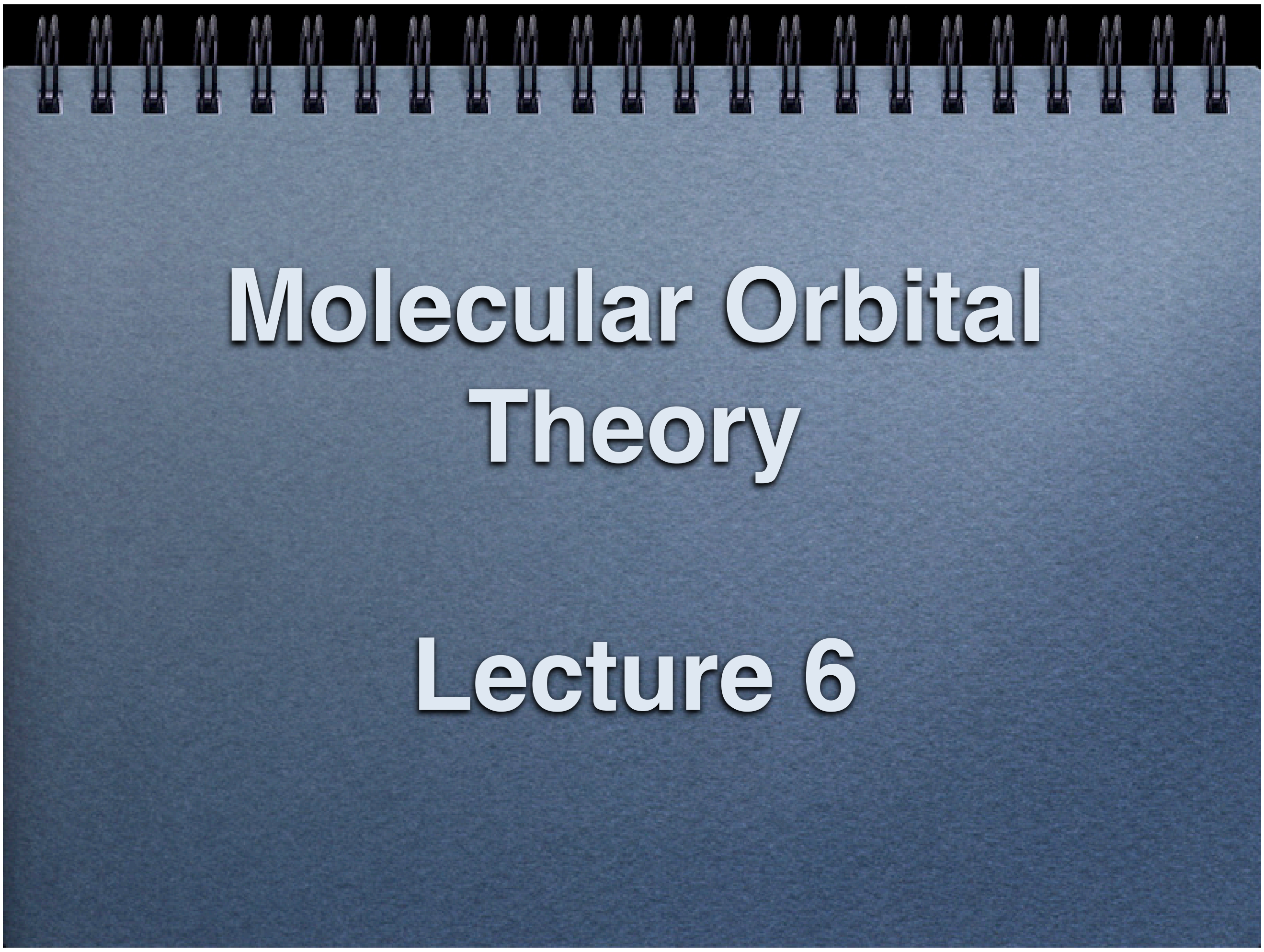
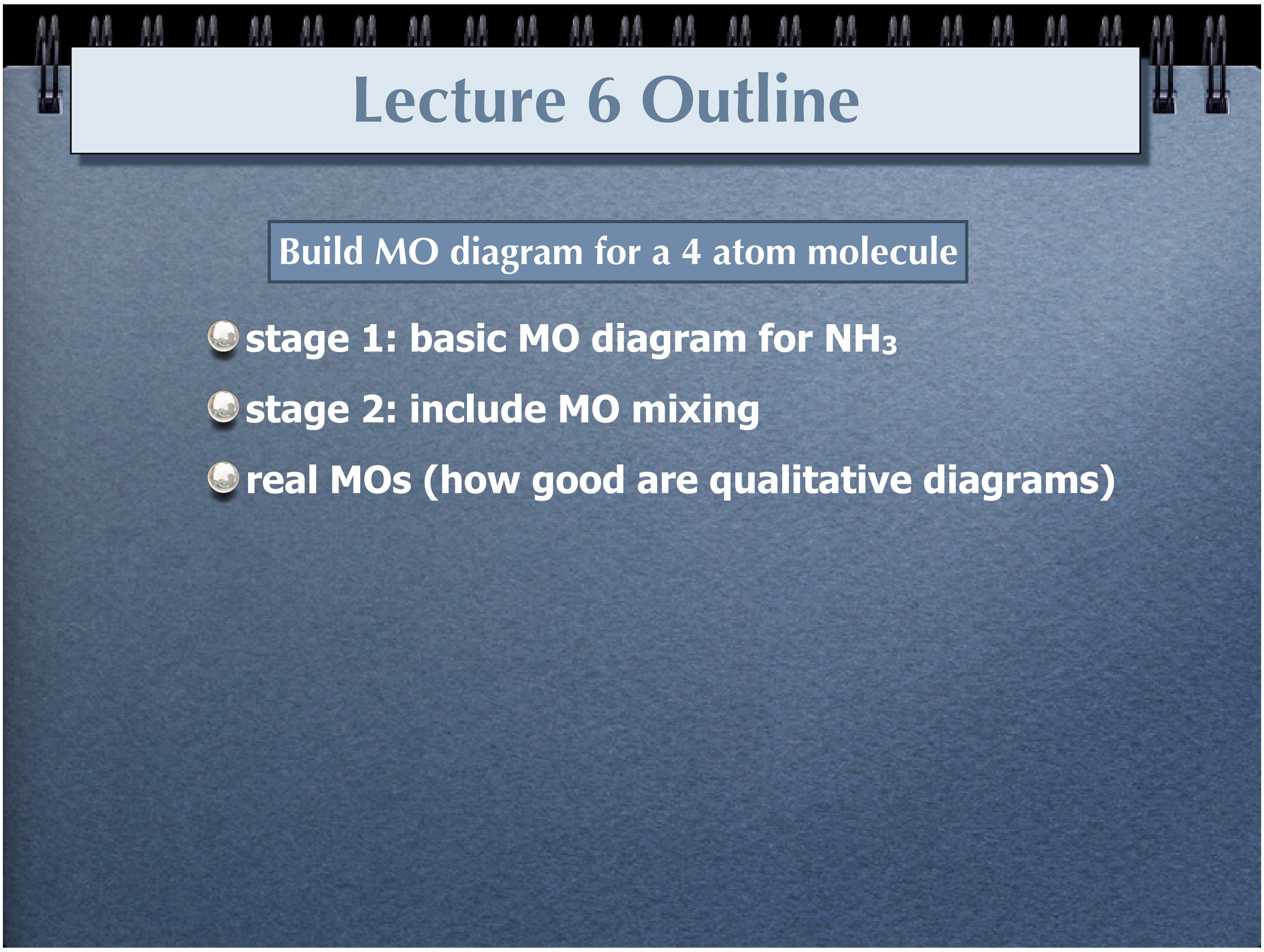


Molecular Orbital Theory

Lecture 6

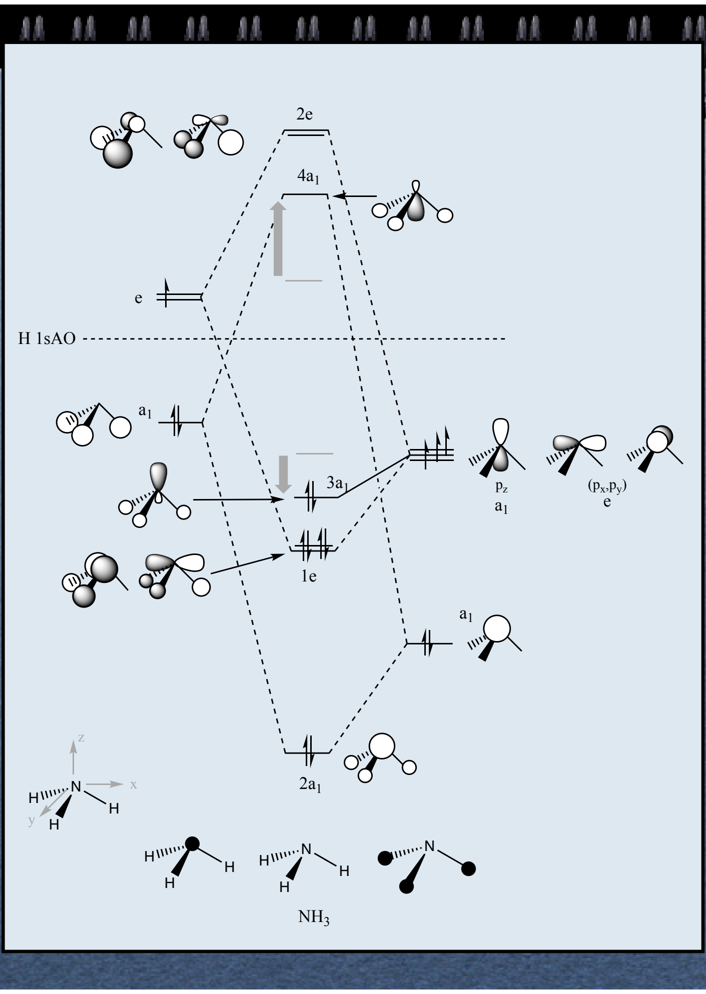


Lecture 6 Outline

Build MO diagram for a 4 atom molecule

- stage 1: basic MO diagram for NH_3
- stage 2: include MO mixing
- real MOs (how good are qualitative diagrams)

MO Diagram of Ammonia



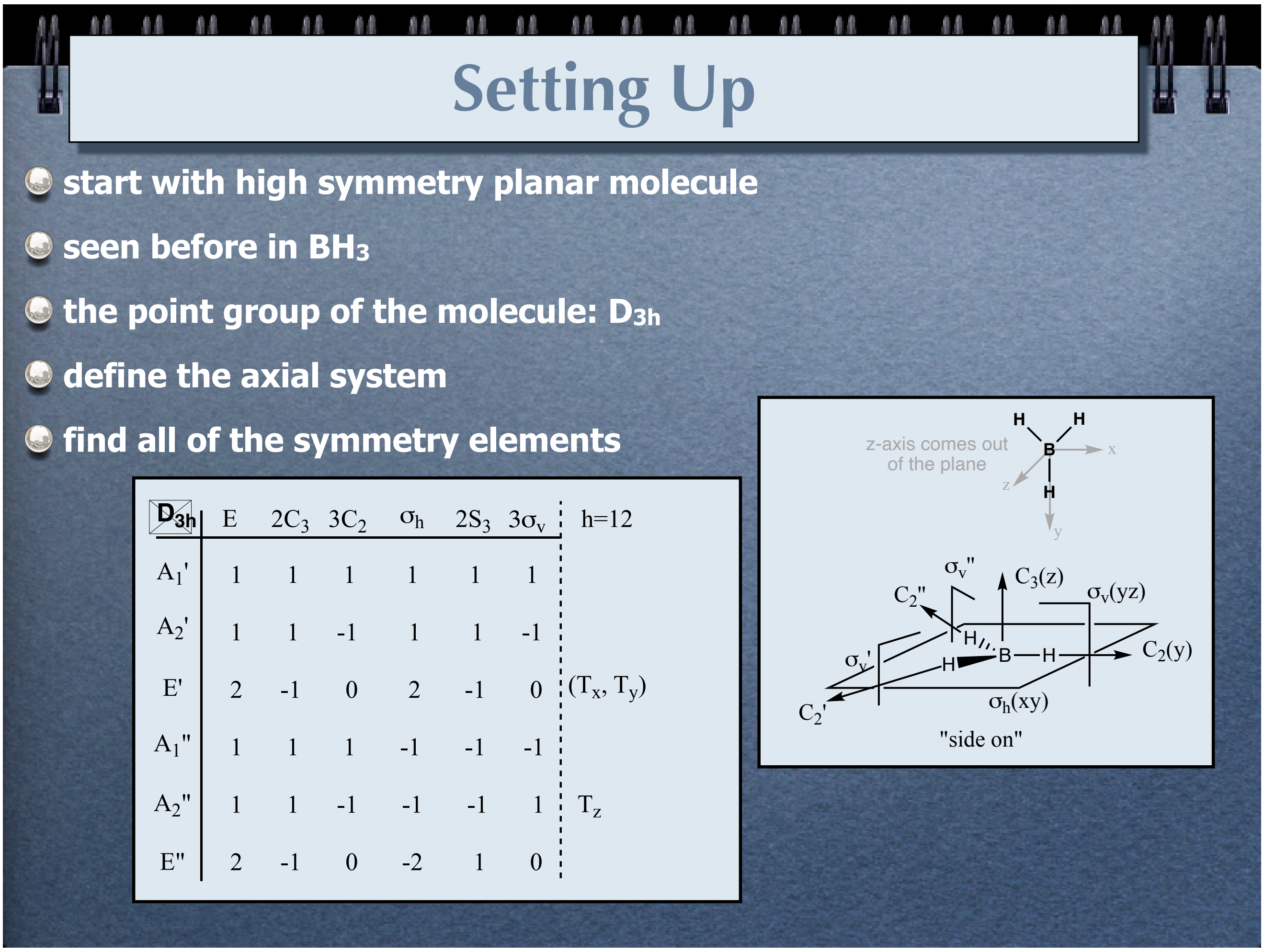
MO checklist

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, sketch out the MOs and analyse the bonding/antibonding character
- ✦ estimate the splitting energy for each pair of MOs, 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 the MO diagram
- ✦ use the MO diagram to understand the structure, bonding and chemistry of the molecule

steps we will use today to form the MO diagram

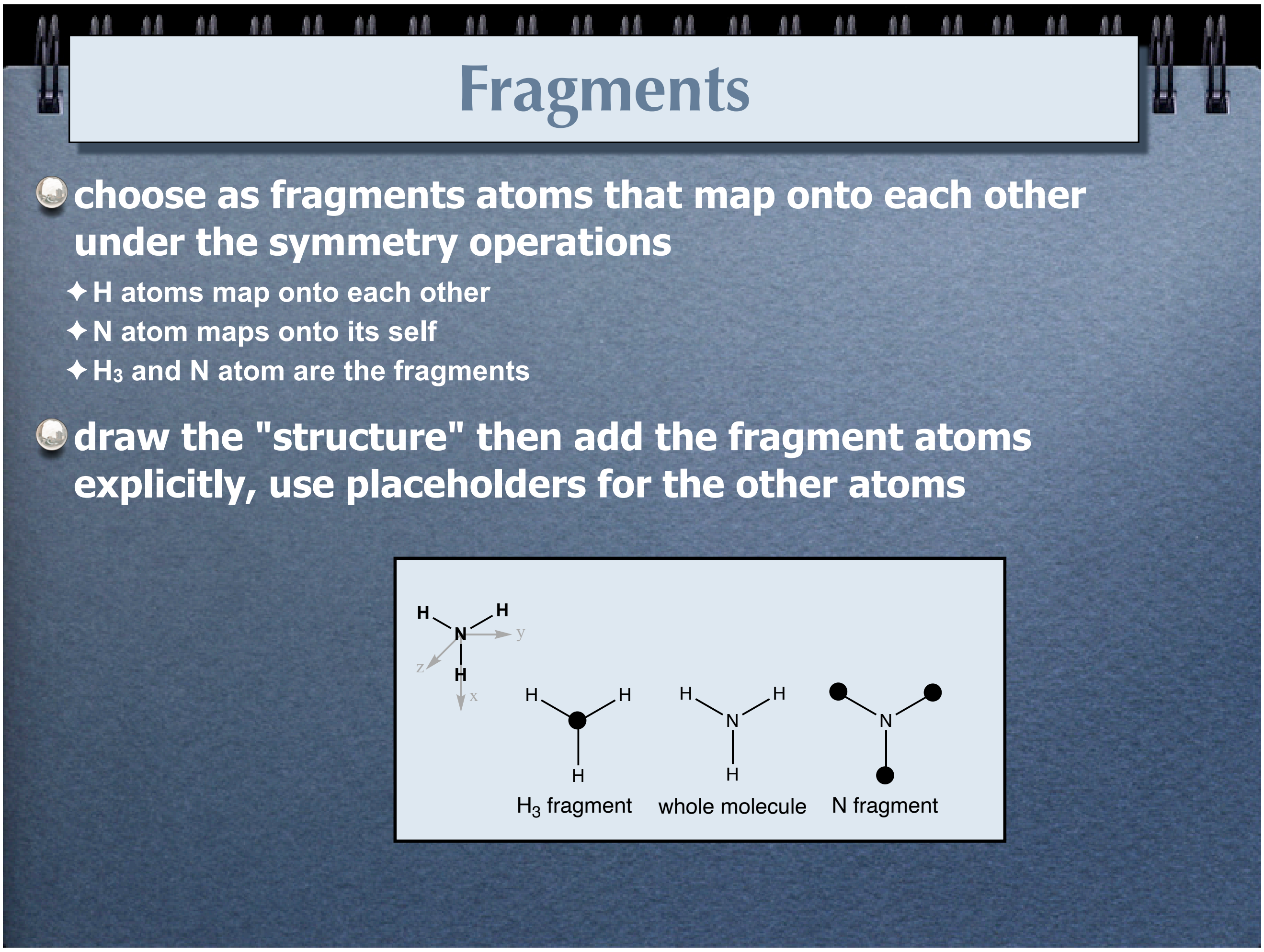
VERY Important!



Setting Up

- start with high symmetry planar molecule
- seen before in BH_3
- the point group of the molecule: D_{3h}
- define the axial system
- find all of the symmetry elements

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	h=12
A_1'	1	1	1	1	1	1	
A_2'	1	1	-1	1	1	-1	
E'	2	-1	0	2	-1	0	(T_x, T_y)
A_1''	1	1	1	-1	-1	-1	
A_2''	1	1	-1	-1	-1	1	T_z
E''	2	-1	0	-2	1	0	

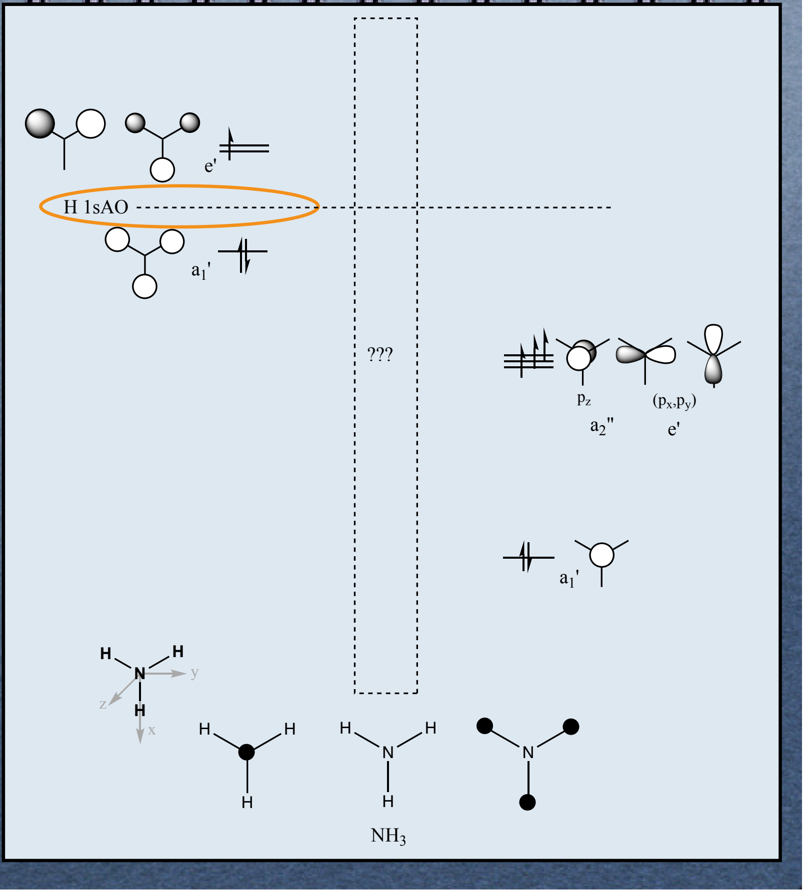


Fragments

- choose as fragments atoms that map onto each other under the symmetry operations
  - ✦ H atoms map onto each other
  - ✦ N atom maps onto its self
  - ✦ H_3 and N atom are the fragments
- draw the "structure" then add the fragment atoms explicitly, use placeholders for the other atoms

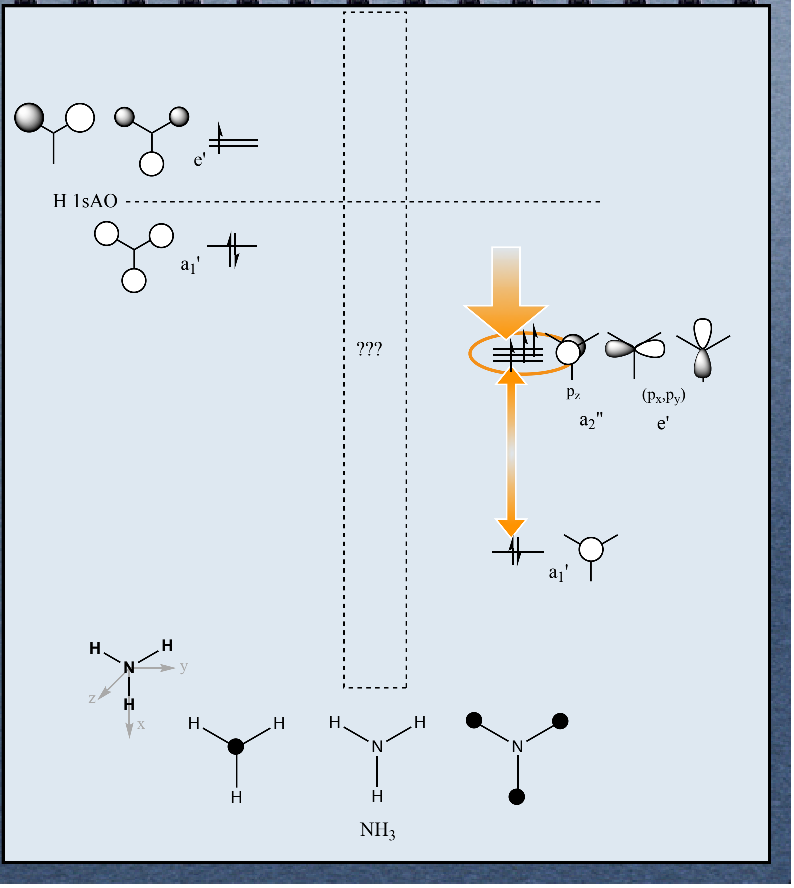
Set Up MO Diagram

- vertical axis: Energy
- add H 1s AO reference level



Set Up MO Diagram

- add fragment orbitals
- N atom: use AOs
  - ✦ N more electronegative => so valence orbitals lie below H 1s reference orbital
  - ✦ moderate 2s-2p energy gap



Symmetry Labels

- sAO is totally symmetric must be a_1'
- pAOs look in the last columns of the character table
  - find T_x, T_y, T_z
  - gives you the axis symmetry label
  - gives the pAO symmetry label

Short-Cuts!

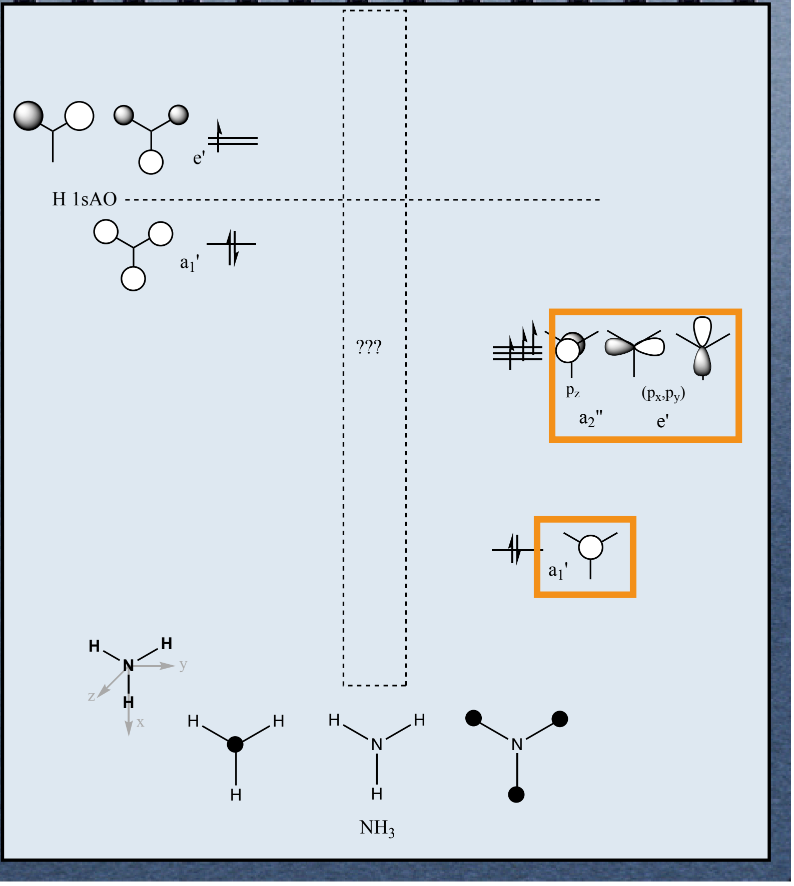
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	h=12
A_1'	1	1	1	1	1	1	
A_2'	1	1	-1	1	1	-1	
E'	2	-1	0	2	-1	0	(T_x, T_y)
A_1''	1	1	1	-1	-1	-1	
A_2''	1	1	-1	-1	-1	1	T_z
E''	2	-1	0	-2	1	0	

$p_x, p_y \rightarrow e'$

$p_z \rightarrow a_2''$

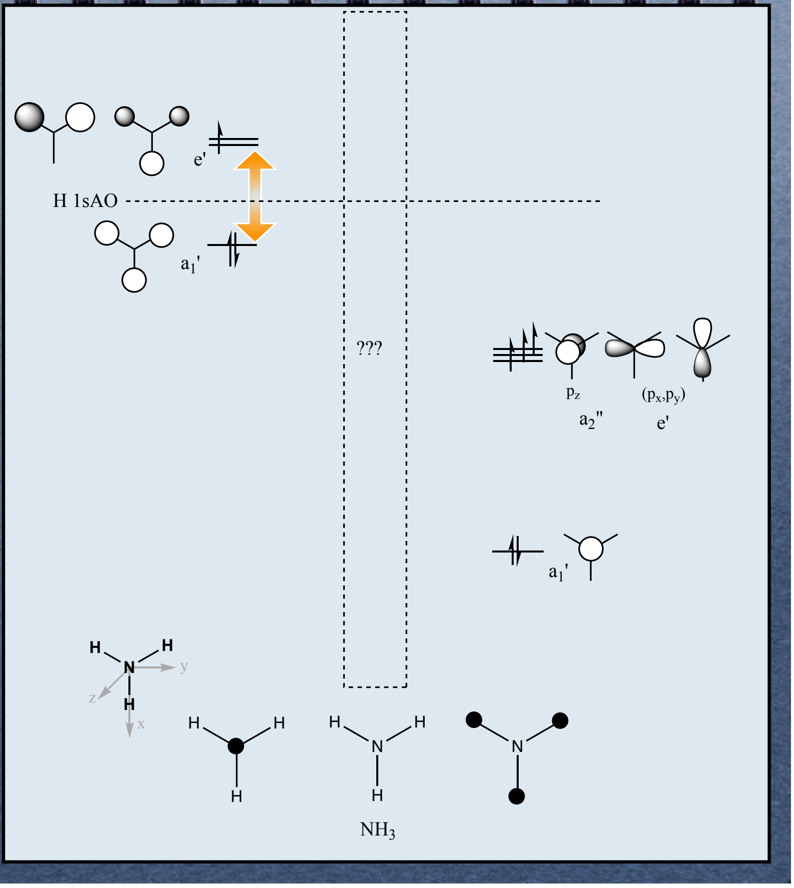
Set Up MO Diagram

- add fragment orbitals
- determine the symmetry



Set Up MO Diagram

- add fragment orbitals
- H_3 fragment orbitals
  - H atoms are further apart than if directly bonded =>stabilisation and destabilisation are less
- given by symmetry adapted FOs
  - a_1' totally symmetric
  - e' same pattern x,y axis
  - derived last lecture

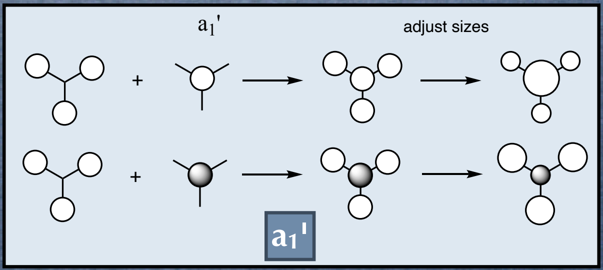


Form the MOs

work out MOs first
then the splitting

Important!

- The a_2'' remains non-bonding
- Only fragment orbitals (FOs) of the same symmetry can combine
- for ammonia: a_1' and e'
- Form MOs by
  - “adding” FOs together “as is”
  - “adding” FOs with ONE FO phase inverted



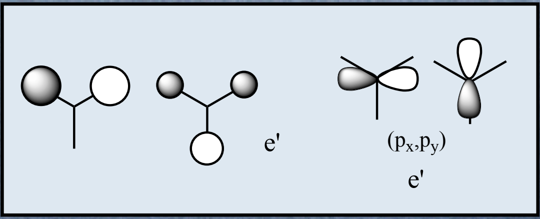
In-Class Activity P1

work out MOs first
then the splitting

Important!

Combine the e' FO orbitals

- for degenerat e orbtials: 2 in so 2 out
- many options!
- combine those that have best overlap



In-Class Activity P1

work out MOs first
then the splitting

Important!

Combine the e' FO orbitals

- for degereat e orbtials: 2 in so 2 out
- many options!
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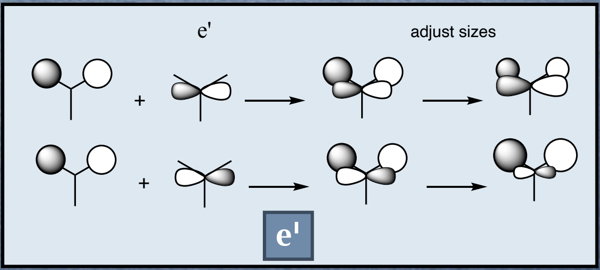
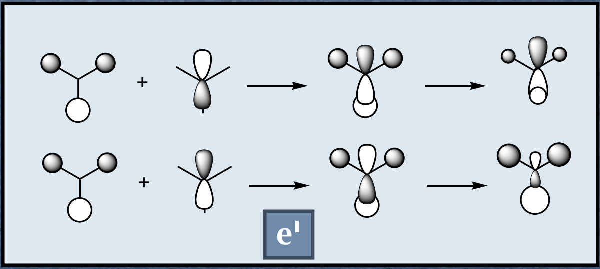
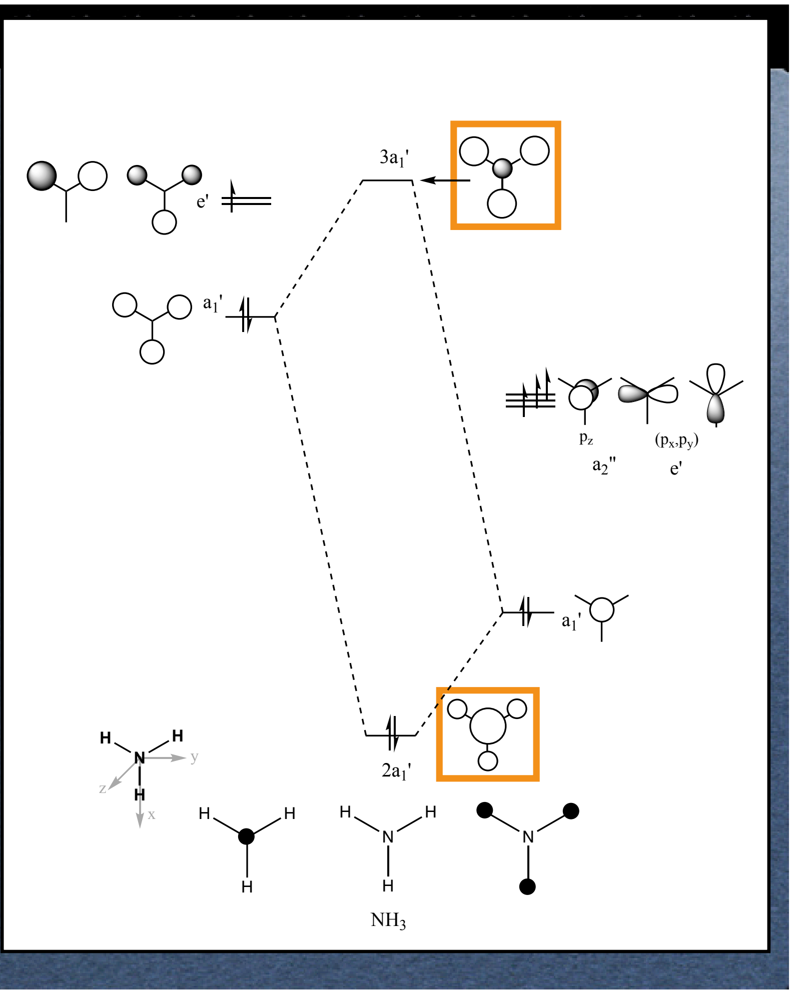




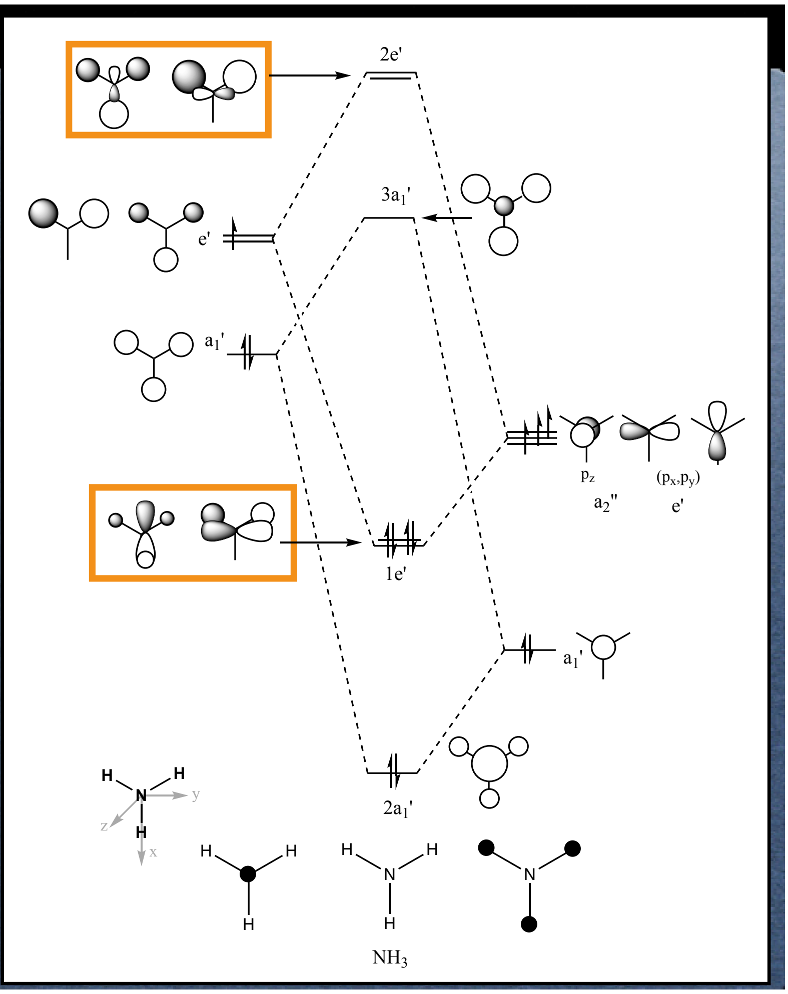
Stage One MO Diagram

- Evaluate splitting
  - ✦ FOs far apart in energy interact only moderately
  - ✦ sAO interactions are moderate
  - ✦ destabilisation is always larger



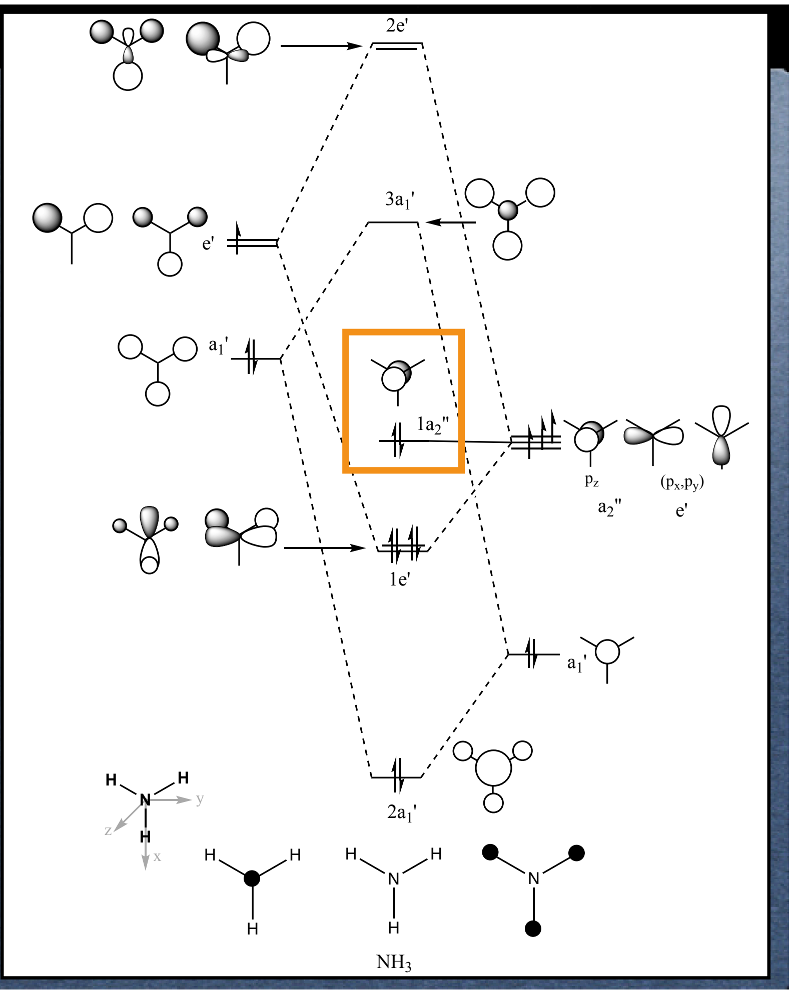
Stage One MO Diagram

- Evaluate splitting
  - ✦ FOs closer in energy interact more
  - ✦ non-direct s-p overlap is moderate, less than s-s
  - ✦ destabilisation is always larger



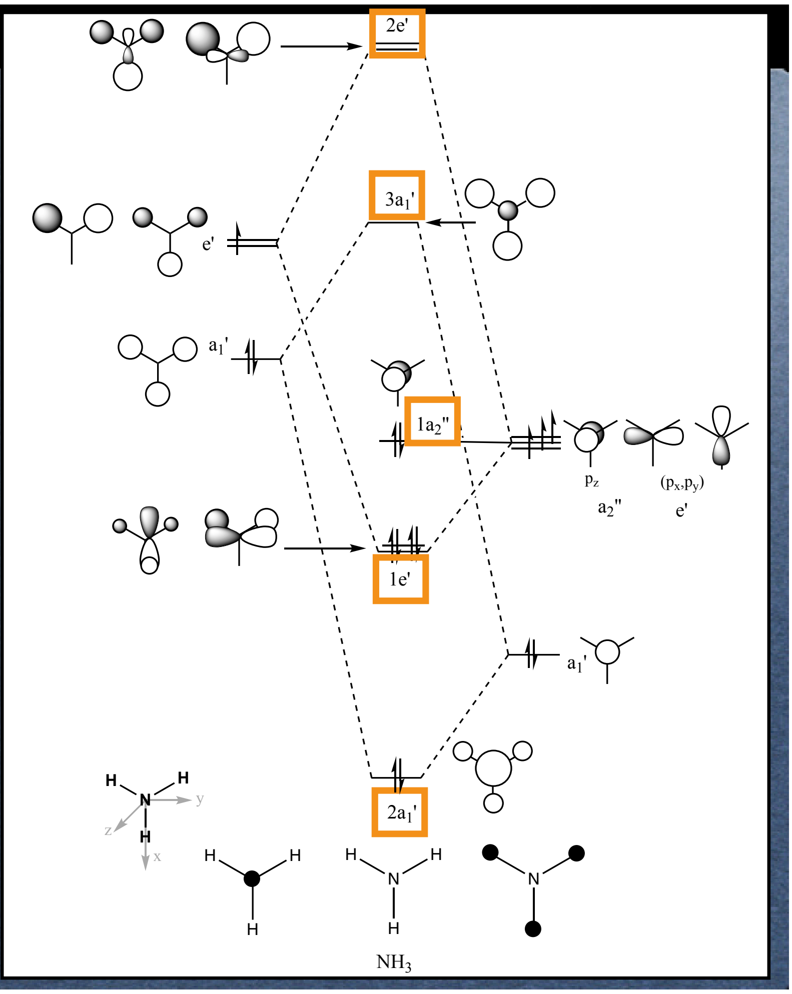
Stage One MO Diagram

- a_2" is non-bonding



Stage One MO Diagram

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

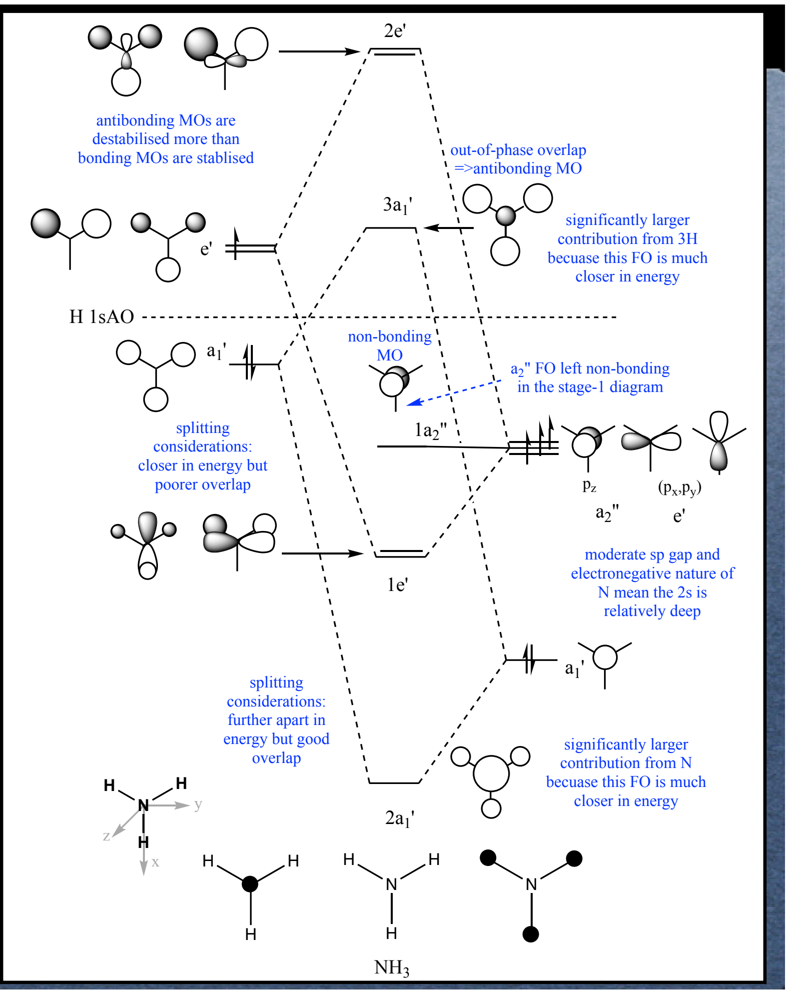


Stage One MO Diagram

Annotate your diagrams!

Important!

do not repeat information



antibonding MOs are destabilised more than bonding MOs are stablised

out-of-phase overlap =>antibonding MO

significantly larger contribution from 3H becuase this FO is much closer in energy

a$_2$'' FO left non-bonding in the stage-1 diagram

splitting considerations: closer in energy but poorer overlap

moderate sp gap and electronegative nature of N mean the 2s is relatively deep

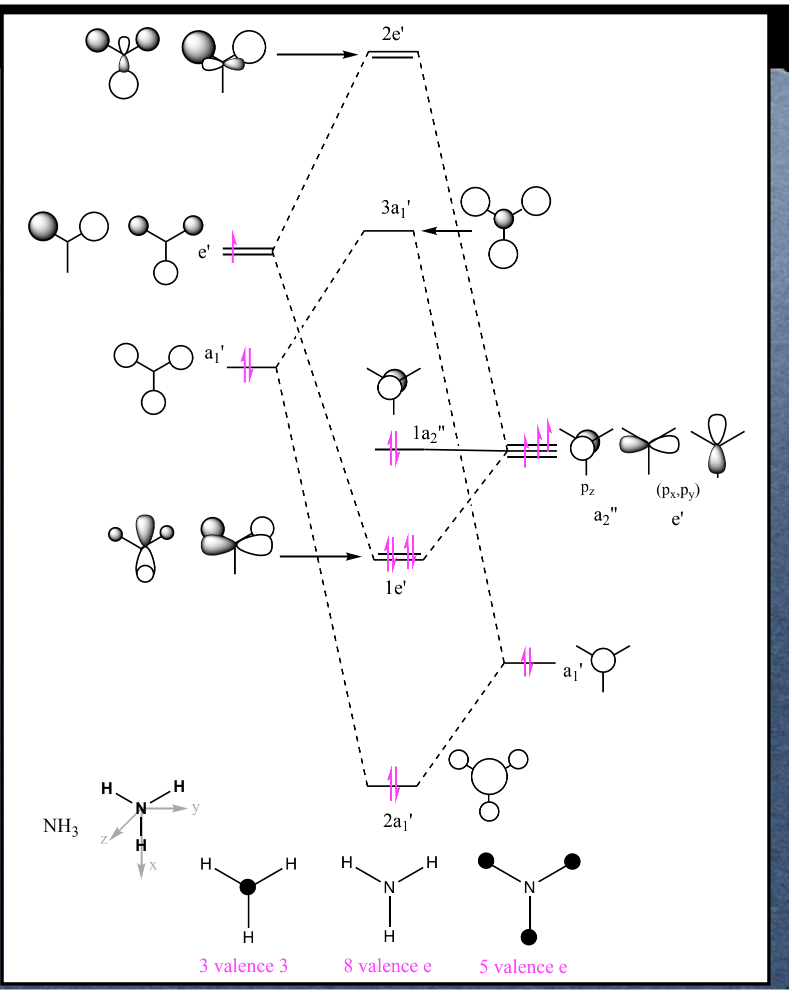
splitting considerations: further apart in energy but good overlap

significantly larger contribution from N becuase this FO is much closer in energy

---

Stage One MO Diagram

- add the electrons!
  - ✦ n has 5 valence e
  - ✦ 3H has 3 valence e
  - ✦ hence ammonia has 8 ve
  - ✦ fill sequentially

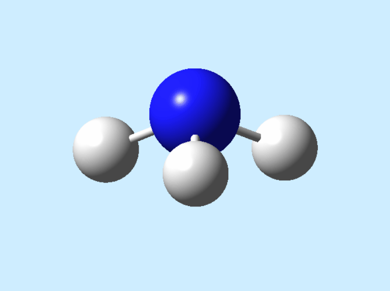


Stage 2: MO Mixing

- **necessary conditions**
  - ONLY MOs of the same symmetry can mix
  - MOs cannot be from the same bonding-antibonding pair
  - 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
- **currently no MOs meet the requirements for mixing**

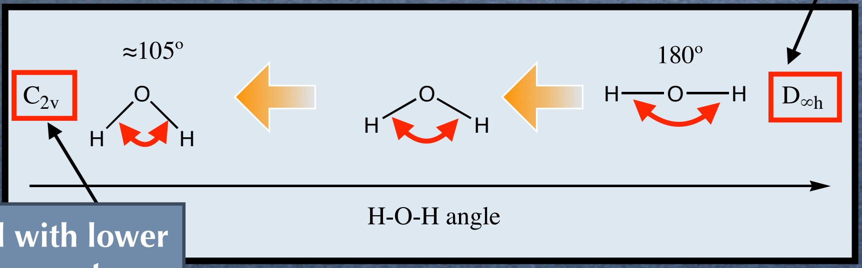
Symmetry Breaking

- **But how does the drop in symmetry start?**
- **nuclear vibrations provide infinitesimal distortion required for MO mixing**
- **vibronic coupling can occur**
  - umbrealla vibrational motion reduces symetry to C_{3v}
  - 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!



Correlation Diagram

- Correlation 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: explains why is H_2O bent (see lecture questions!)



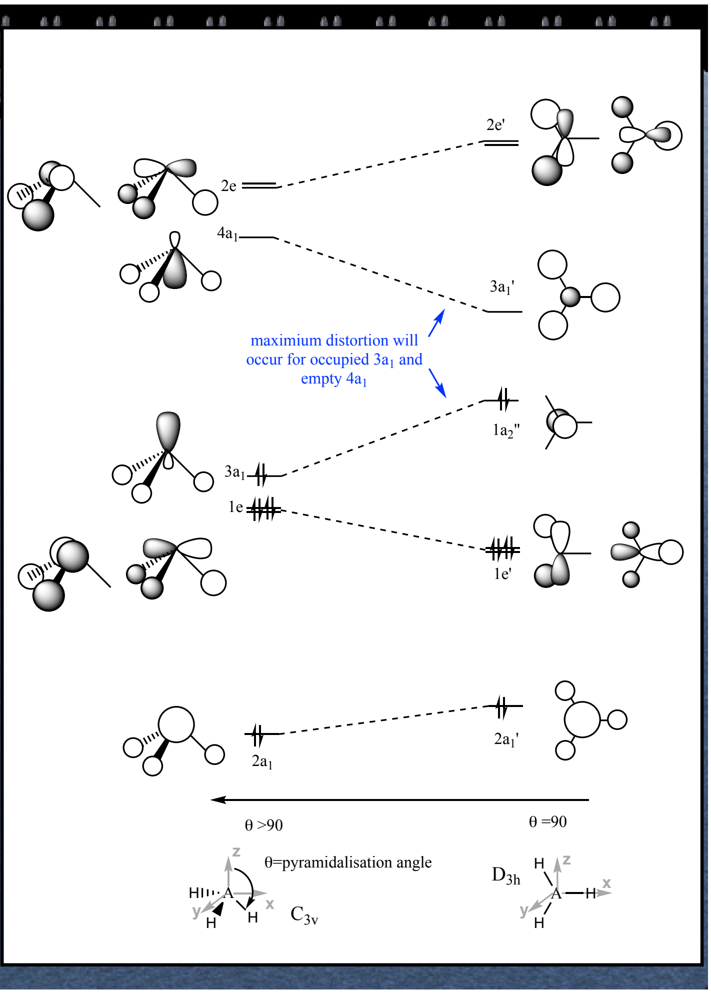
start with high symmetry

end with lower symmetry

Energy of MOs

start with high symmetry

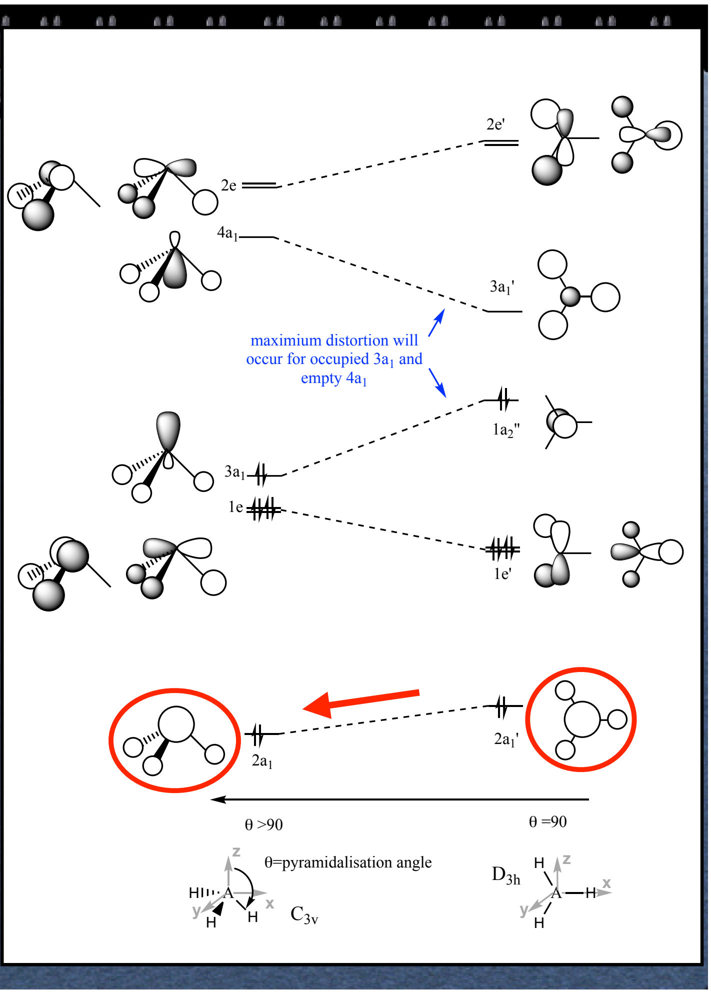
- NH_3 start with planar and distort via pyramidalisation



Energy of MOs

start with high symmetry

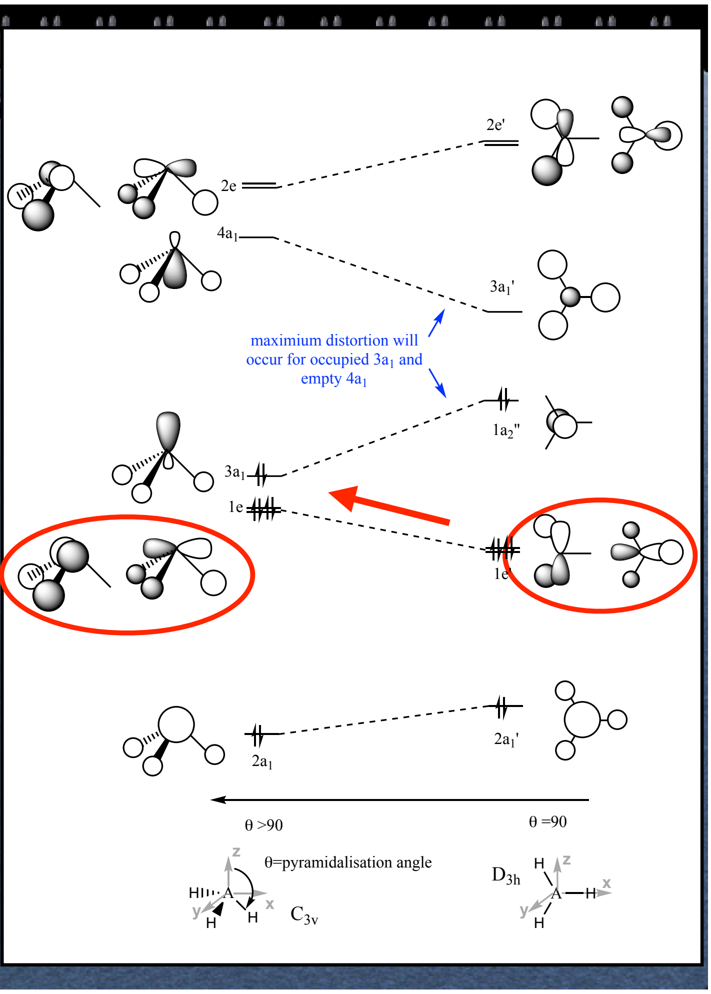
- then examine how MOs change under geometric distortion
- $2a_1'(2a_1)$ stabilised
  - ✦ N-H bonds essentially unchanged
  - ✦ BUT H···H through space bonding overlap increases
  - ✦ net result small stabilisation



Energy of MOs

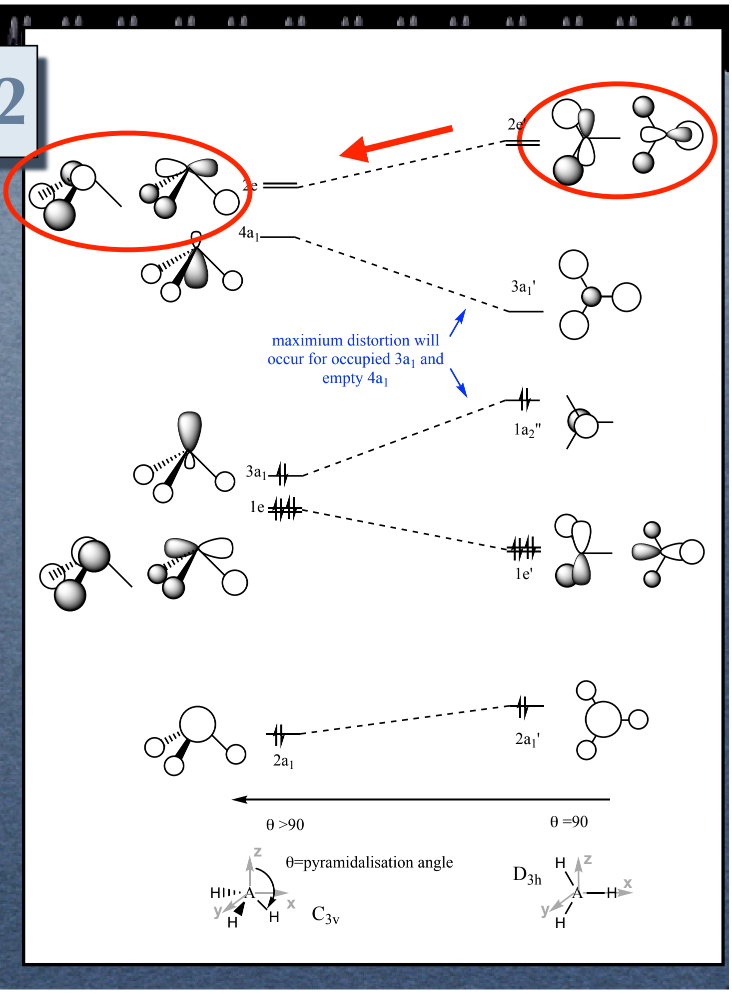
start with high symmetry

- then examine how MOs change under geometric distortion
- $1e'(e)$ destabilised
  - ✦ p-s bonding overlap is reduced
  - ✦ and H···H through space anti-bonding overlap increases
  - ✦ net result destabilisation (larger than a_1 is stabilised)



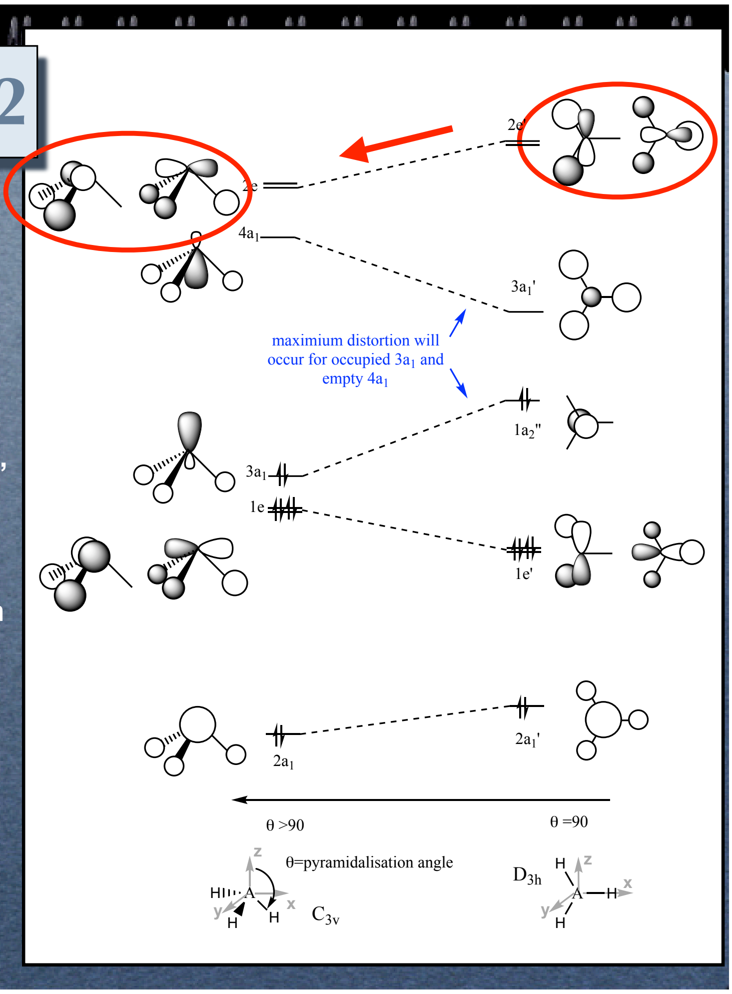
In-Class Activity P2

- why are the 2e'(e) MOs stabilised?



In-Class Activity P2

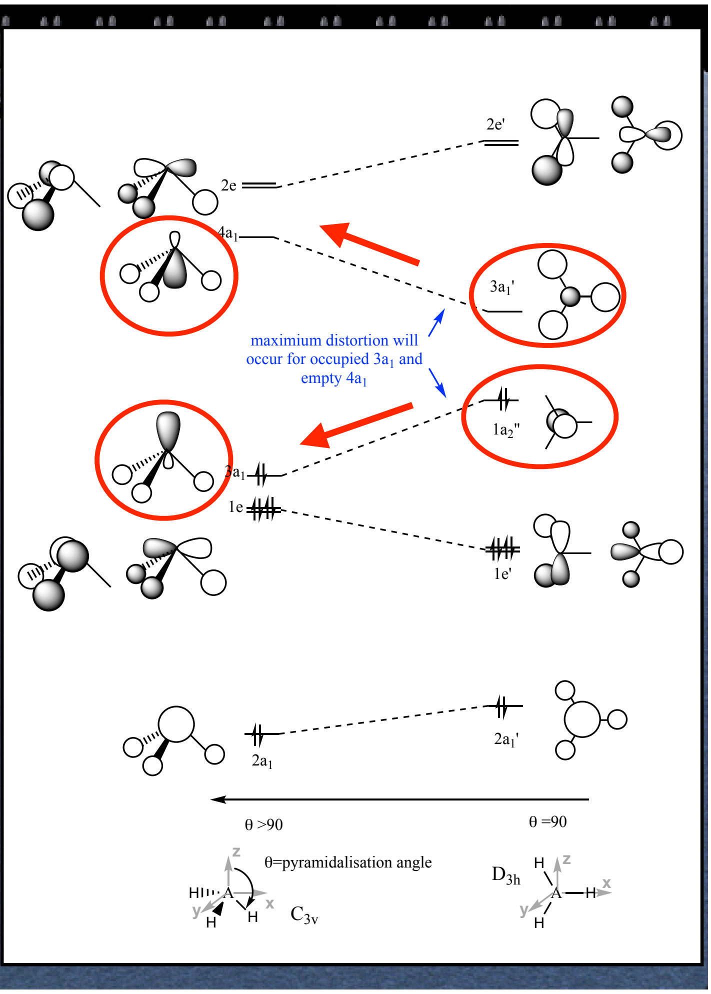
- why are the 2e'(e) MOs stabilised?
  - p-s anti-bonding overlap is reduced, stabilising molecule
  - and H···H through space anti-bonding overlap increases
  - net result stabilisation (smaller than 1e is destabilised)



Energy of MOs

- the 1a$_2$" → 3a$_1$
- and 3a$_1$'→ 4a$_1$
- MO mixing can occur!
  - ✦ same symmetry
  - ✦ not same bonding-antibonding pair
  - ✦ stabilises total E
  - ✦ MOs are in HOMO-LUMO region
  - ✦ one is occupied
  - ✦ one is non-bonding
  - ✦ MOs are close in energy

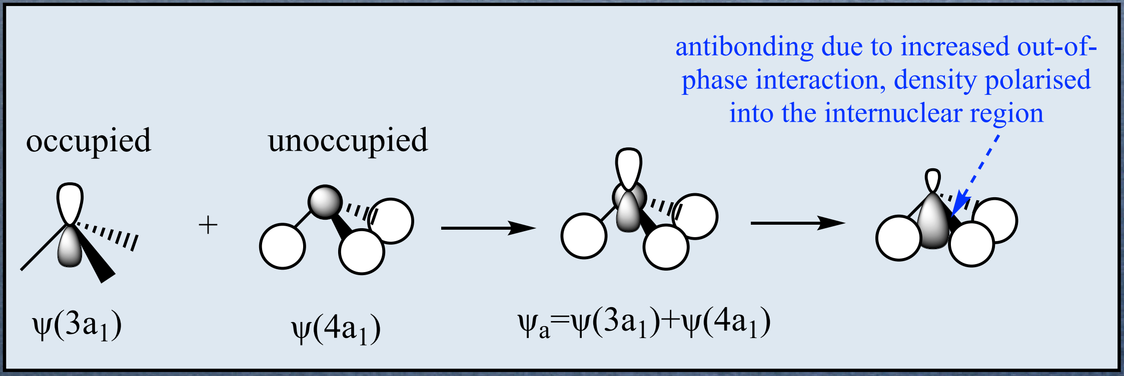
LARGE mixing!



maximium distortion will occur for occupied 3a$_1$ and empty 4a$_1$

Generate the mixed-MOs

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



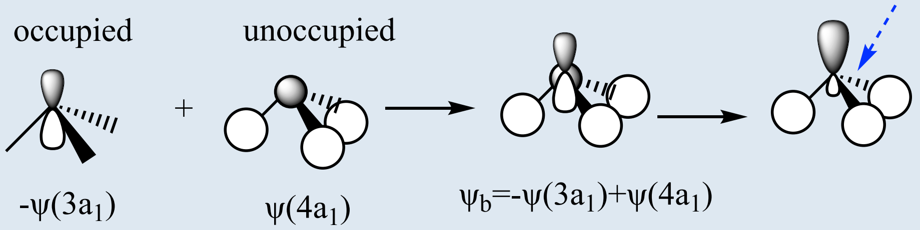
antibonding due to increased out-of-phase interaction, density polarised into the internuclear region

In-Class Activity P3

- **mixing orbitals**
  - ✦ "add" MOs together "as is"
  - ✦ "add" MOs with ONE MO phase inverted
  - ✦ inspect to determine which is the bonding mixed MO

In-Class Activity P3

- **mixing orbitals**
  - ✦ "add" MOs together "as is"
  - ✦ "add" MOs with ONE MO phase inverted
  - ✦ inspect to determine which is the bonding mixed MO

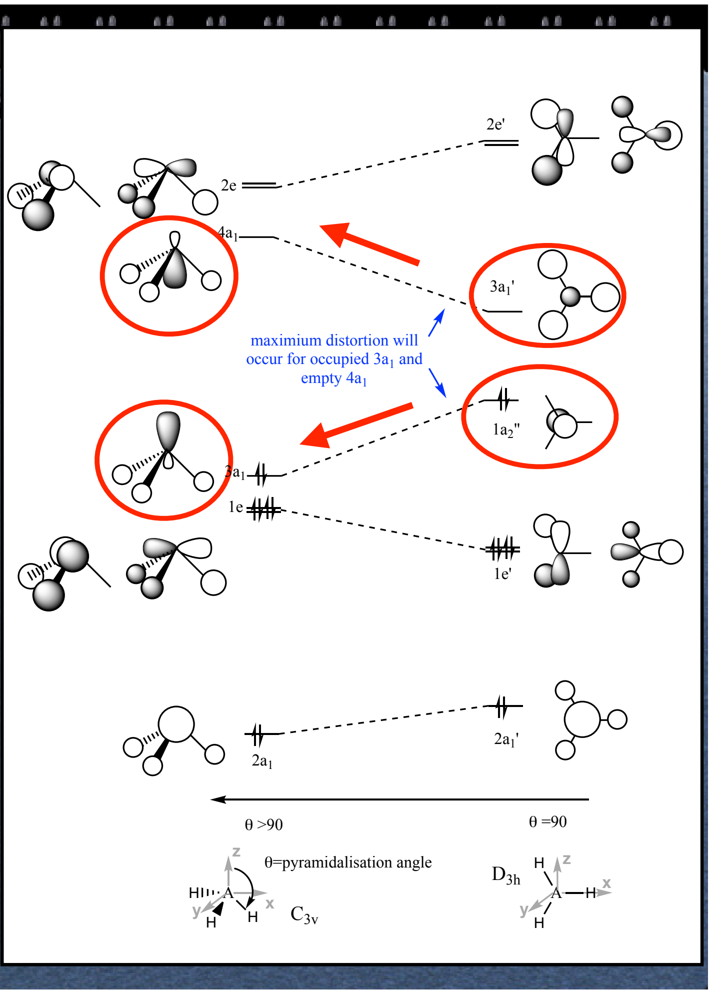


non-bonding/slightly bonding due to increased in-phase interaction, density polarised outside of internuclear region

Energy of MOs

LARGE mixing!

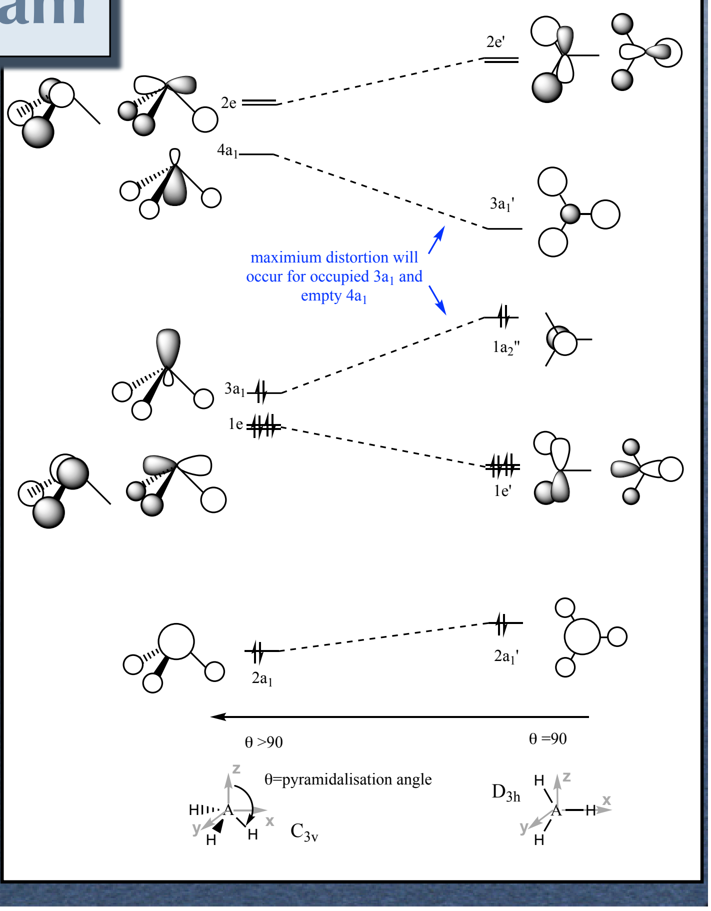
- the $1a_2''$ → $3a_1$
  - occupied so strongly stabilises the whole molecule
- the $3a_1'$→ $4a_1$
  - unoccupied so can go very high in energy without penalty



maximium distortion will occur for occupied $3a_1$ and empty $4a_1$

Correlation Diagram

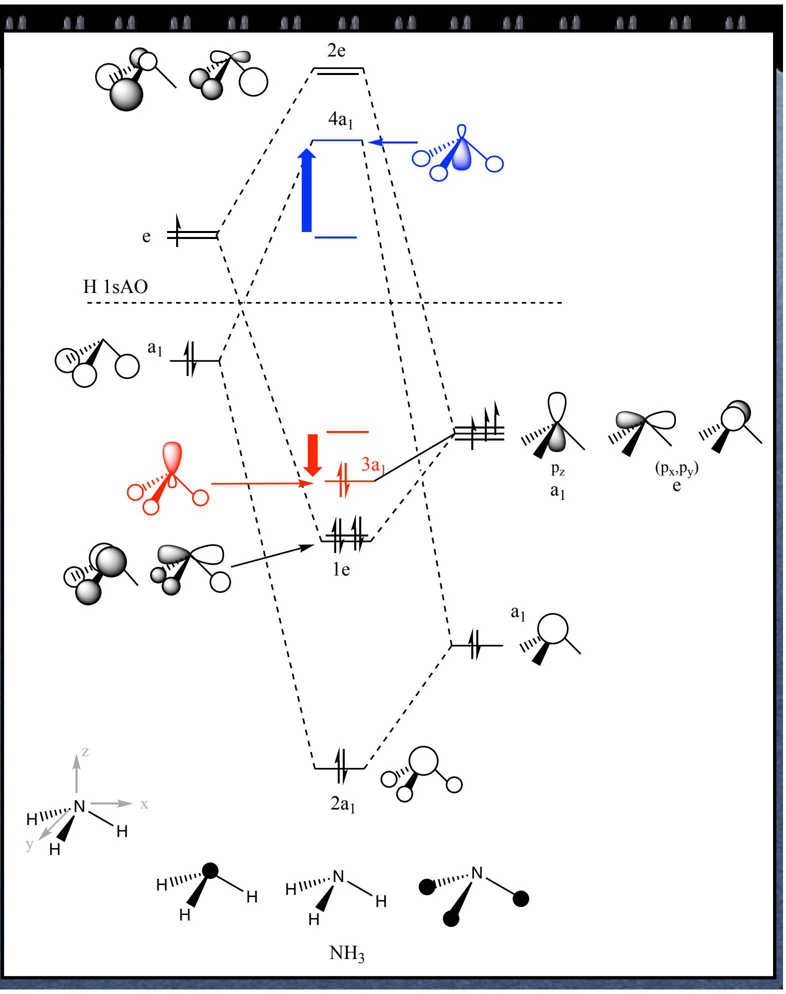
- Orbital changes
  - AOs move with the atoms
  - form or shape of AOs remains constant
  - !! except for MOs which undergo mixing
- Molecular stability
  - examine how occupied MOs change under geometric distortion
  - look for occupied MOs which show a large change in energy
  - these orbitals drive the change in shape



maximium distortion will occur for occupied $3a_1$ and empty $4a_1$

Final MO Diagram

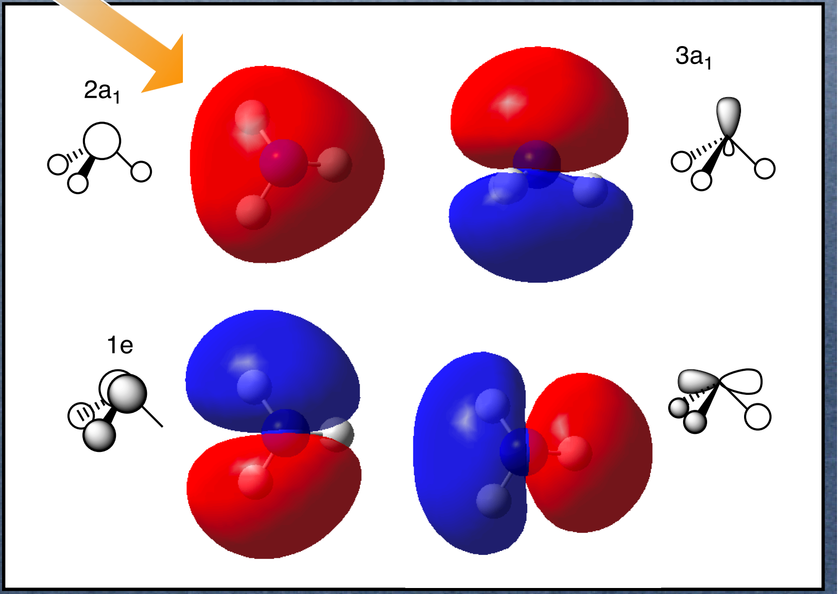
- **strong mixing:**
  - ✦ $4a_1$ MO unoccupied goes up
  - ✦ $3a_1$ MO non-bonding goes down



"Real" MOs

computed molecular orbitals

we have "solved" the Schrödinger equation!!!



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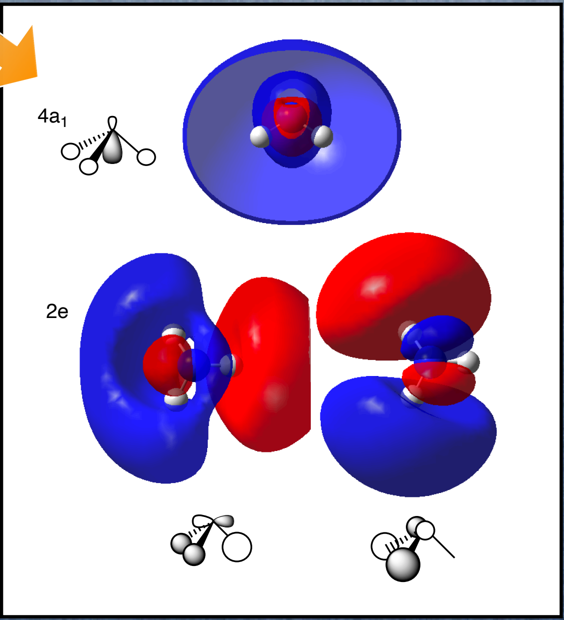
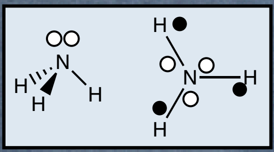


Experimental Evidence

- **Photoelectron spectrum**
  - ✦ energy required to eject an electron from each MO
- **“traditional” theory:**
  - ✦ expect 3 equivalent bonds and 1 lone pair = 2 peaks in photo-electron spectrum

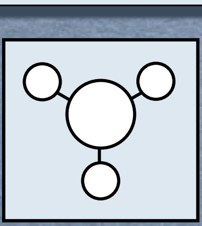


BUT

- ✦ have 3 peaks in photo-electron spectrum which relate to delocalised $2a_1$, $1e$ and $3a_1$ MOs
- ✦ $1a_1$ and $4a_1$ are outside standard detector range

Delocalisation

where have the bonds gone???



- **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**

MO checklist

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
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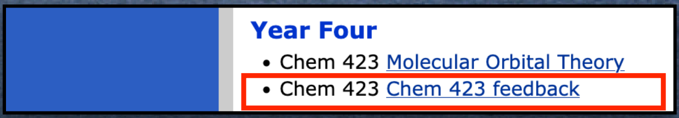
  - ✦ combine fragment orbitals of the same symmetry, sketch out the MOs and analyse the bonding/antibonding character
  - ✦ estimate the splitting energy for each pair of MOs, draw in the MO energy levels and MOs (in pencil!)
  - ✦ determine the number of electrons in each fragment and hence the central 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 the MO 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 where A= main group element
- be able to discuss symmetry breaking and vibronic coupling
- be able to explain and illustrate MO mixing for these molecules
- 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 critically evaluate VSEPR theory, localised 2c-2e bonding and the delocalised MO picture of bonding

feedback: on-line!



Year Four

- Chem 423 Molecular Orbital Theory
- Chem 423 Chem 423 feedback

Symmetry Breaking

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

Noether's Theorem

Anything that does not change under an operation has a conservation law!

- translation -> linear momentum conserved
- rotation -> angular momentum (l) is concerved
- move in time -> energy (mass) is conserved
- reflection -> parity is conserved

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