Molecular Orbitals in Inorganic Chemistry

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Outline

- choosing fragments
- orbital symmetry (again!)
- bonding and antibonding character of orbitals
- complex MOs -> decompose into LCAOs
- a complex MO diagram: B_2H_6

Complex Fragments

- **MO diagrams combine two fragments**

Symmetry Fragments	Molecular Fragments

- **Symmetry fragments**
  - atoms that transform onto each other under operations of the point group
  - “equivalent atoms” in terms of NMR
- **Molecular fragments**
  - small molecules for which the MOs are well known
  - like AH_2 or liner AB or AH_3

Example:

- **CH_2O**
  - formaldehyde
  - molecular fragments CH_2 and O
  - symmetry fragments H_2 and CO
  - use molecular fragments as there is a single atom

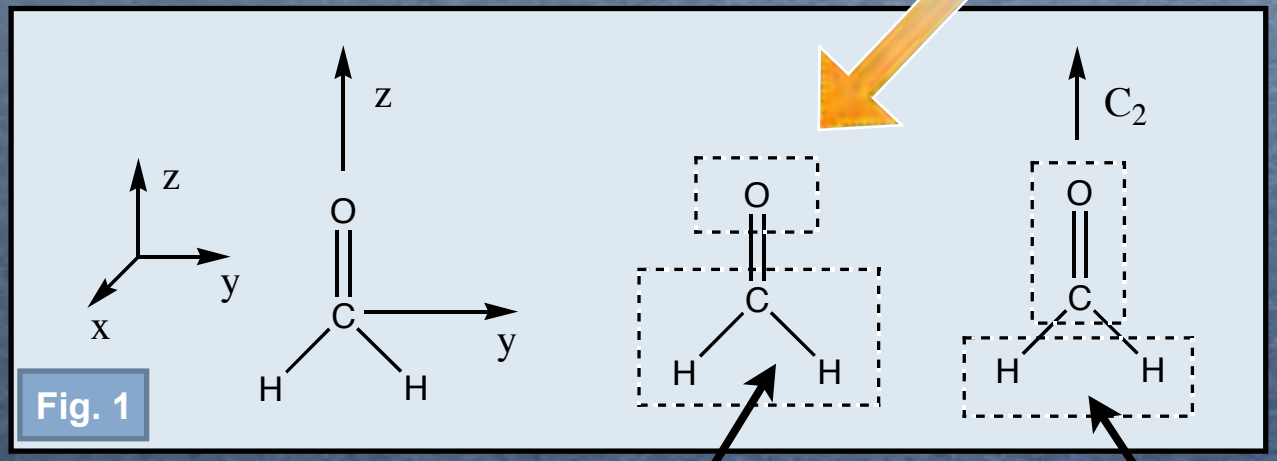


Fig. 1

CH_2 fragment like H_2O will have the same MOs

H's map onto each other under C_2

Example:

BH_3

- boron trihydride
- molecular fragments H_2 and BH
- symmetry fragments H_3 and B
- use the symmetry fragments as there is a single atom

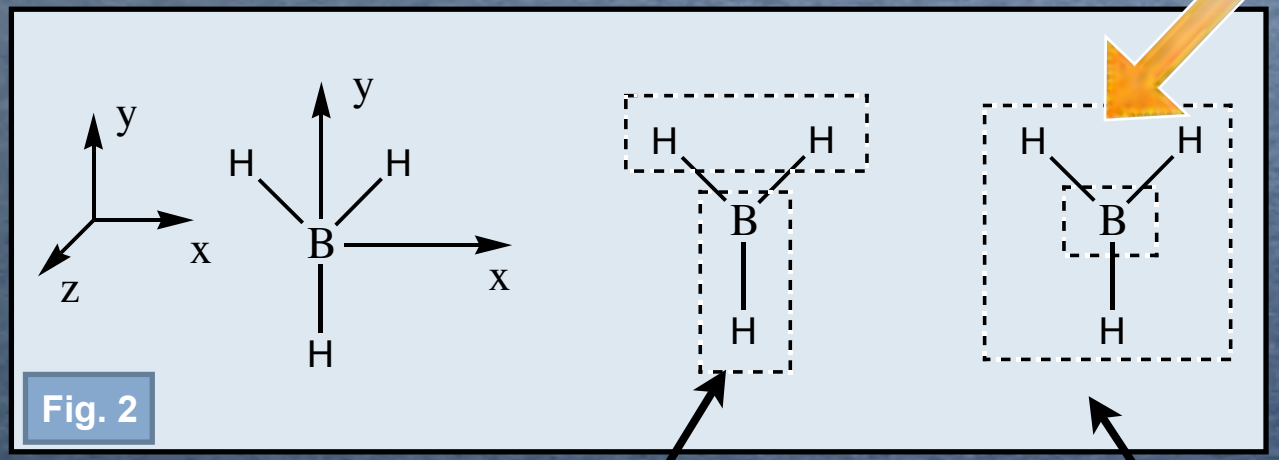


Fig. 2

preferred

H_2 and BH fragments will have the same MOs as diatomics

H's map onto each other under C_2

In-Class Activity

- C_2H_4
  - ethane
  - determine the symmetry fragments
  - determine the molecular fragments
  - which is the better one to use and why?

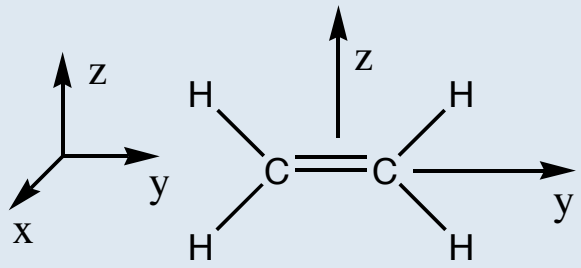


Fig. 3

Orbital Symmetry

Short-cuts

- look at the phase pattern!
- orbitals with the same phase pattern as an axis have the same symmetry label as the axis

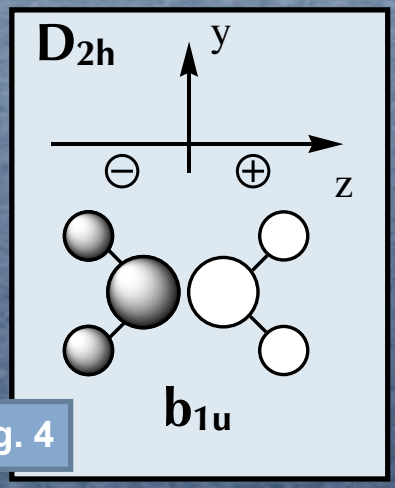


Fig. 4

same symmetry as the z-axis

Orbital Symmetry

Short-cuts

- look at the phase pattern!
- orbitals with the same phase pattern as a dAO have the same symmetry as the corresponding cartesian function

look at the last column on your character tables: it gives the symmetry label (IR) of the binary cartesian functions

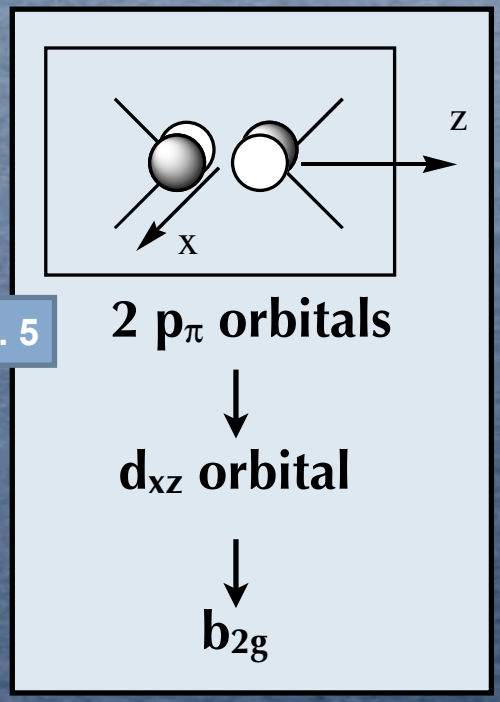


Fig. 5

same symmetry as the dxz AO

Orbital Symmetry

- **if there are no short-cuts possible**
  => use a representation table

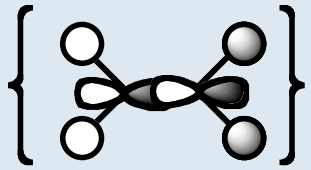
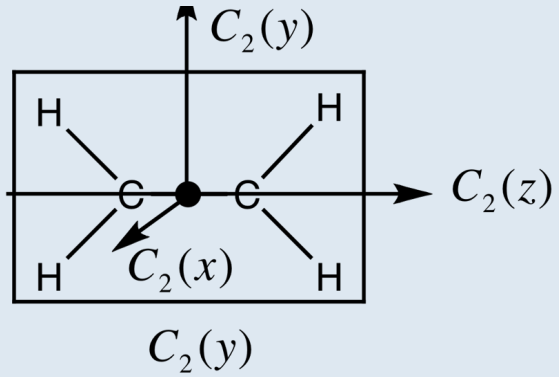
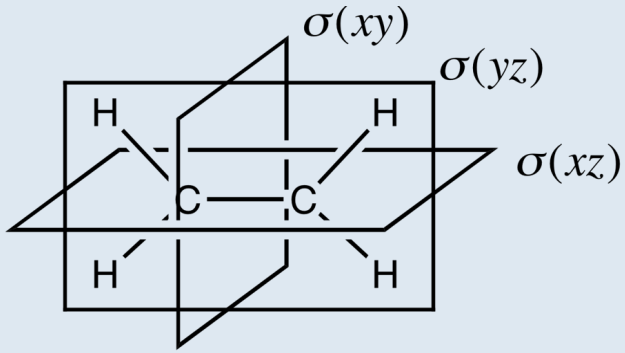
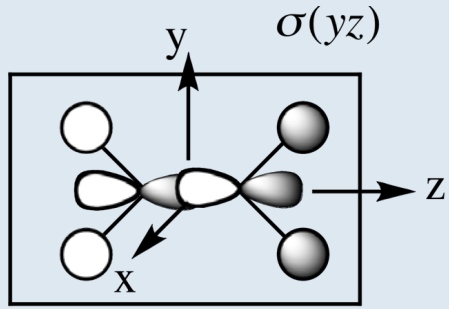
D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	
Γ 	1	1	-1	-1	-1	-1	1	1	b_{1u}

Fig. 6







In-Class Activity

- test yourself!
- socrative quiz

socrative quiz!

WHZ9KBWC3

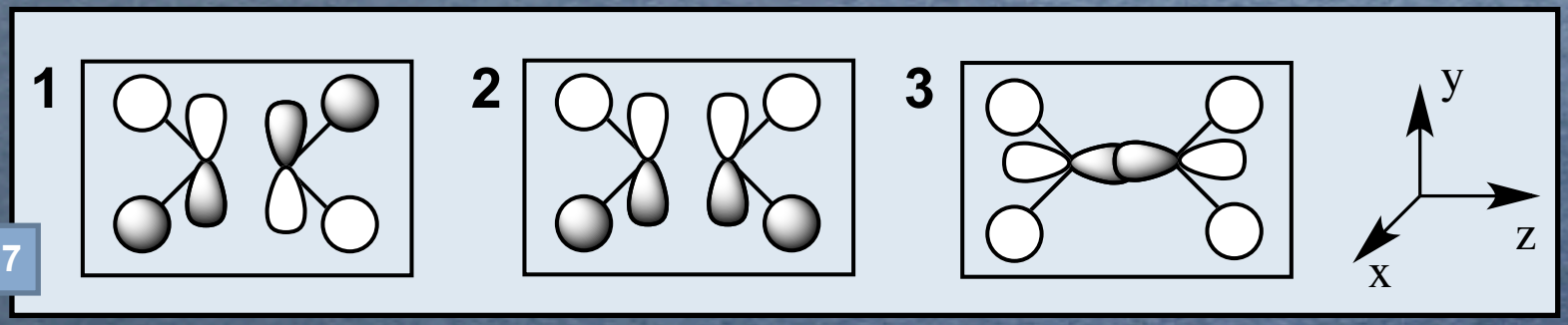


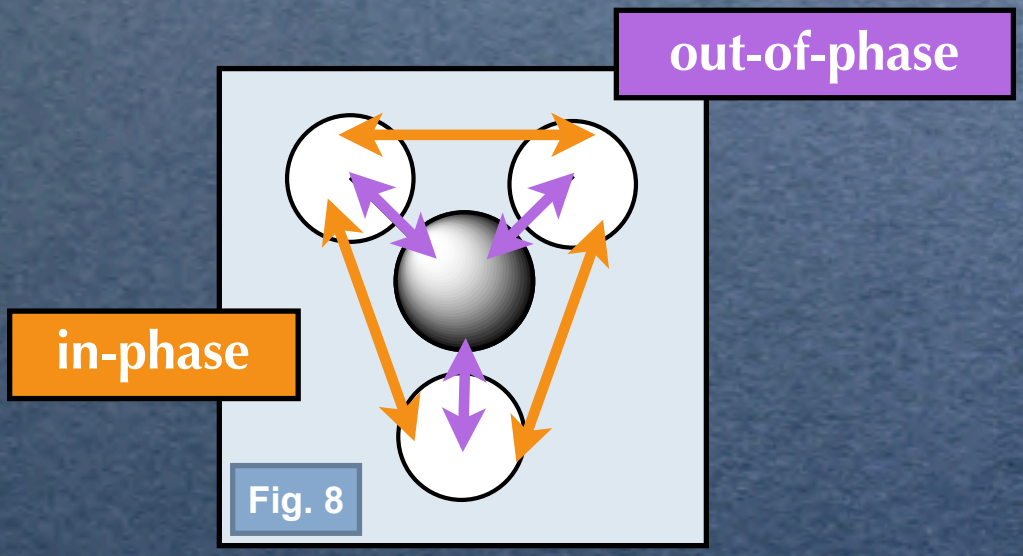
Fig. 7

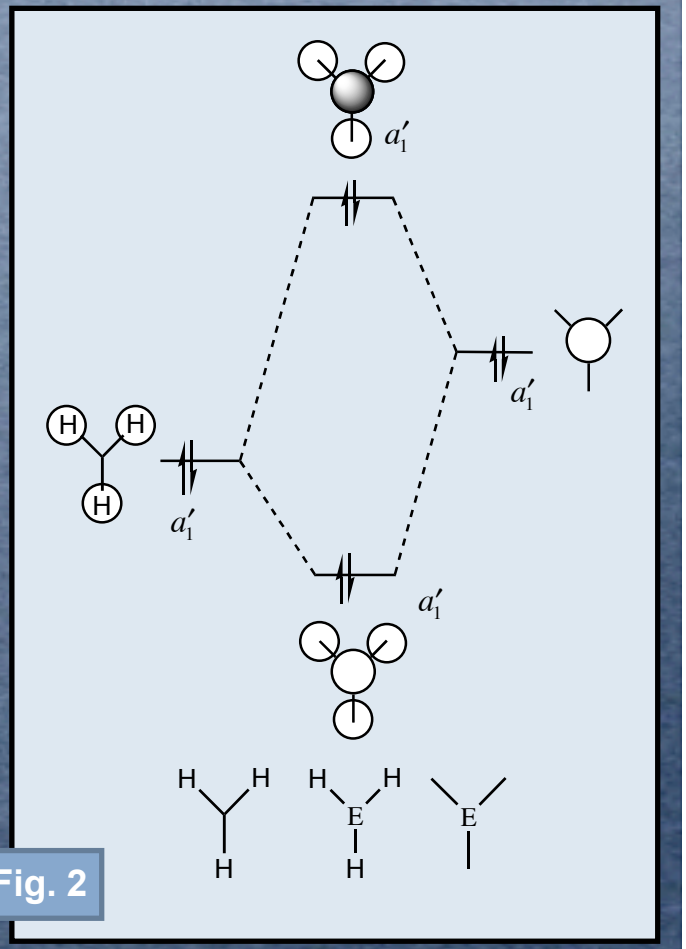
- determine the symmetry of these MOs
  - these are MOs from C_2H_4 which belongs to the D_{2h} point group
  - assume the centre of the axis system lies on the centre of inversion for the molecule

Bonding vs Anti-bonding

Bonding

- bonding => in-phase overlap
- anti-bonding => out-of-phase overlap





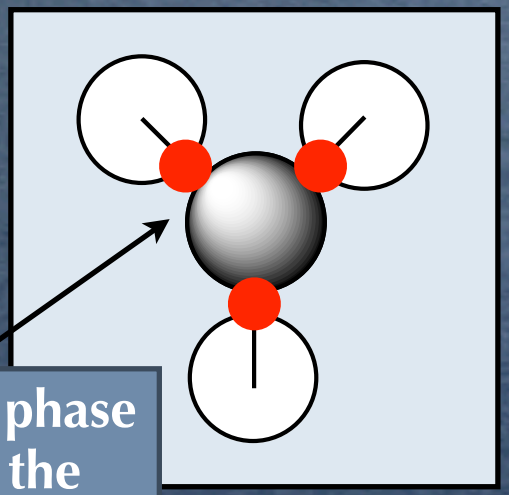
Bonding vs Anti-bonding

Bonding

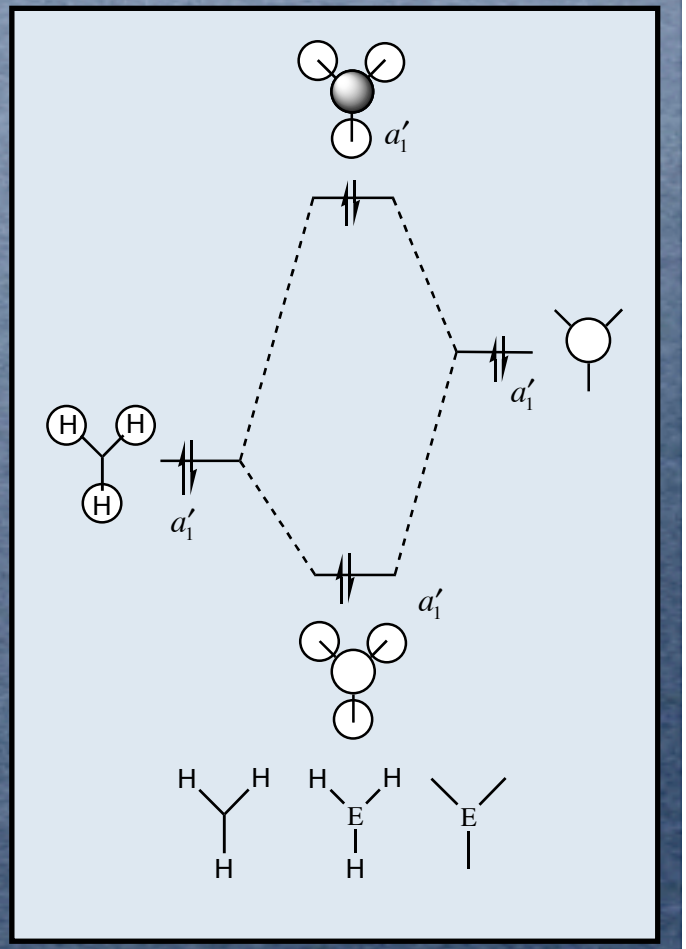
- bonding => in-phase overlap
- anti-bonding => out-of-phase overlap

Nodes

- occur where phase changes
- raises the energy of an orbital, more nodes indicates increasing anti-bonding character
- nodes at atoms are less important



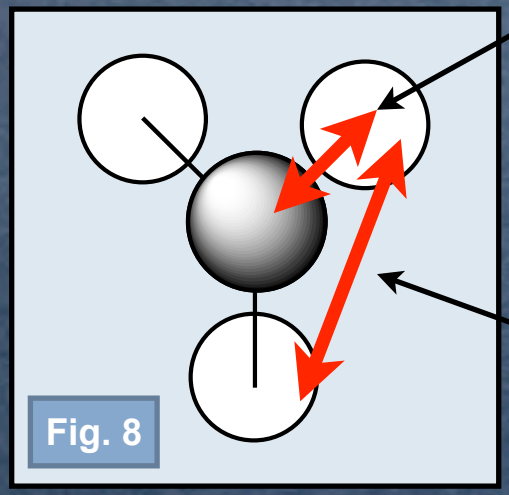
nodes where phase changes in the internuclear region



More Complex MOs

- **Complex MO**
  - has both bonding and anti-bonding components
- **Bonding character is a sliding scale**
  - σ (s) interactions are much stronger than π (p) type interactions
  - the closer the orbitals the stronger the interaction (bonded vs non-bonded)

this MO has only sAOs so interactions are stronger than π or p interactions



orbitals are close => strong (antibonding) interaction

orbitals are far apart => weak (bonding) interaction

Important!

In-Class Activity

- **test yourself!**

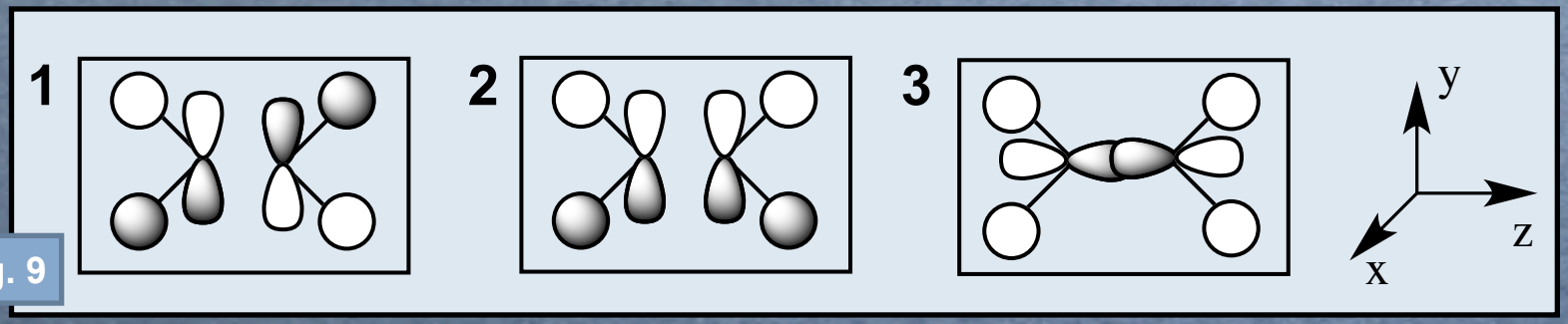


Fig. 9

- **annotate a diagram of MO1 identifying the bonding/ antibonding interactions**
- **what is the relative energy ordering of these MOs?**
- **HINTS**
  - look at ALL of the interactions
  - what is the type of interaction (s or p)?
  - what is the distance between the interacting orbitals?
  - for similar MOs how many nodes are there?

LCAO for complex MOs

- **in research we often work in "reverse"**
  - optimise a molecule
  - confirm the minima (frequency analysis)
  - compute the MOs
- **you will have seen the "MO window" for gaussview**
- **dithiocarbamate ligands**
  - used as ligands for many TM and coinage metal complexes
  - used in nanoparticle synthesis

$S_2C{=}NR_2$

Important!

poor attempts in last years exam

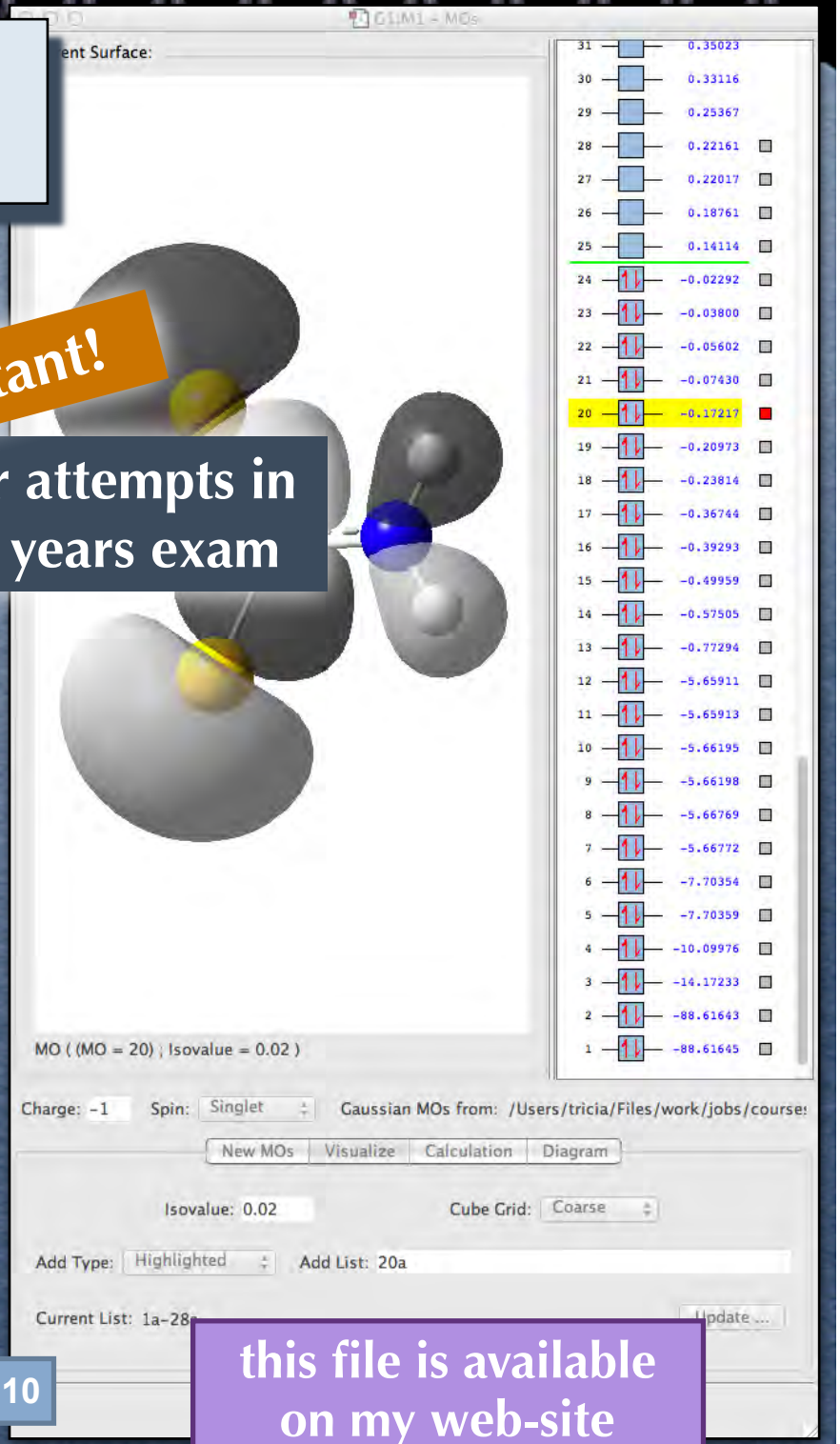


Fig. 10

this file is available on my web-site

LCAO for complex MOs

- **which MOs are important??**
  - not the deep core orbitals: AO-like
  - “jump” in energy
  - not the high energy unoccupied MOs: too diffuse
  - LUMO+4 and above
  - yes to valence MOs!
  - yes to lower energy unoccupied MOs

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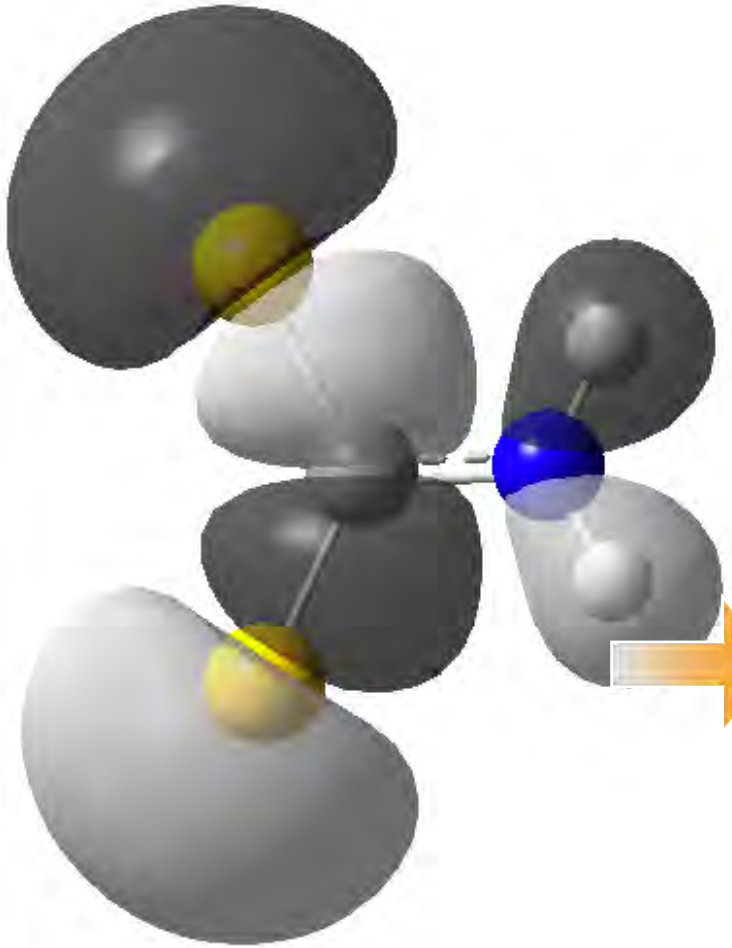

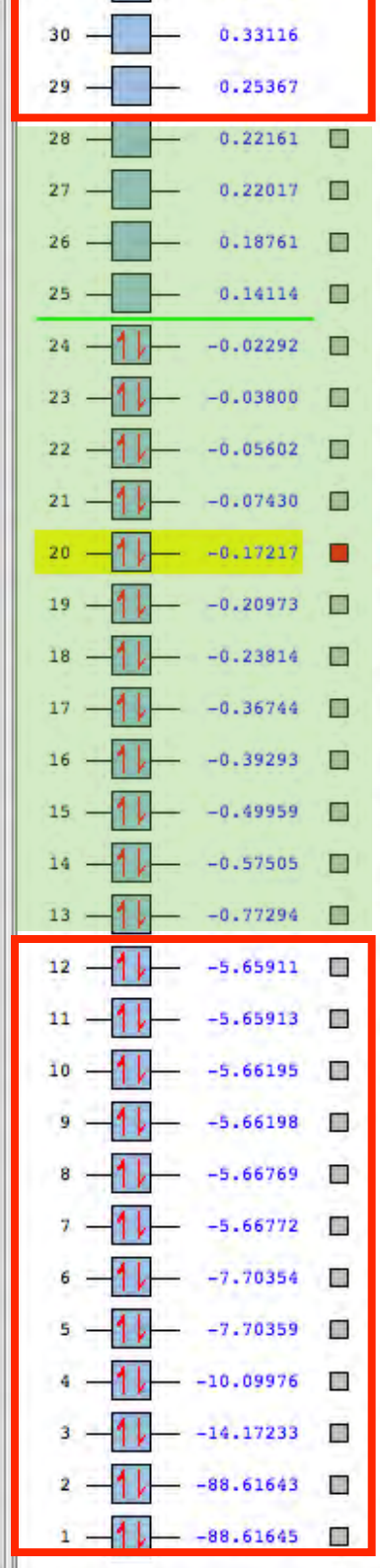

Fig. 10

MO ((MO = 20) ; Isovalue = 0.02)

LCAO for complex MOs

- **decompose the real MOs into LCAO components**
  - examine MO look for AO contributions
  - very small contributions are ignored
  - relate to known fragment orbitals
  - relative size is important

Look at Fig 11 in your notes

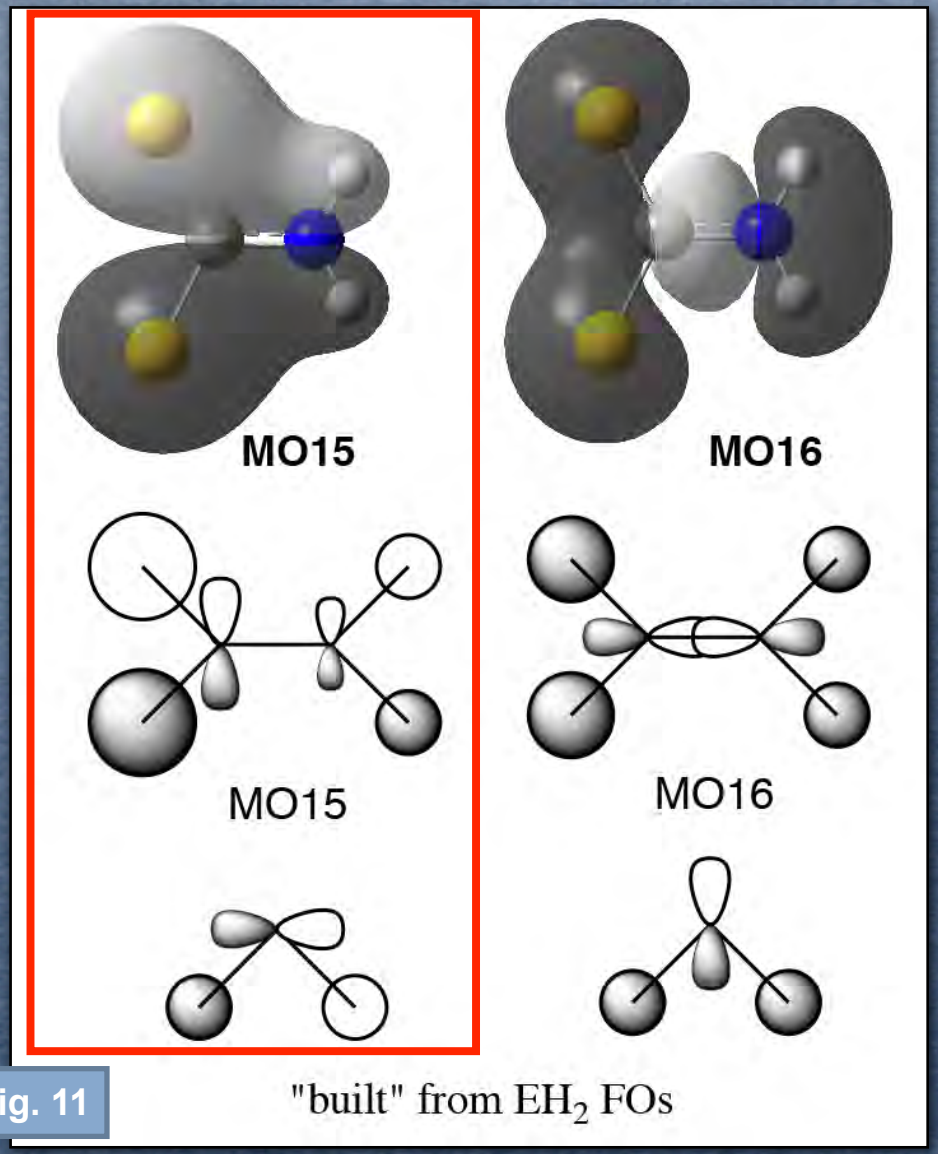

Fig. 11 "built" from EH_2 FOs

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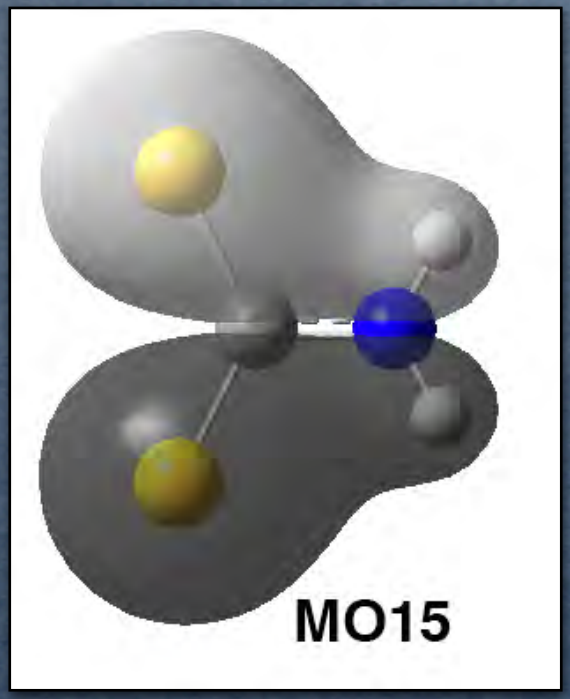
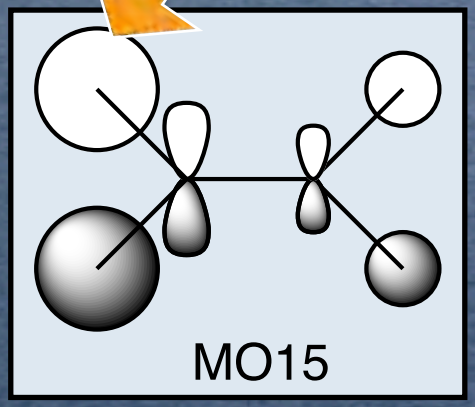
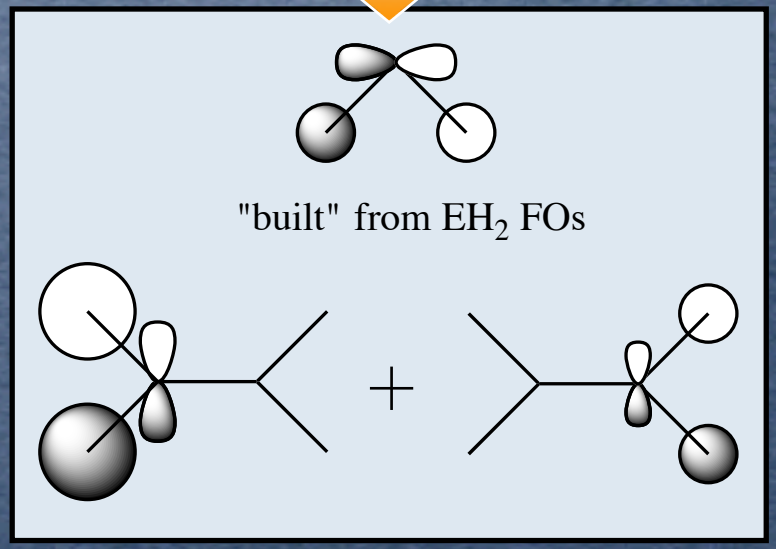


larger contribution



combined "b_1" MOs from EH_2 fragments



LCAO for complex MOs

- **decompose the real MOs into LCAO components**
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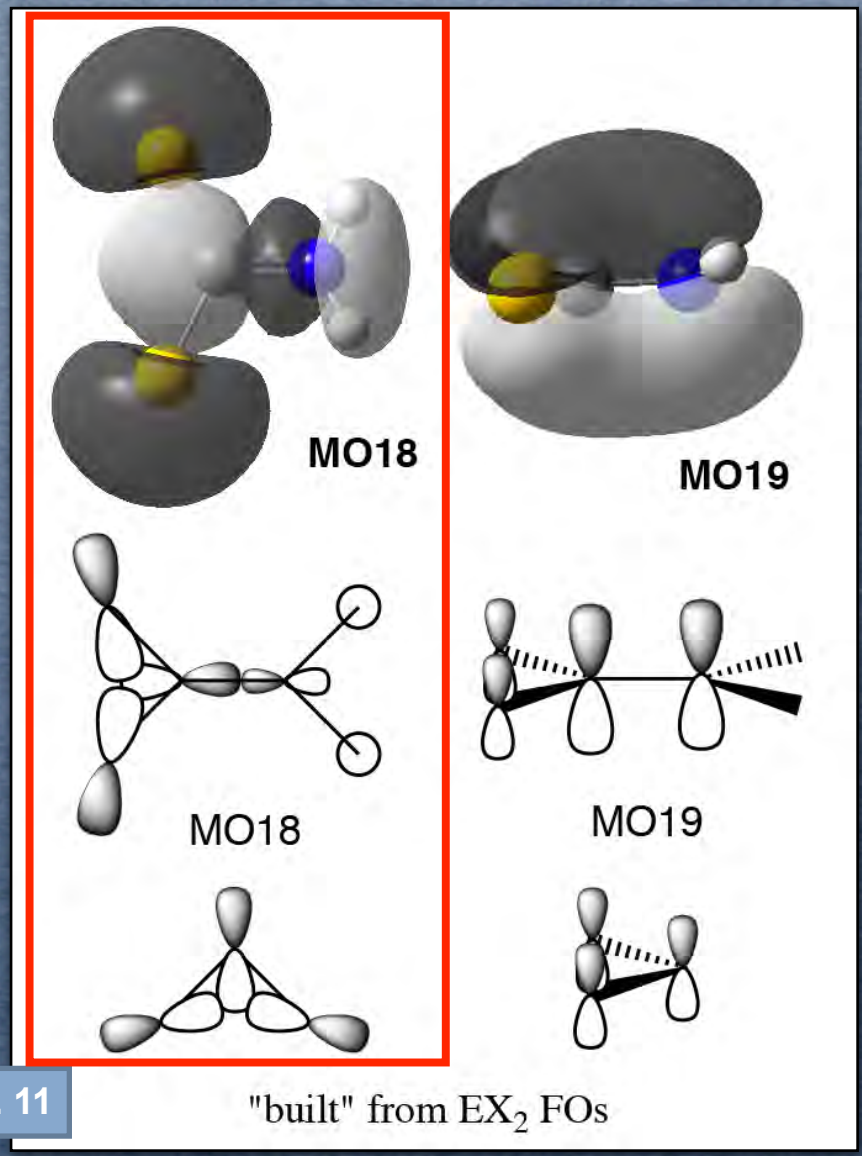

Fig. 11 "built" from EX_2 FOs

LCAO for complex MOs

- **decompose the real MOs into LCAO components**
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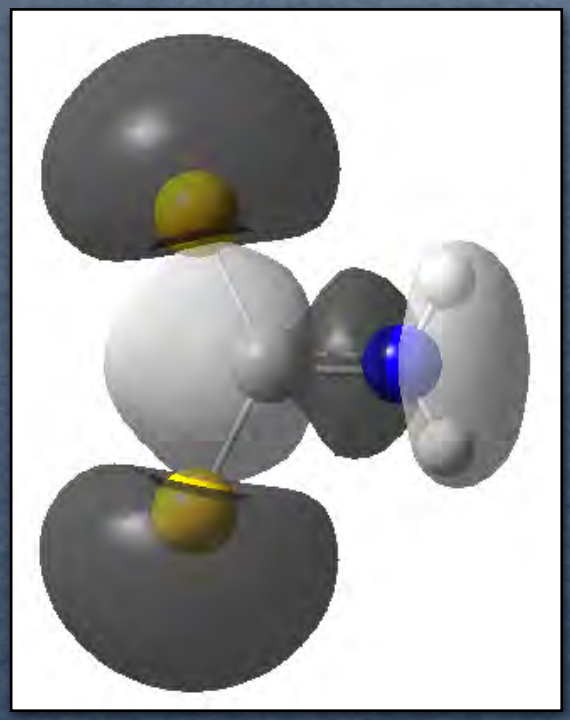
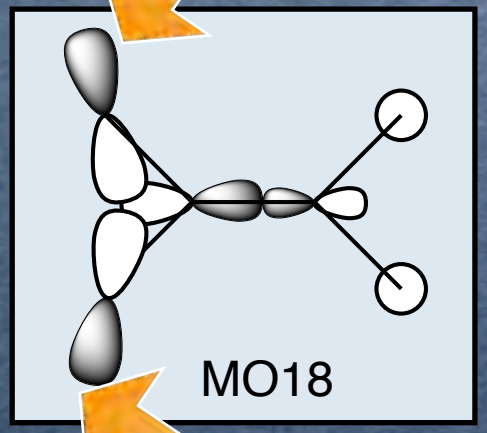
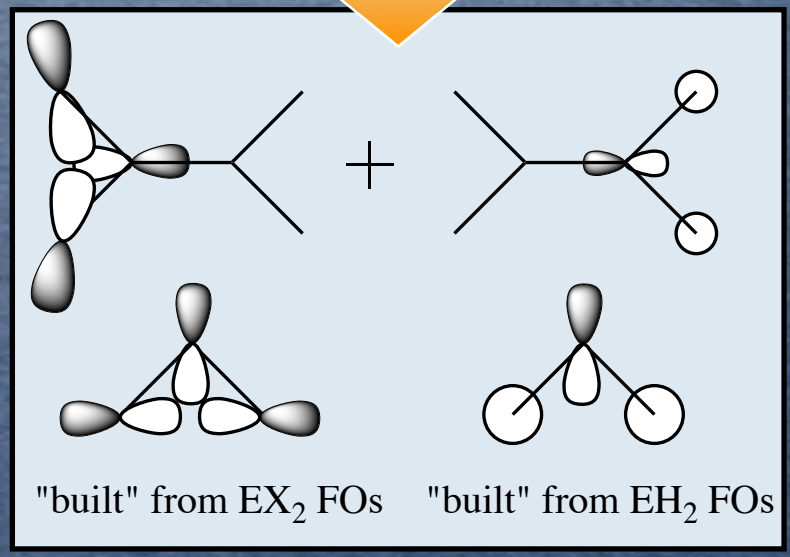


larger contribution



combined "a_1" MOs from EX_2 and EH_2 fragments



orientation!!
draw what you see, FO does not lie along the bonds

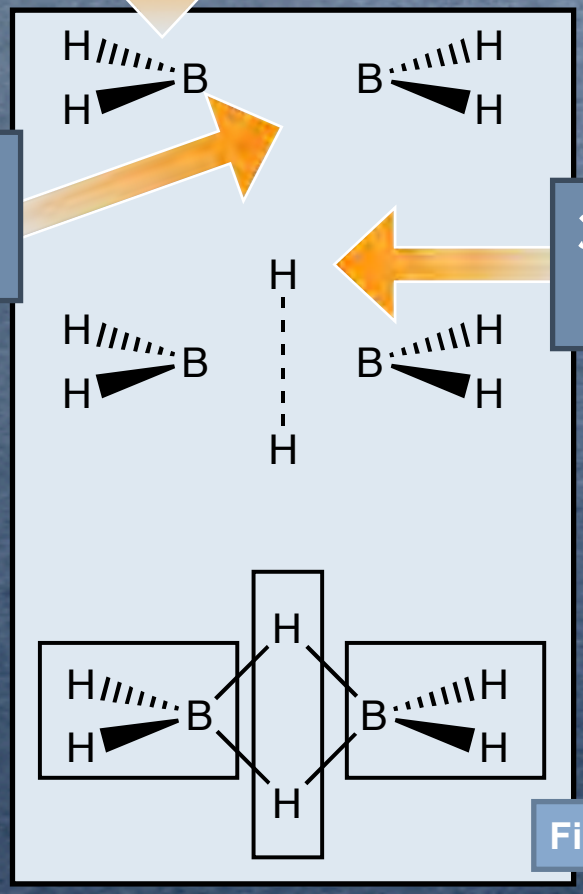
Complex MO Diagrams

- **complex molecules are built up by combining a series of fragments**

1. know the BH_2 fragment

2. combine two BH_2 fragments => intermediate MO diagram

3. add H_2 across centre =>final MO diagram



3 fragments!! form intermediate MO diagram

Fig. 13

Diborane

- **We could expect the bonding in B_2H_6 to be similar to that of ethane**
- **VSEPR theory**
  - does not work!
  - make an *ad-hoc* correction
  - 3 center two electron "bent" bonds
- **Molecular Orbital Theory**
  - MOs are easily developed
  - no special corrections required
  - stability and bonding of diborane explained

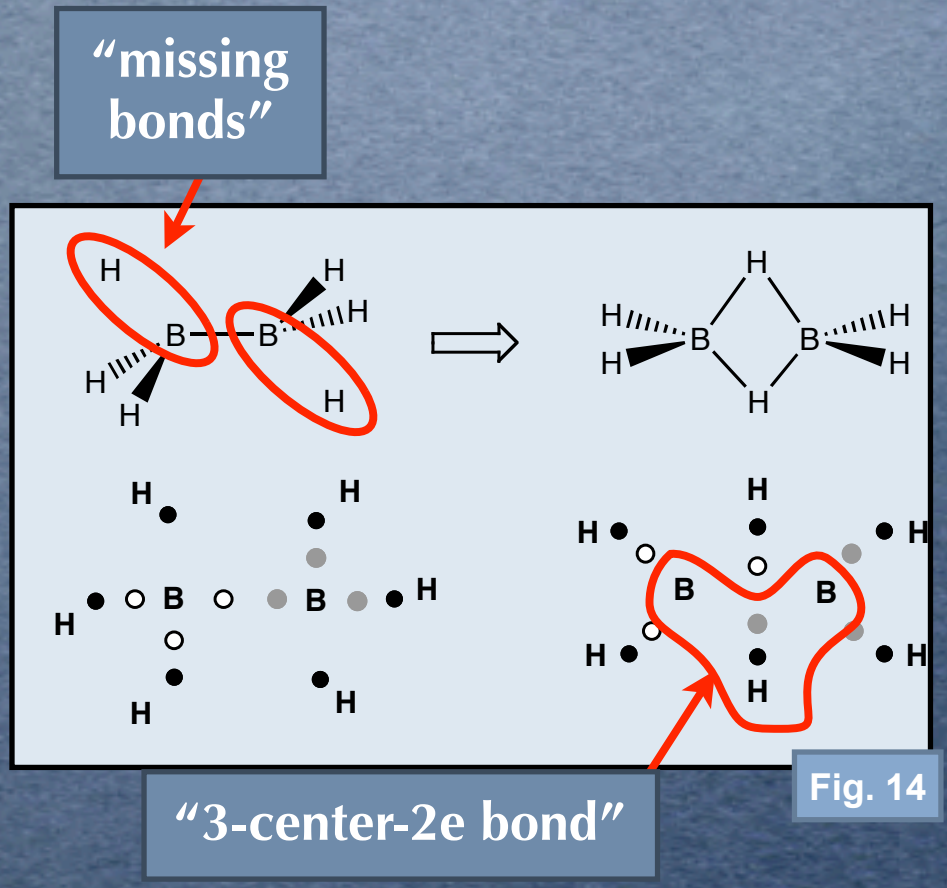


Fig. 14

Revision: MO checklist

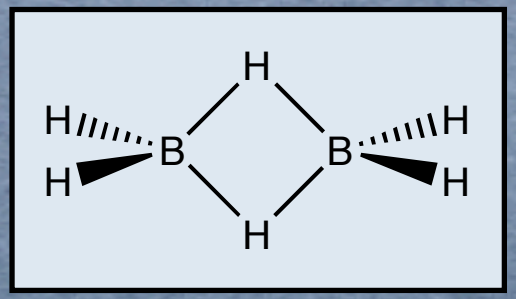
Steps to construct a MO diagram

1. determine the molecular shape and identify the point group of the molecule
2. define the axial system and find all of the symmetry operations on the molecule
3. identify the chemical fragments, and put them along the bottom of the diagram
4. determine the energy levels and symmetry labels of the fragment orbitals
5. combine fragment orbitals of the same symmetry, estimate the splitting energy and 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. use this checklist!
9. analyse the MO diagram

Setting Up

- determine molecular shape
- identify the point group of the molecule: D_{2h}

convince yourself of this for homework



- define the axial system
- find all of the symmetry elements
  - 3 C_2 axes
  - 3 σ planes
  - centre of inversion, i

convince yourself of this for homework

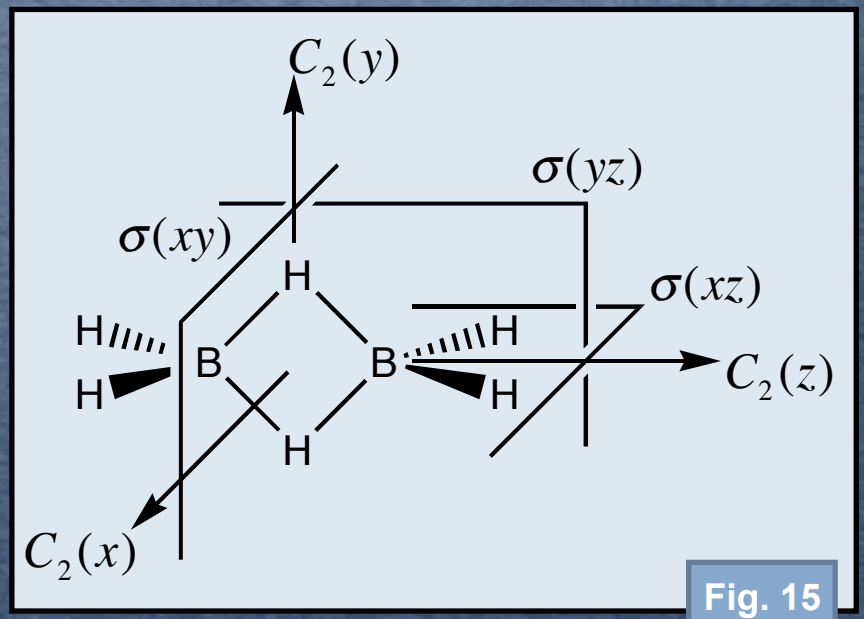


Fig. 15

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Intermediate Diagram

- **treat two BH_2 fragments first**
  - know orbitals for EH_2
  - combine these two in intermediate diagram
  - include orbitals up to LUMO+1
  - requires electronic configuration of fragment
  - B=3 valence e and 2H=2 valence e
  - fragment =5e therefor keep up to b_2 orbital

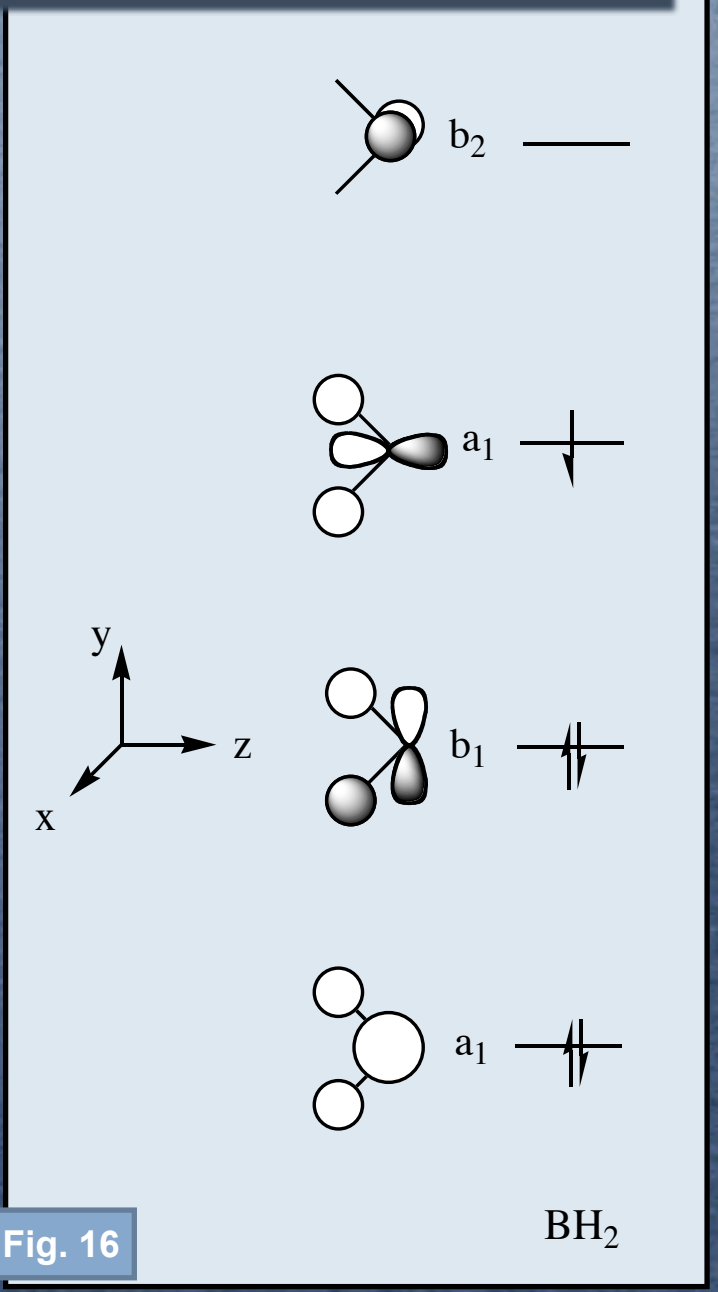

Fig. 16

Revision: MO checklist

Steps to construct a MO diagram

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8. use this checklist!
9. analyse the MO diagram

Form B_2H_4 Fragment

- combine fragment orbitals of the same symmetry
- FIRST work out the MOs
- THEN the splitting energy:
  - degenerate orbitals have a large interaction
  - but BH_2 units are NOT directly bonded and hence have a weaker interaction
  - still moderated by overlap strength: s vs p_σ vs p_π
- make an educated guess that can be justified
- exact ordering will require computation

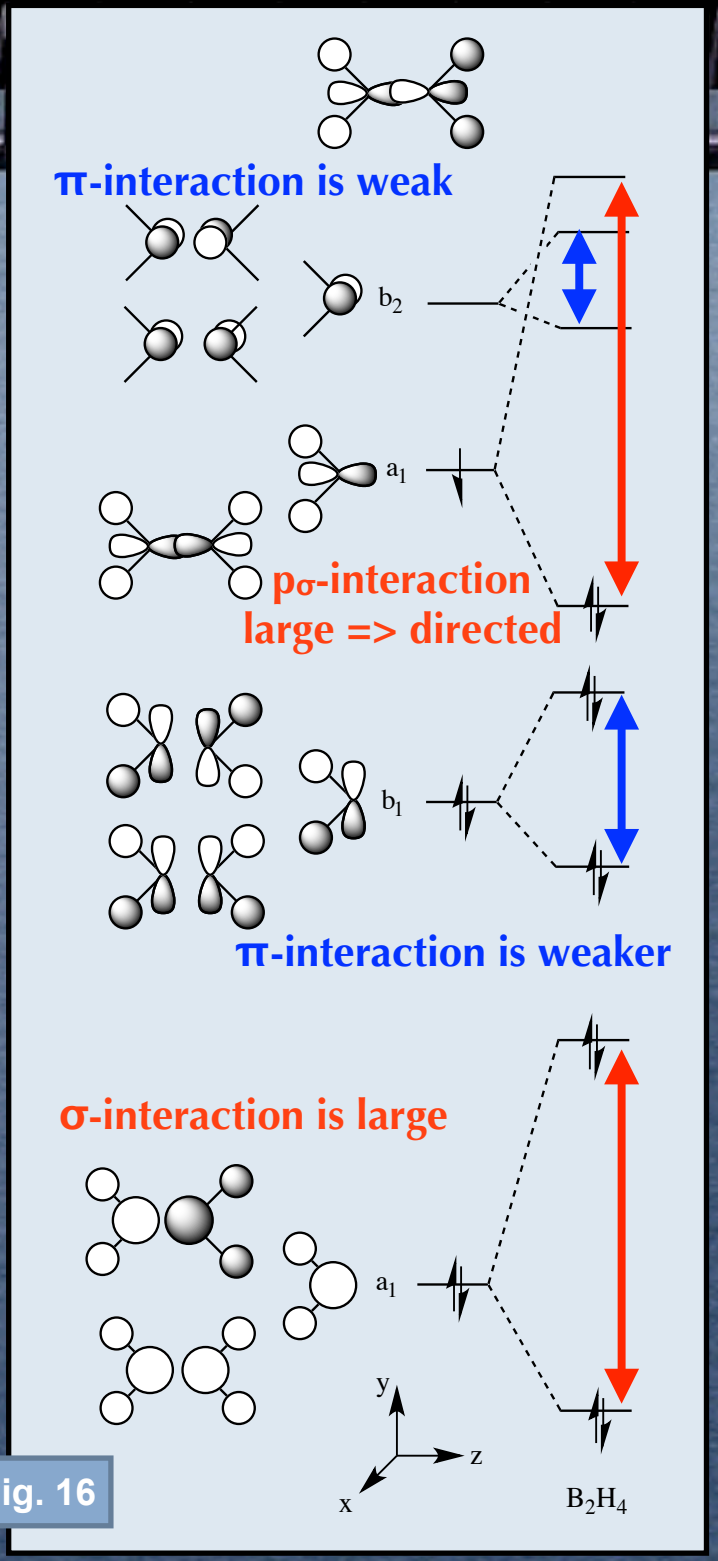


Fig. 16

Symmetry Labels?

- totally bonding MO

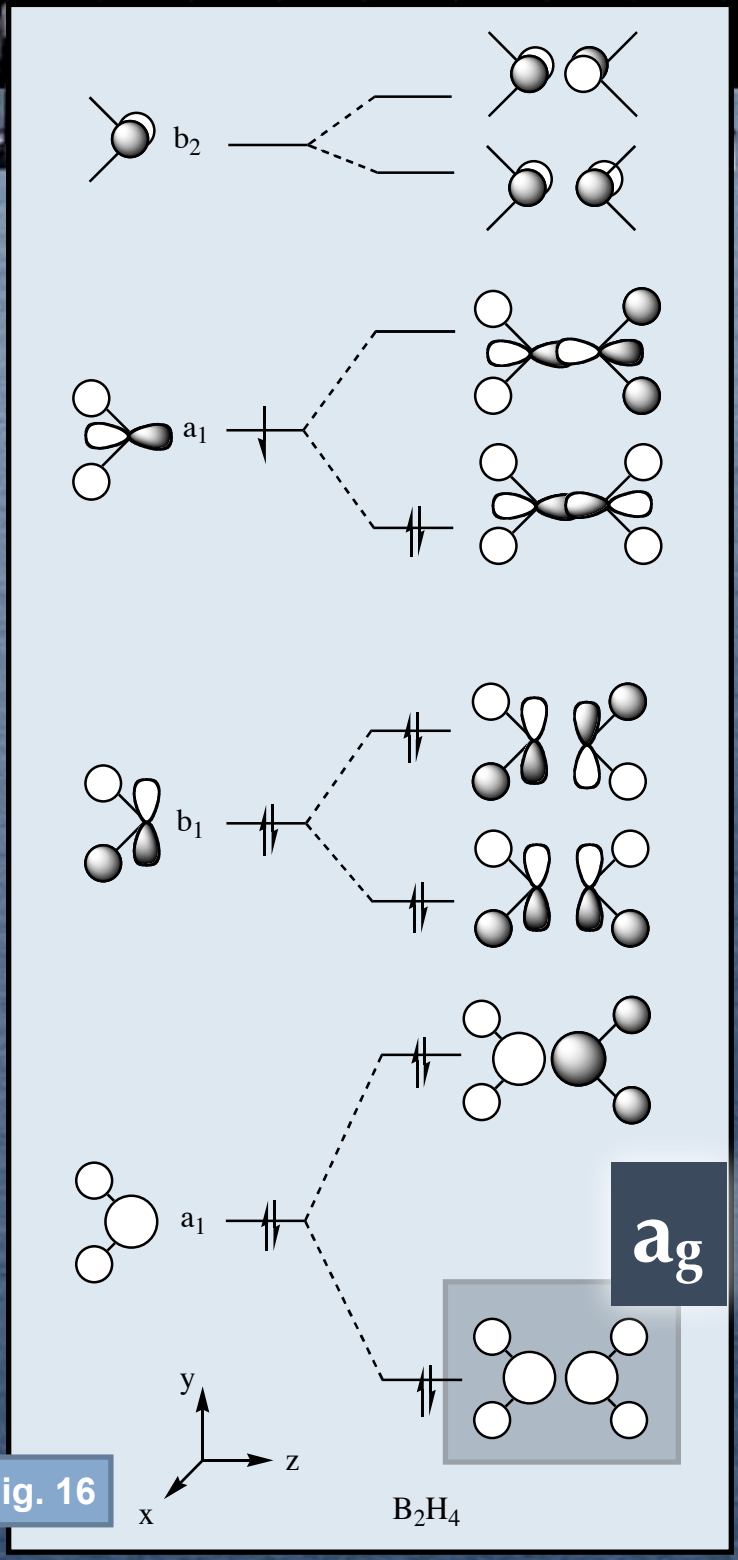
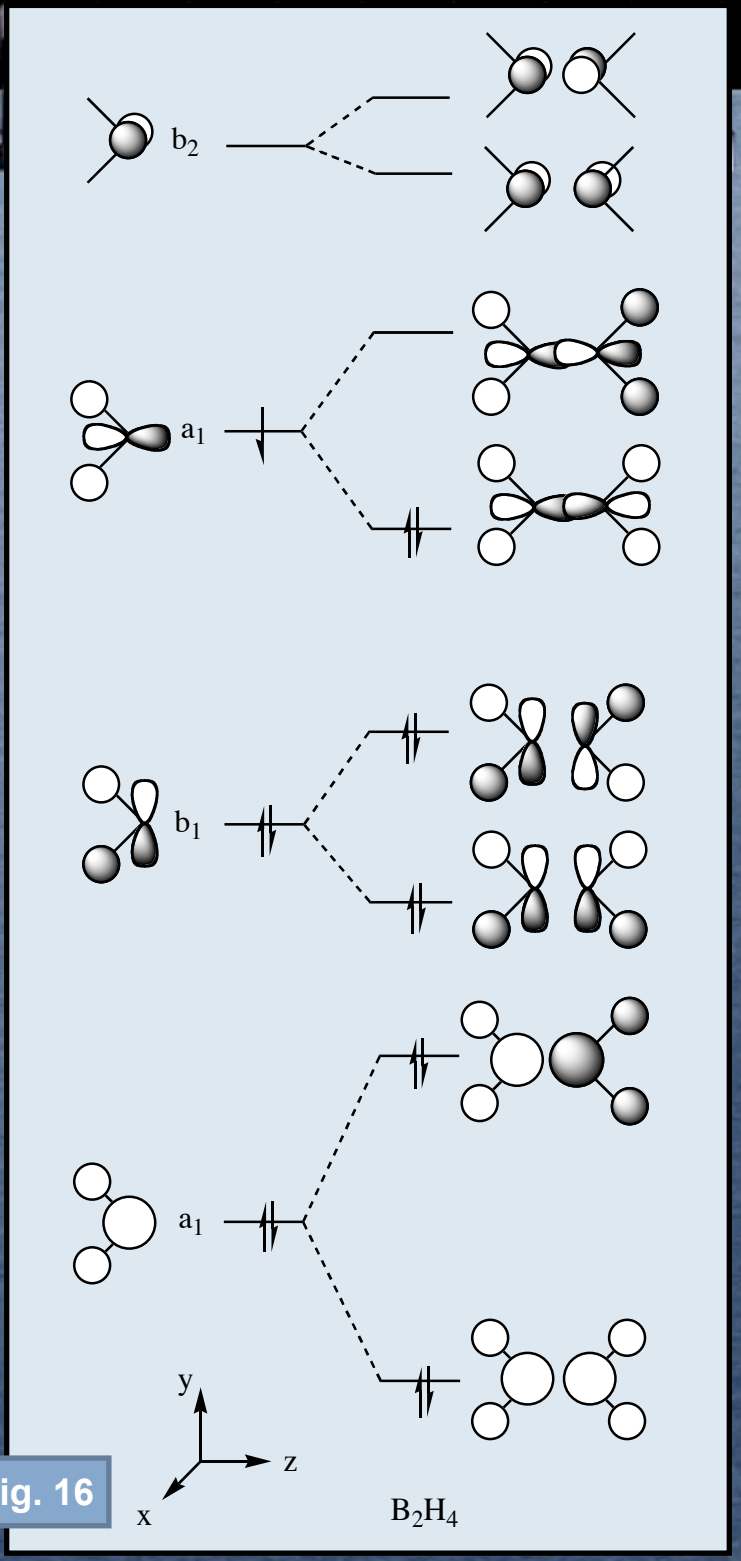


Fig. 16

Symmetry Labels?

- totally bonding MO
- which symmetry label is associated with each of the axes?
  - x-axis = b_{3u}
  - y-axis = b_{2u}
  - z-axis = b_{1u}

see the character table



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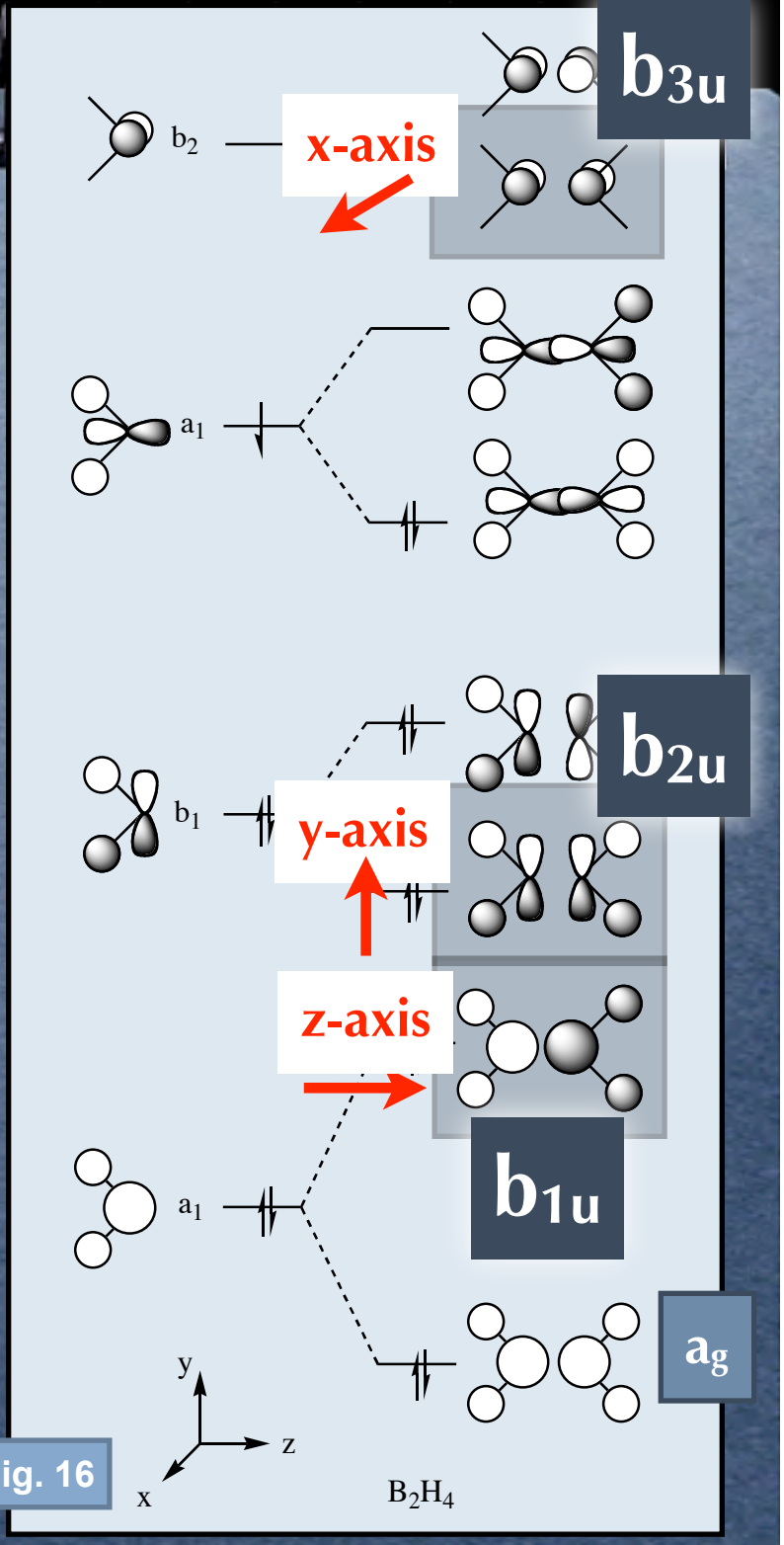

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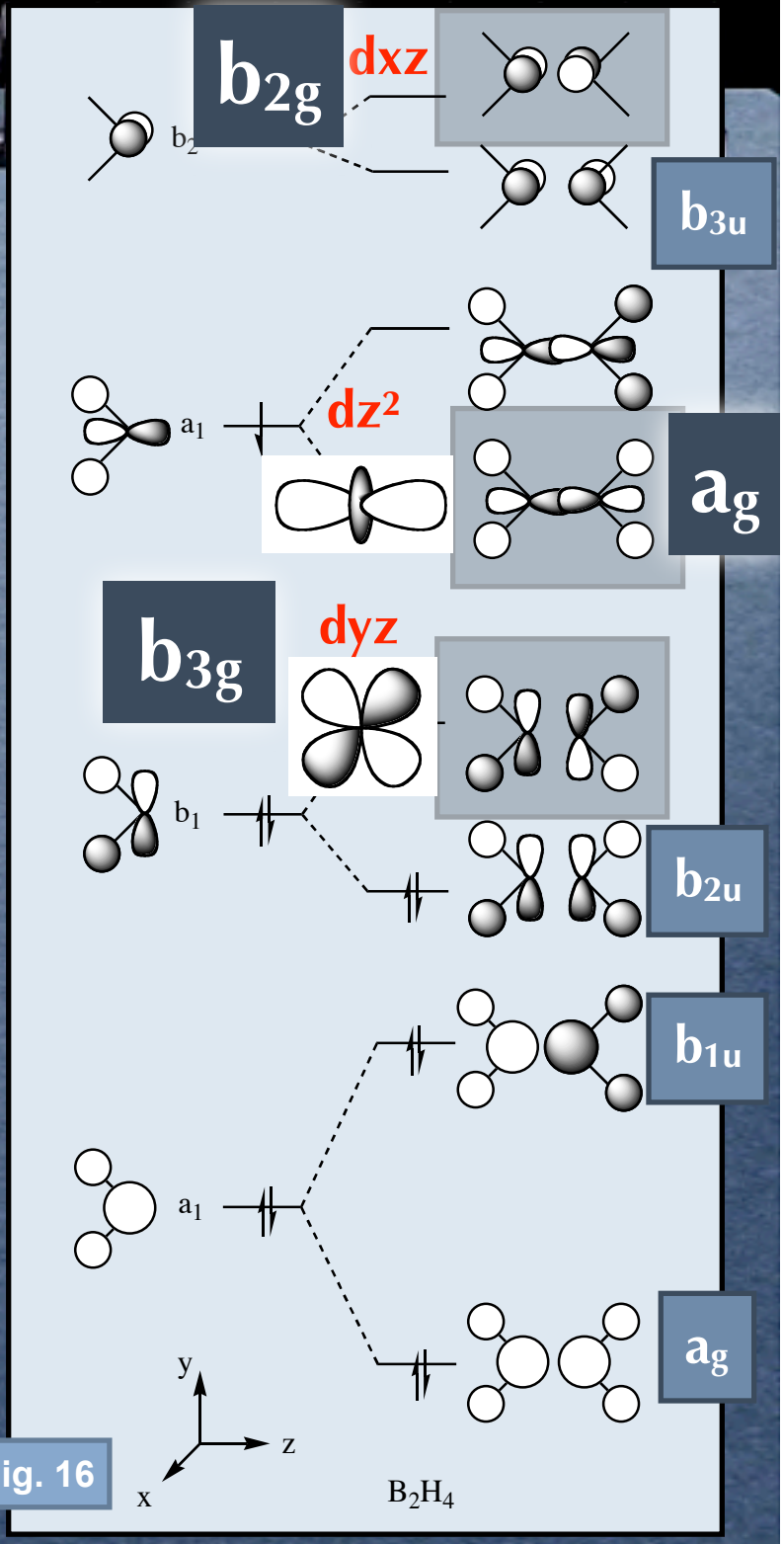
- which MOs have the same phase pattern as dAOs?



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  - x-axis = b_{3u}
  - y-axis = b_{2u}
  - z-axis = b_{1u}
- which MOs have the same phase pattern as dAOs?
- final MO: use representation table

Fig. 19

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
Γ { }	1	1	-1	-1	-1	-1	1	1

b_{1u} symmetry

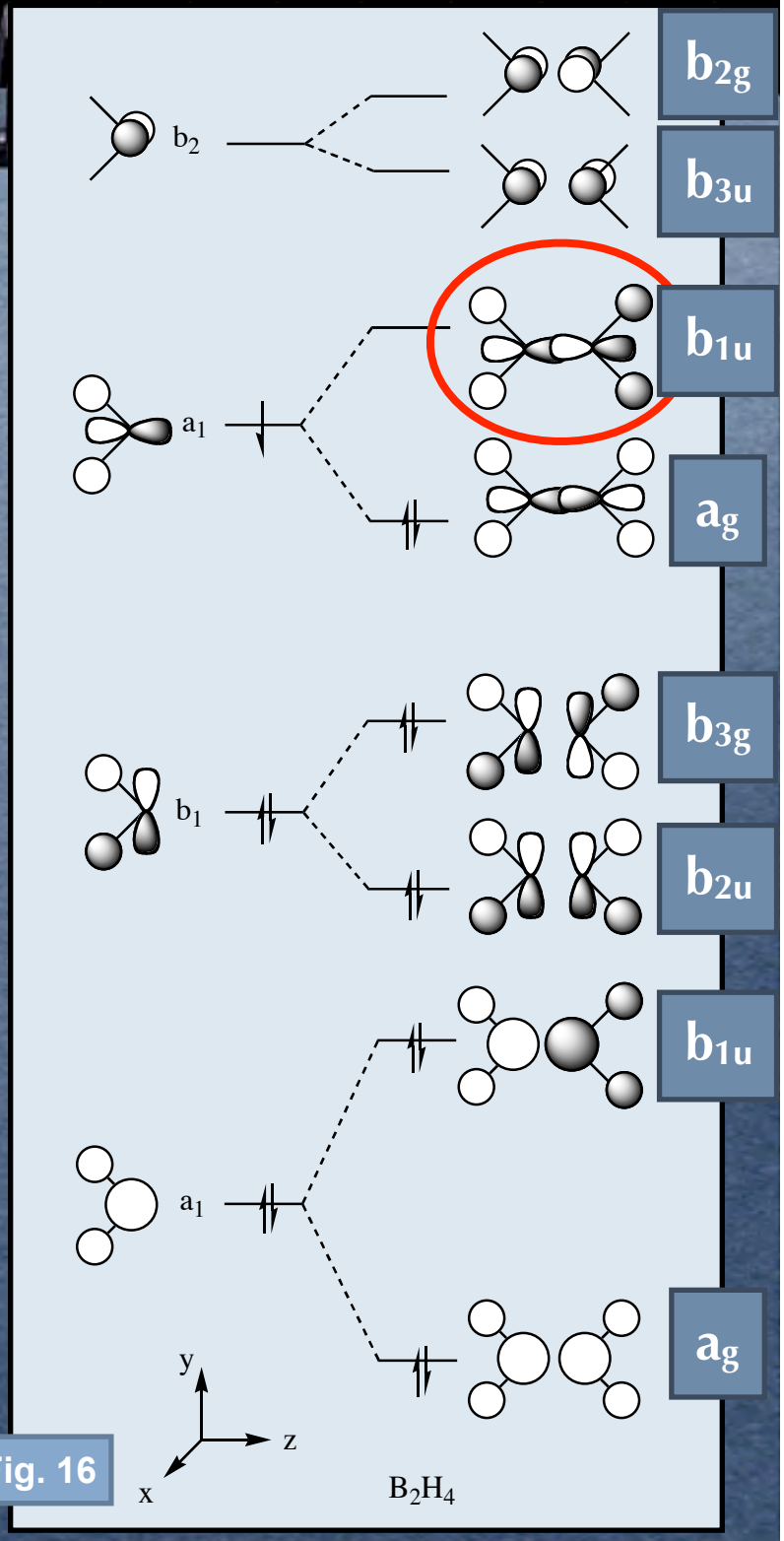


Fig. 16

Fragments:

- use the molecular fragments because it is easier to work out the interactions of degenerate fragments

two BH_2 fragments

we already know MOs for AH_2 from H_2O

add H_2 across

MOs for H_2 are very simple!

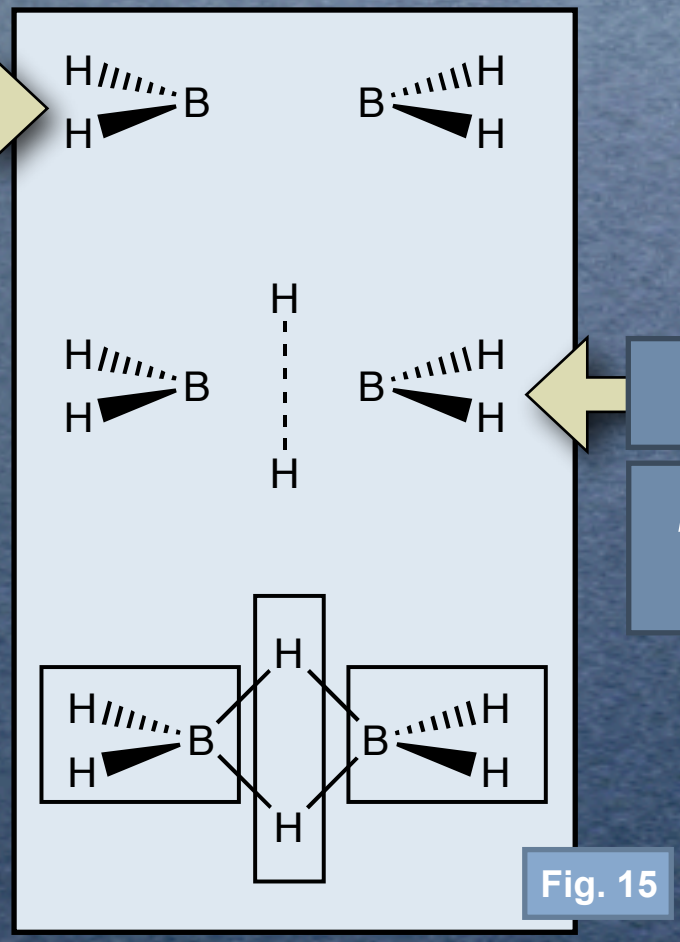


Fig. 15

Set-Up

- **Where will the H_2 orbitals lie?**
- **the H atoms are not directly bonded**
  - means small splitting energy
  - means fragments are almost non-bonding
  - so they will lie near non-bonding orbitals of B_2H_4 fragment

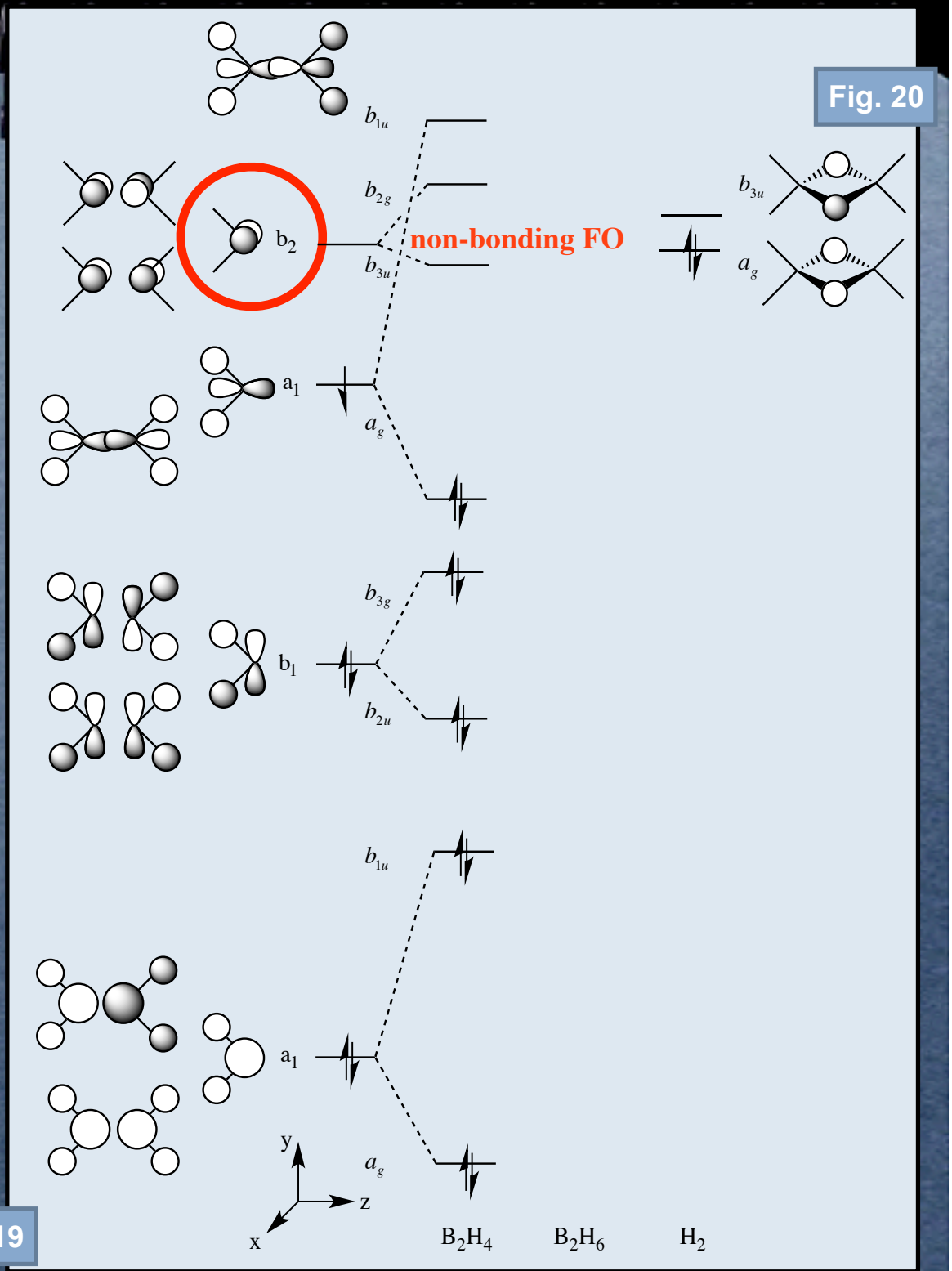


Fig. 19

MO Diagram

- **Combine orbitals of the same symmetry**
- **a_g**
  - lowest B_2H_4 a_g orbital is too deep and will not interact
  - the energy levels are not very close, but overlap is good stabilisation is medium

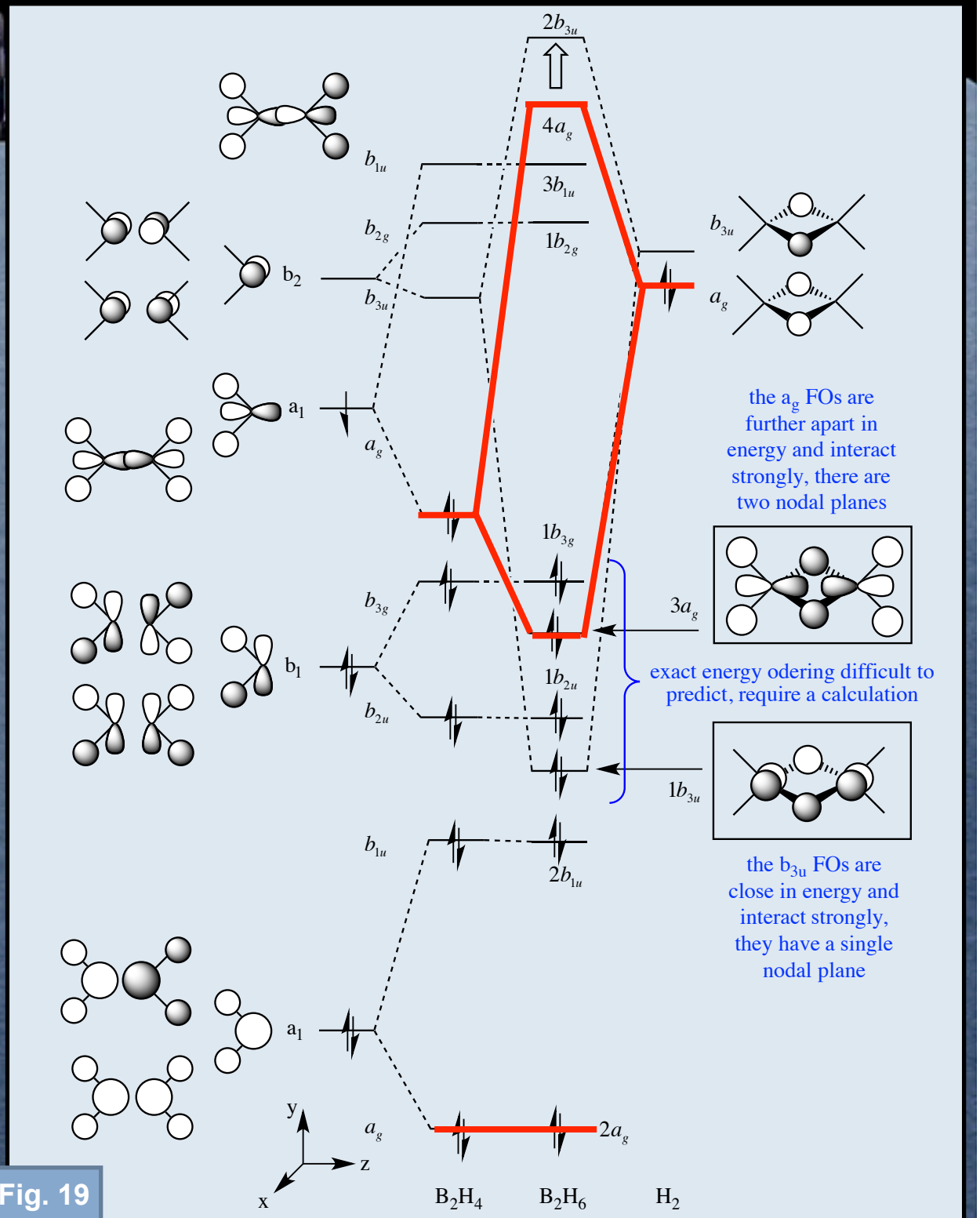


Fig. 19

MO Diagram

- **Combine orbitals of the same symmetry**
- **b_{3u}**
  - there is only one b_{3u} orbital on B_2H_4 fragment
  - the energy levels are almost degenerate, stabilisation is large

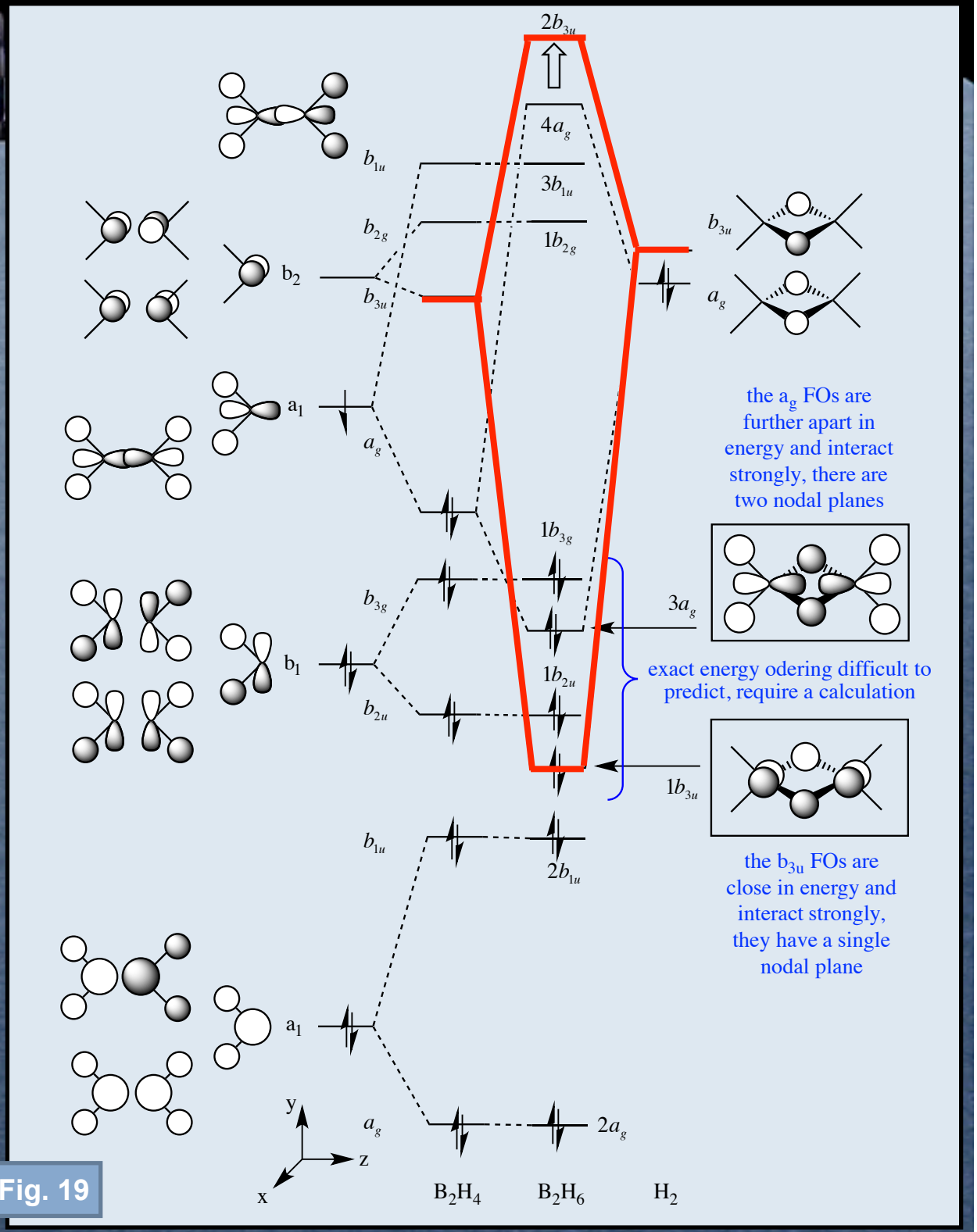


Fig. 19

Revision: MO checklist

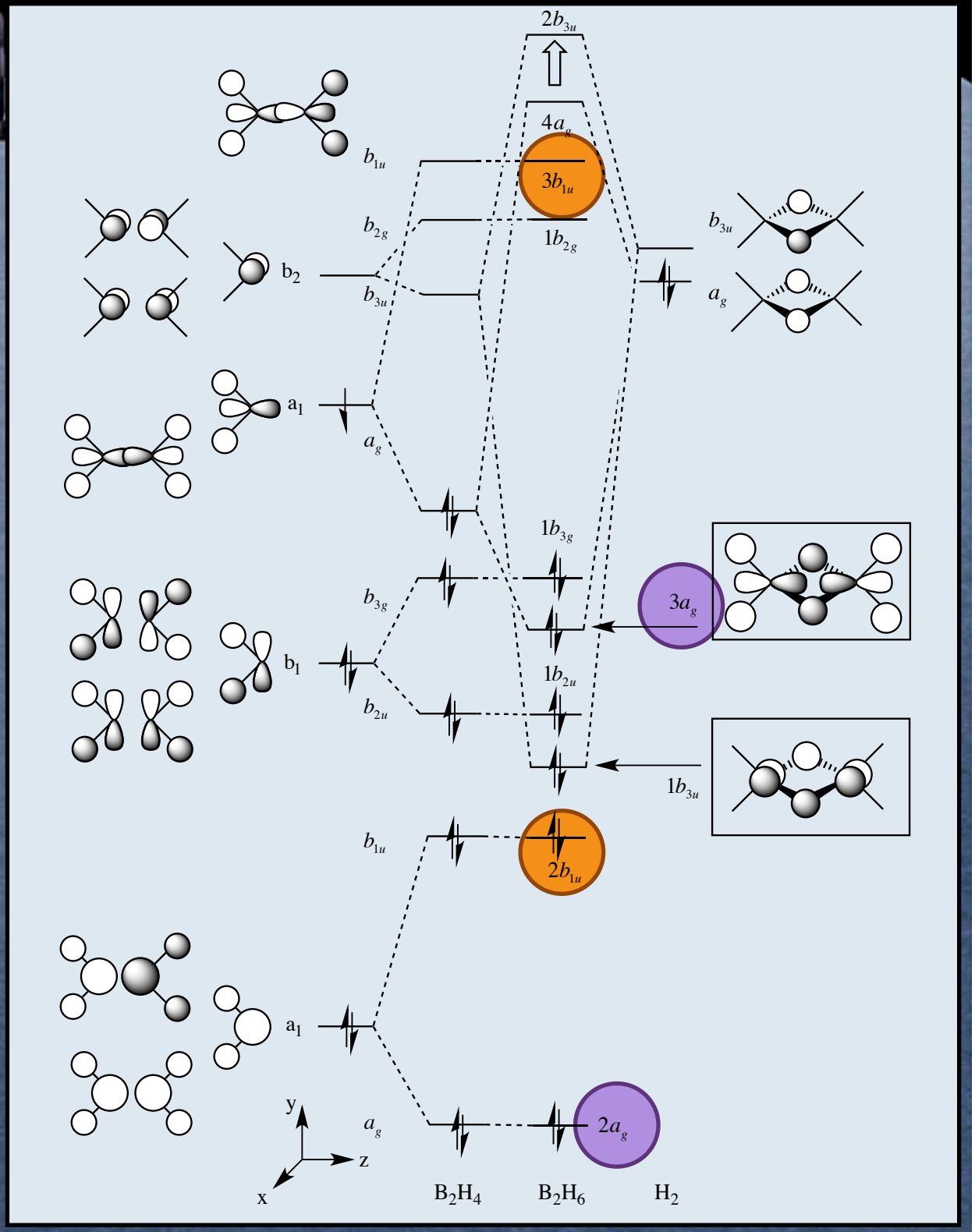
Steps to construct a MO diagram

1. determine the molecular shape and identify the point group of the molecule
2. define the axial system and find all of the symmetry operations on the molecule
3. identify the chemical fragments, and put them along the bottom of the diagram
4. determine the energy levels and symmetry labels of the fragment orbitals
5. combine fragment orbitals of the same symmetry, estimate the splitting energy and 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. use this checklist!
9. analyse the MO diagram

MO Diagram

- **Configuration**
  - 10e from B_2H_4 fragment and 2e from H_2 =12e
- **Only MOs of the same symmetry mix**
  - must also be close in energy
  - greatest between occupied and unoccupied orbitals
- **a_g and b_{1u} ?**
  - b_{1u} too far apart in energy
  - a_g both occupied

NO mixing!



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Analysis

- 4 of the occupied MOs are non-bonding with respect to the bridging H atoms

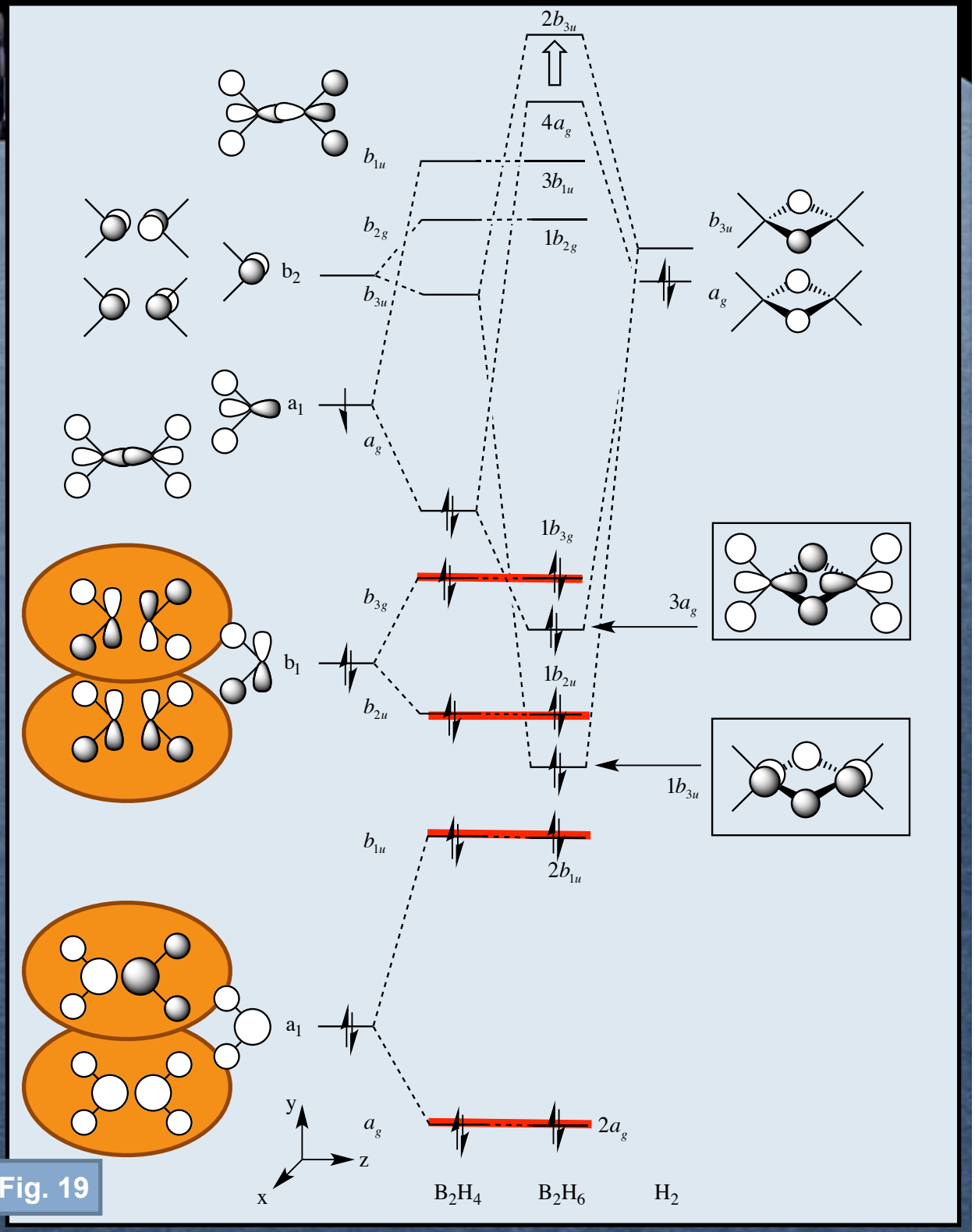


Fig. 19

Analysis

- 4 of the occupied MOs are non-bonding with respect to the bridging H atoms
- 2 of the occupied MOs describe bonding with the bridging H atoms
- natural description which doesn't require us to invoke "add-hoc" corrections to a theory

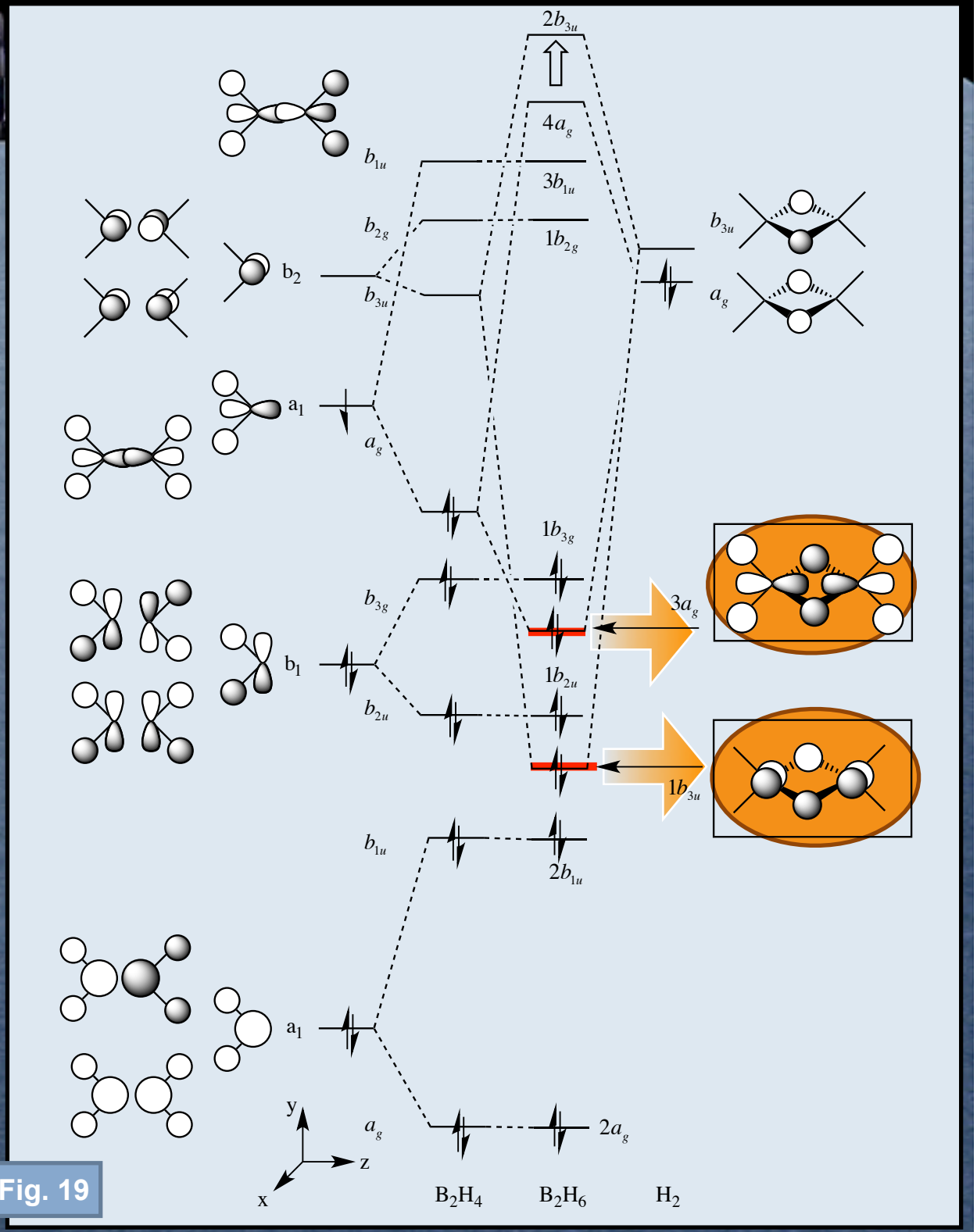


Fig. 19

Analysis

- 4 of the occupied MOs are non-bonding with respect to the bridging H atoms
- 2 of the occupied MOs describe bonding with the bridging H atoms
- natural description which doesn't require us to invoke "add-hoc" corrections to a theory
- LUMO is essentially non-bonding between BH_2 units (and H_2)
- low energy for a LUMO
- can accept electrons without destabilising the molecule

$B_2H_6^{2-}$ is stable!

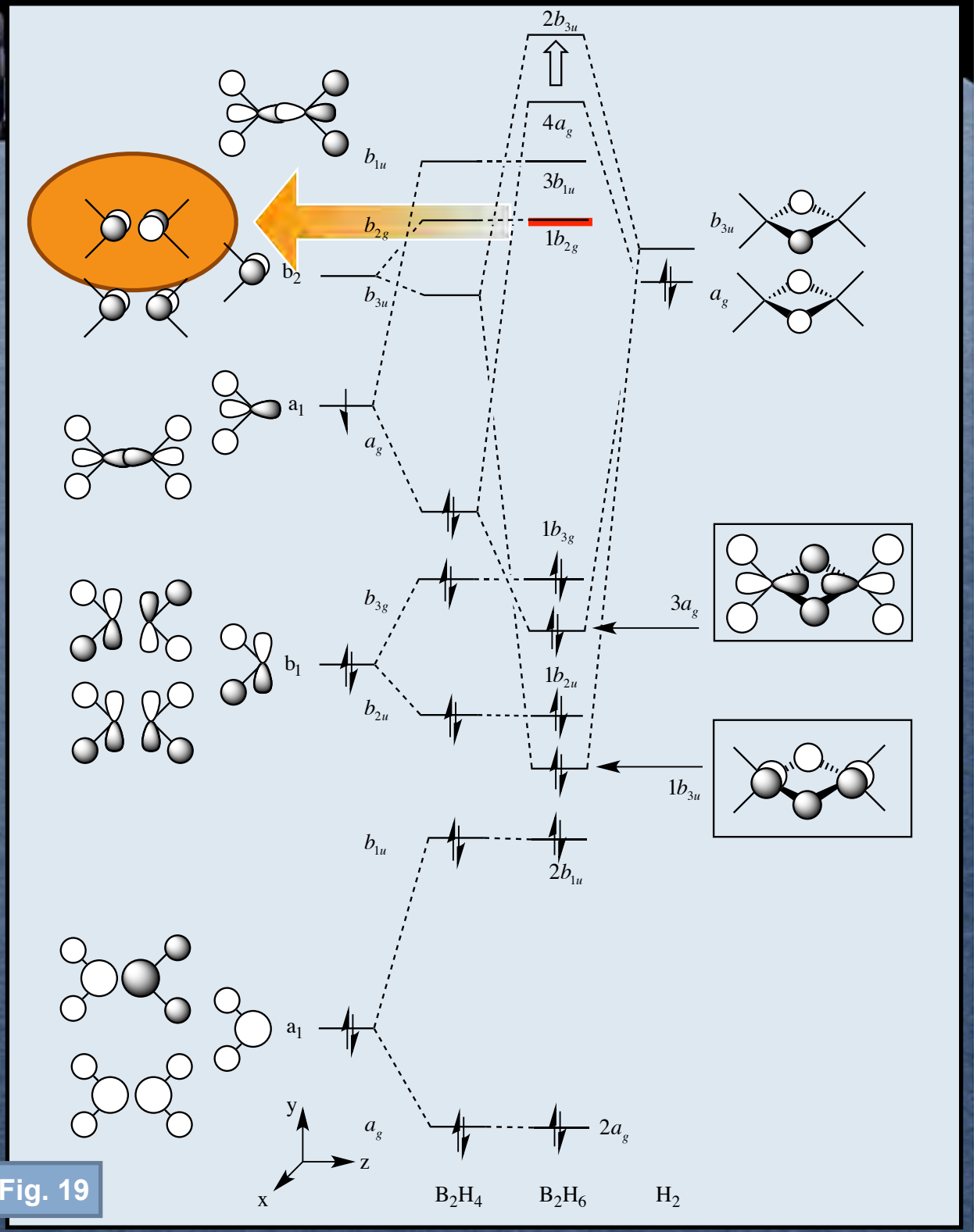
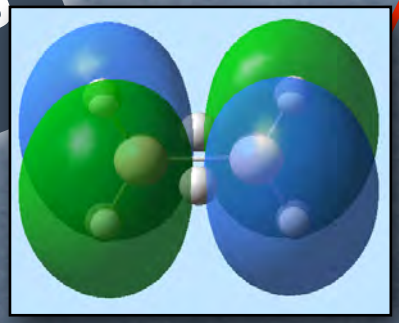


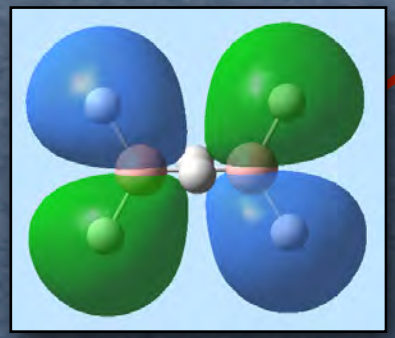
Fig. 19

Analysis

- qualitative MO diagram

exact ordering can vary





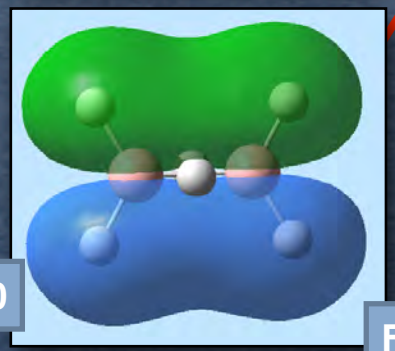


Fig. 20

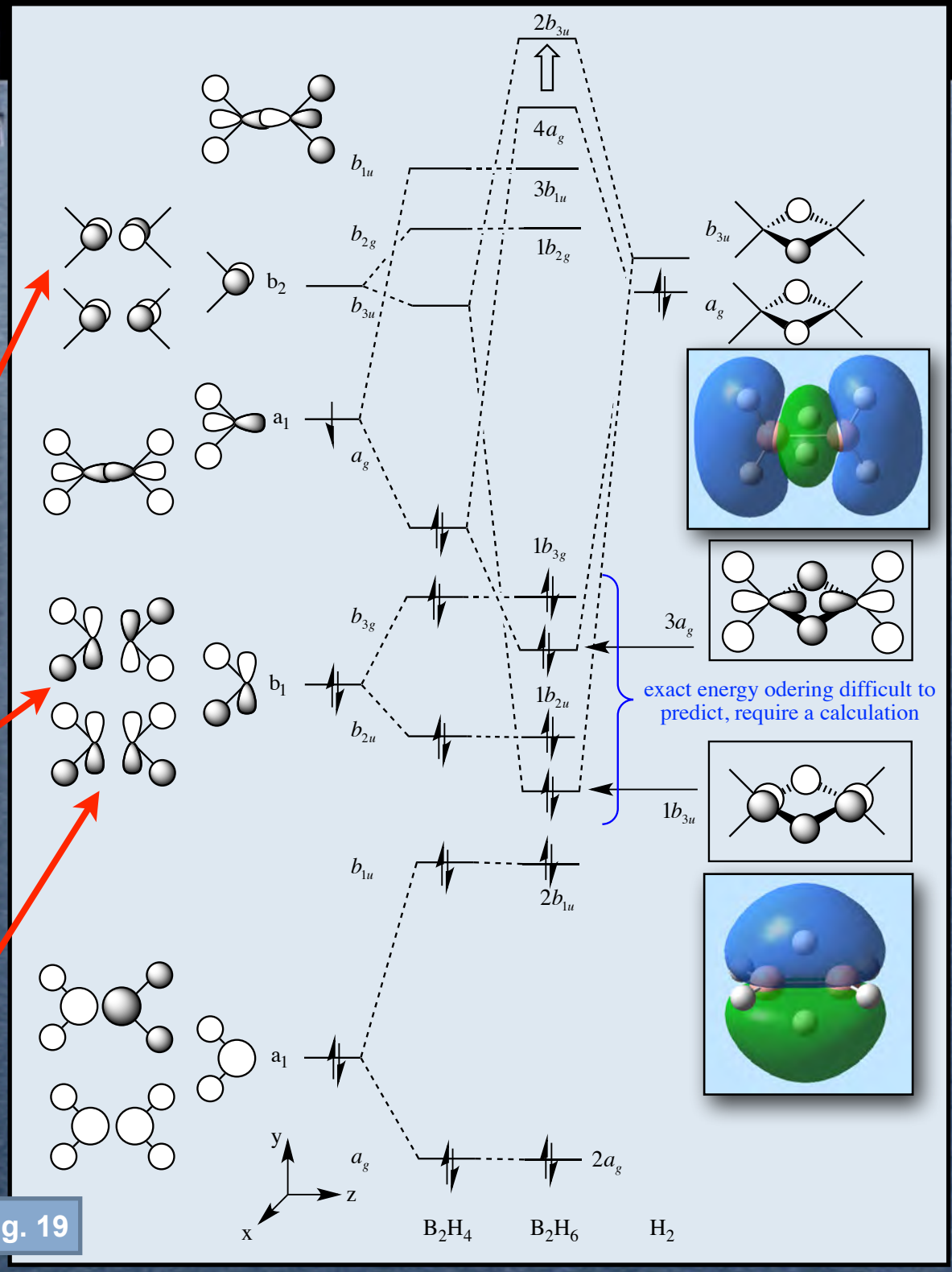


Fig. 19

Key Points

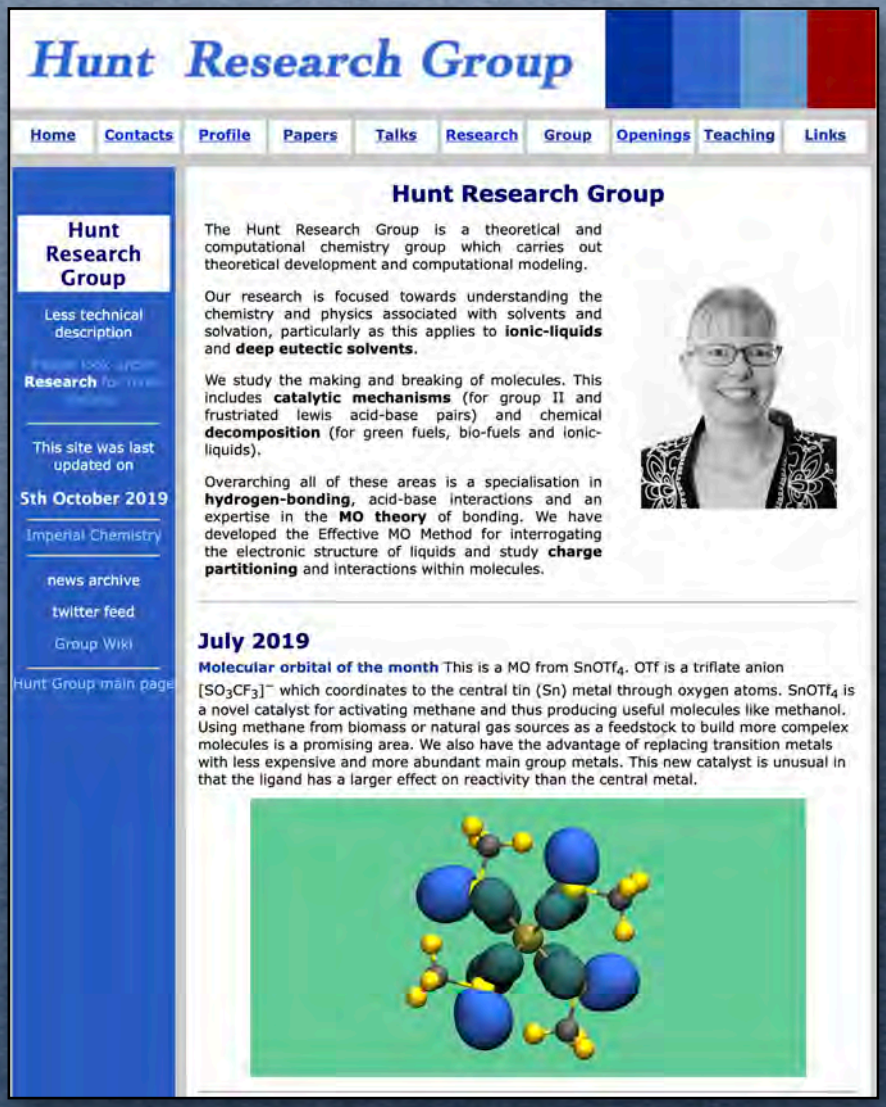
- be able to differentiate between symmetry and molecular fragments and be able to choose fragments that make generating the MO diagram easier
- be able to quickly determine the symmetry of MOs using character tables and "short-cuts"
- be able to explain the bonding/antibonding qualities of a set of MOs and annotate a diagram showing the key characteristics
- be able to represent complicated computed MOs in terms of LCAOs
- be able to discuss the bonding in B_2H_6 with respect to VSEPR theory, delocalisation, and MO theory. Be able to justify the stability of $B_2H_6^{2-}$
- be able to form a MO diagram for A_2H_2, A_2H_4, A_2H_6 and analyse the MO diagram for information relating to structure and bonding

Finally

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

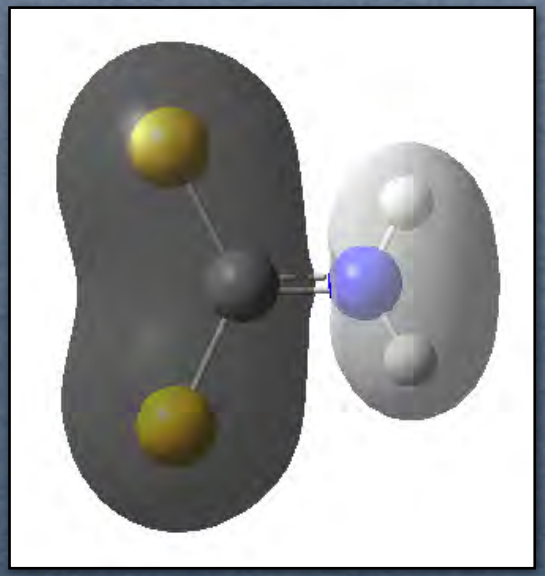
See my web-site

- 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!!

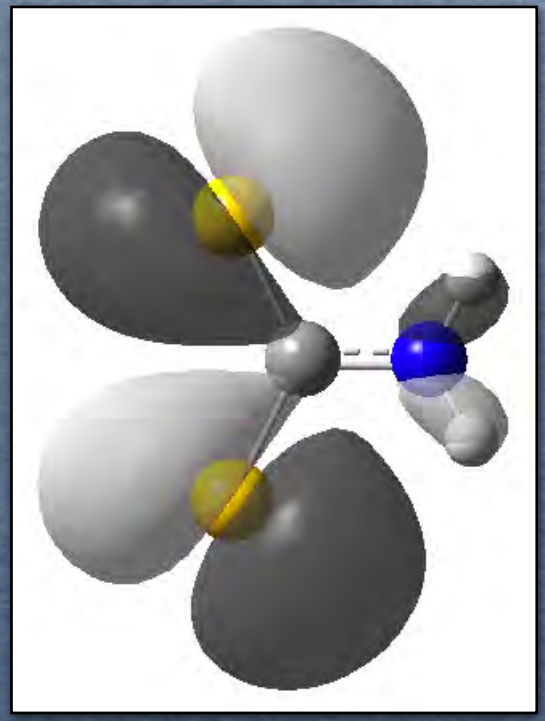


In-Class Activity

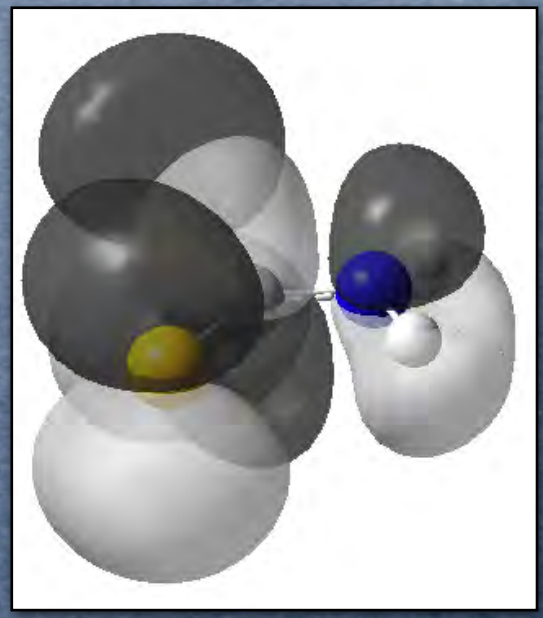
- **draw the LCAO for MO14, M24 and MO25**



MO 14



MO 24
HOMO



MO 25
LUMO