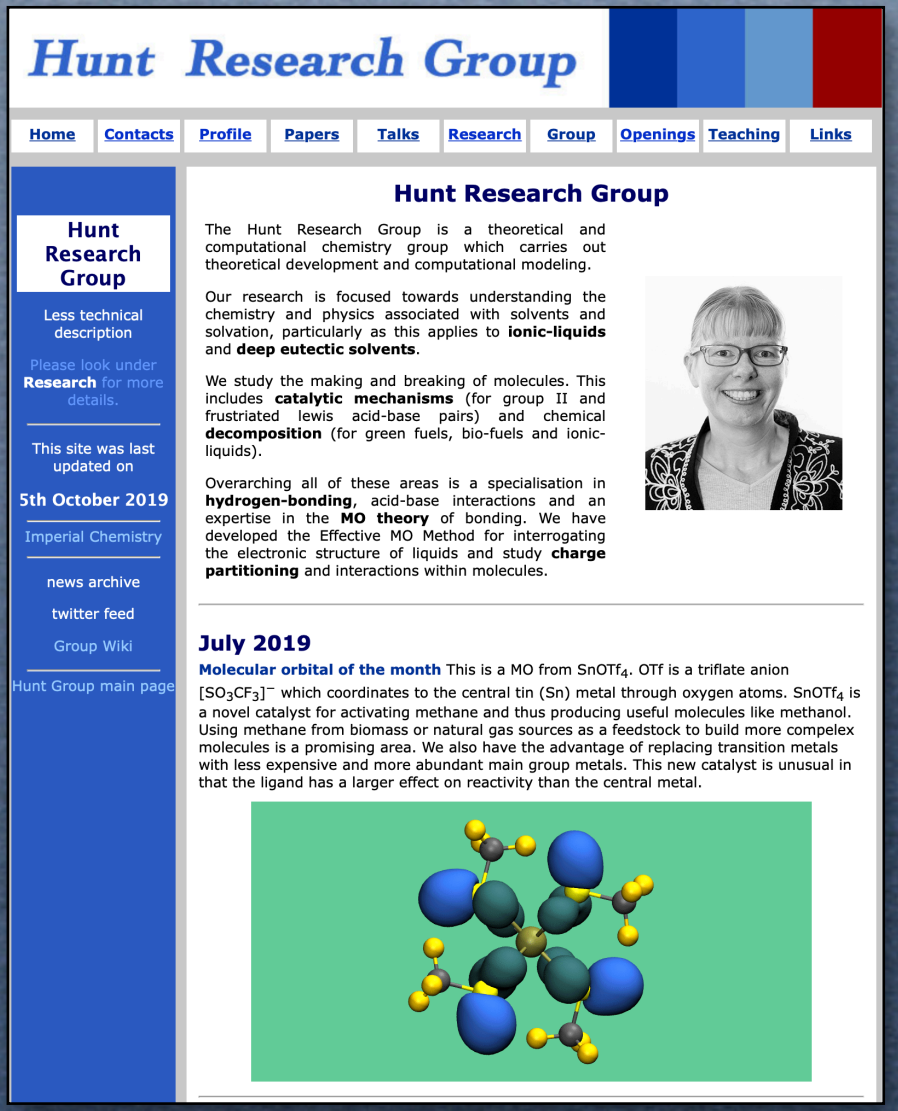
- determine the molecular shape and identify the point group
- define the axial system and all of the symmetry operations
- identify the chemical fragments, put them on the bottom of the diagram
- determine the energy levels and symmetry labels of the fragment orbitals (use H1s as a reference)
- combine 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

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!!