The MO Diagram of Ammonia

Introduction

- previously you have seen the MO diagram of H_2O and practiced forming the MO diagram of BH_3 (Workshop 2 in Chem207)
- this lecture we will go through forming the MO diagram of NH_3 a
- we will then look at the real MOs and compare these to a PES

MO diagram check list

important

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

Set-up

- for some molecules we construct the MO diagram for the highest symmetry and then we lower the symmetry to produce a **correlation diagram**
- the highest symmetry for an EH_3 molecule is D_{3h}
- the first steps have been covered in earlier courses/lectures for planar BH_3
- **Figure 1** has the shape, molecular point group, axial system and the symmetry elements for the D_{3h} point group

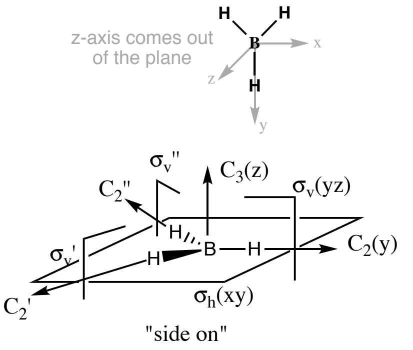


Figure 1 Symmetry elements for NH_3

Determine the fragments

- the fragments for NH_3 are the central N atomic orbitals and the H_3 fragment
    - we choose as fragments the atoms that map onto each other under the symmetry operations of the group
        - H atoms map onto each other but not N
        - the N atom maps onto itself
    - draw the structure of the whole molecule, explicitly write in the fragment atoms and leave place holders for the other atoms, **Figure 2**

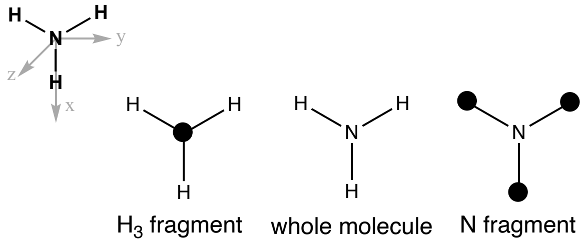


Figure 2 Drawing the fragments with place holderss

Determine the fragment energies, orbitals and symmetry labels

- set up for the MO diagram as shown in **Figure 3** below:

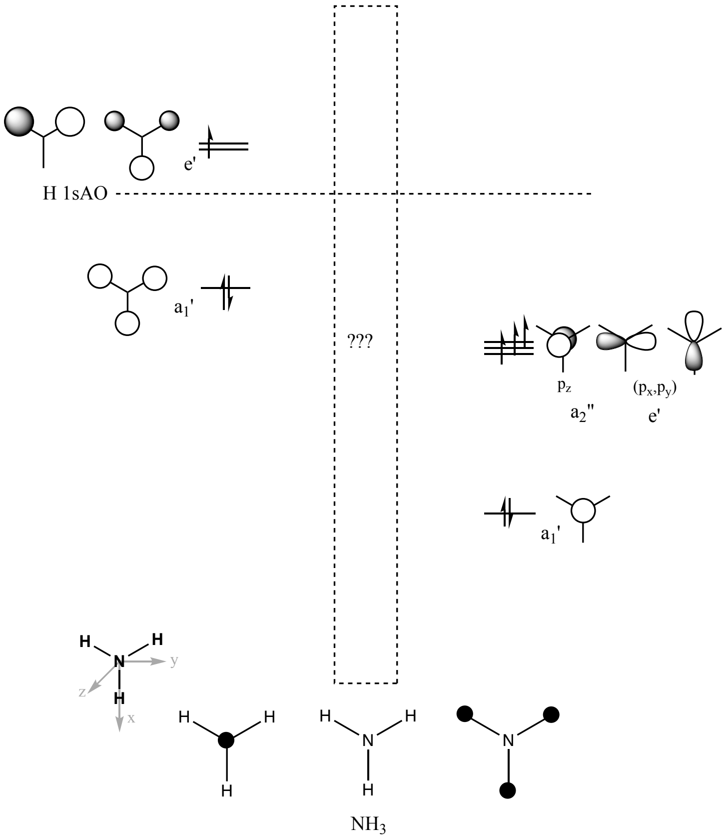


Figure 3 Bare MO diagram

- N is more electronegative than H and so the N p fragment orbitals (FOs) will lie lower than the single H 1s AOs, N has a smaller sp gap than O
- we know the symmetry adapted fragment orbitals for the H_3 fragment, in ammonia the hydrogen atoms are **further apart** than they would be in H_3 and therefore they **interact less**, stabilisation of the bonding, and destabilisation of the antibonding FOs is less and thus the overall splitting energy or **energy gap is small**.

important

- we know these from determining the symmetry FOs but we could also determine the symmetry of these fragments by examining how the orbitals transform under the symmetry operations of the D_{3h} point group, or we could use some **short-cuts**
  - totally bonding orbitals and sAOs are always **totally symmetric** and have the highest symmetry, in this case a_1'
  - the pAOs have the same symmetry as the T_x, T_y and T_z so the p_x and p_y have e' symmetry labels and p_z is a_2''
  - the symmetry adapted H_3 orbital symmetries are already known, or can easily be determined via the phase "pattern" method

Form the basic or stage one MO diagram

- first work out the MOs and then determine from their interactions the energy splitting, last place the MOs and MO energy levels on the diagram
- remember the general rules
  - **only fragment orbitals of the same symmetry can combine**.
  - **fragment orbitals only interact once**
  - if there is more than one fragment orbital of the same symmetry, we generally combine the lowest energy orbitals first, if there is no matching FO then the FO becomes a non-bonding MO
  - form the bonding/antibonding pairs, take orbitals of one fragment and "add" them to the orbitals of the other fragment, do this once "as is", and once with the phase of all components reversed (ie adding the negative)
  - the MO has a **larger component from the FO closest in energy**
- for ammonia we combine first the orbitals of a_1' and e' symmetry
  - the lowest energy a_1' FOs on N (2s a_1 FO) and H_3 (totally bonding a_1') are combined, leaving the N p_z a_2'' FO non-bonding
  - then the e' orbitals are formed, for degenerate FOs combine the "pairs" of FOs that have the best overlap
- formation of the a_1' symmetry MOs are shown in **Figure 4**

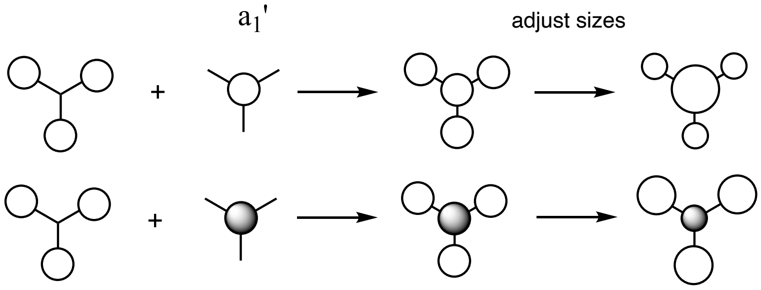


Figure 4 Forming bonding and antibonding MOs for a_1' MOs

In-Class Activity P1

- form the e' MOs for planar NH_3

Figure 5 Forming bonding and antibonding MOs for e MOs

- **justify the splitting** for each MO bonding antibonding pair
    - sAOs that are "close" interact more and the N-H bond distance is quite small, however there is quite a large energy difference between the fragment orbitals which will reduce the splitting, thus overall there is a moderate splitting for the a_1' MOs
    - pAOs that overlap end-on with another orbital have strong interactions, as the sAO is brought off linear this decreases, but the FOs are closer in energy increasing the interaction, thus overall the e' MOs also have a moderate splitting, but less than the a_1' MOs

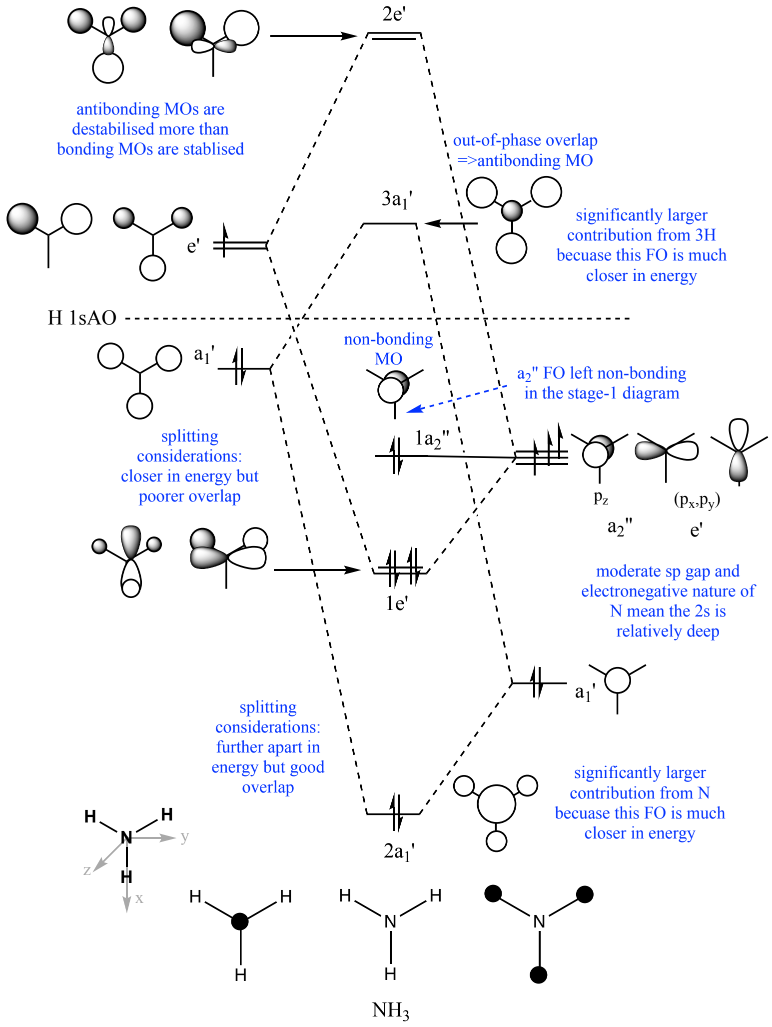


Figure 6 Basic MO diagram

- MOs are labelled by their symmetry, and sequentially starting with the lowest energy orbitals
- I have **annotated** this MO diagram. I expect you to annotate your MO diagrams, explaining key features.

Add the electrons

- determine the number of electrons for each fragment
    - each H contributes one 1s electron =3e
    - the nitrogen atom contributes 5 valence electrons =5e
    - the total electrons for the diagram is 8e
- then fill the MOs sequentially starting at the lowest energy MOs
    - follow the Pauli exclusion principal and Hund's rule.

important

Molecular orbital mixing

- next look for mixing, **necessary conditions**:
  - only MOs of the same symmetry can mix
  - MOs cannot be from the same bonding-antibonding pair
  - mixing must stabilise the total energy of the molecule
- mixing tends to be **large** when at least one of these criteria are met:
  - MOs are close in energy
  - one of the MOs is non-bonding or unoccupied
  - MOs are in the HOMO-LUMO region
- no MOs in the D_{3h} configuration meet these requirements for "planar" NH_3

Symmetry breaking

- BUT NH_3 undergoes **vibronic coupling**, the umbrella vibrational motion of the NH_3 molecule couples the MOs which leads to a distortion
- the umbrella motion reduces the symmetry to C_{3v}, folding the H-atoms down and now we need to evaluate what happens to the MOs under this condition
- vibronic coupling ONLY occurs when there has been a breakdown of the Born-Oppenheimer approximation
- this is also a form of **symmetry breaking** and it results in fundamental changes to the electronic and nuclear structure of a molecule

What is a correlation diagram?

- a correlation diagram shows how orbital interactions change as one geometric parameter (distance or angle) is varied, they tell us the most stable geometry (atomic arrangement) based on the electronic structure
- I've produced the correlation diagram for ammonia in **Figure 7**

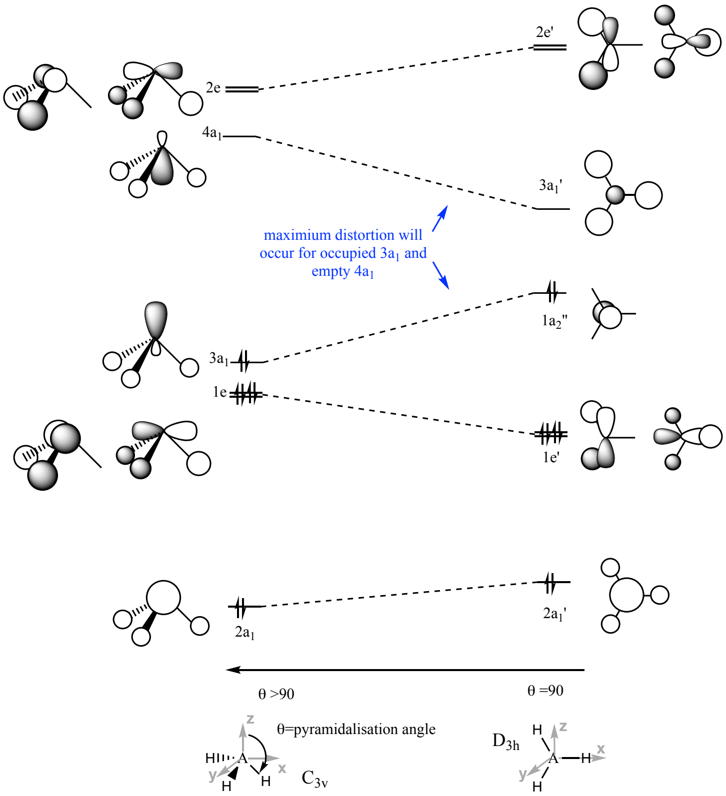


Figure 7 Correlation diagram for NH_3

- we start by constructing the MO diagram for the high symmetry molecule, then we allow the symmetry to lower
- the change in point group on distortion from D_{3h} to C_{3v}, means that the symmetry labels of the orbitals change
  - e' → e MO
  - a_1' → a_1 MO
  - a_2'' → a_1 MO
- the change in symmetry has no significant effect on the e' or the deep a_1' MOs however, we need to examining the "bonding" vs "antibonding" character of orbitals to determine if they are stabilised or destabilised on the drop in symmetry.
  - the $2a_1'$ MO is slightly stabilised due to an increase in the (through space) H sAO bonding overlap, this is a result of the H atoms getting slightly closer together as the molecule distorts. There is no change in the sAO A-H overlap because these are sAOs.
  - the 1e' bonding MOs are destabilised due to a reduction in the bonding overlap of the central element pAO with the H sAOs, and an increase in the through space H sAO antibonding interaction, both interactions contribute to destabilisation and hence the shift in energy is larger than for the $2a_1'$ MO.

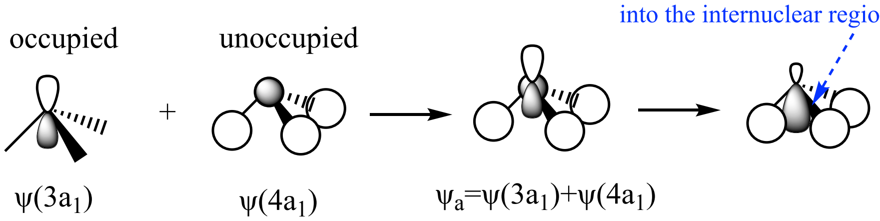
In-Class Activity P2

- What are the main reasons the 2e' antibonding MOs go *down in energy*?

Induced mixing on symmetry breaking

- very interesting things happen to the D_{3h} $1a_2''$ and $2a_1'$ MOs!
  - the $1a_2''$ (D_{3h}) MO becomes $3a_1$ (C_{3v}), and $3a_1'$ (D_{3h}) MO becomes $4a_1$ (C_{3v}), these orbitals now have the same symmetry and can potentially mix
  - note that no mixing occurs until the molecule is infinitesimally distorted from planar
- the extent of mixing is determined by the rules for MO mixing:
  - only MOs of the same symmetry can mix: *these are both a_1*
  - the MOs cannot be from the same bonding antibonding pair, *applies*
  - mixing must stabilise the total energy of the molecule, *yes*
  - mixing tends to be large when at least one of the following criteria are met: MOs are close in energy, one of the MOs is non-bonding or unoccupied, MOs are in the HOMO-LUMO region, *these are close in energy one is non-bonding and these are the HOMO and LUMO*
  - thus we can expect mixing to be large!

- remember mixing is carried out by "adding" the MOs once as is, and once with the phase of one MO reversed, **Figure 8** shows the positive combination



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

Figure 8 Mixing MOs (once as is)

In-Class Activity P3

- following the format of the diagram in **Figure 8**, determine the other mixed orbital by forming $-\psi(3a_1) + 4\psi(a_1)$, note that the first orbital is the negative of $\psi(3a_1)$

Figure 9 Mixing MOs (once with phase of one MO reversed)

- occupied MOs dominate the total energy of the molecule
  - the $4a_1$ MO is unoccupied its destabilisation does not affect the total energy of the molecule and can go very high without penalty
  - stabilisation of the $3a_1$ MO stabilises the whole molecule
  - this is why MO mixing tends to be large for orbitals in the HOMO-LUMO region and where one orbital is occupied and the other unoccupied
- some more comments on mixing
  - in reality *all orbitals of the same symmetry mix* very slightly but we only represent the largest effects that stabilise the molecule the most.
  - when we mix MOs we are really making MOs out of all the FOs that contribute to these MOs, there is a **general rule: n FOs make n MOs**
  - for ammonia 3FOs have produced 3MOs, the FOs are the H_3 a_1 FO, and the N 2s AO and $2p_z$ AO, the final mixed MOs are the $2a_1$, $3a_1$ and $4a_1$. The effect on the deep $2a_1$ MO is small and is not shown on MO diagrams
  - people will sometimes add extra connection lines in the MO diagram to represent the mixing of all three FOs
- MO changes
  - notice that the AOs move with their nuclear centres
  - for most MOs the contributing AOs remain similar irrespective of the geometry the molecule takes on.
  - however if mixing occurs then *the shape of MO changes.*

important

- the geometry of a molecule is determined by ALL of the MO interactions
  - but one or two occupied orbitals can dominate
  - for ammonia one interaction clearly dominates over the others, and NH_3 is bent because of the stabilisation of the $3a_1$ MO
  - generally the greater the mixing the greater the distortion from planar, but at some point this will be impacted by other effects

Final MO diagram

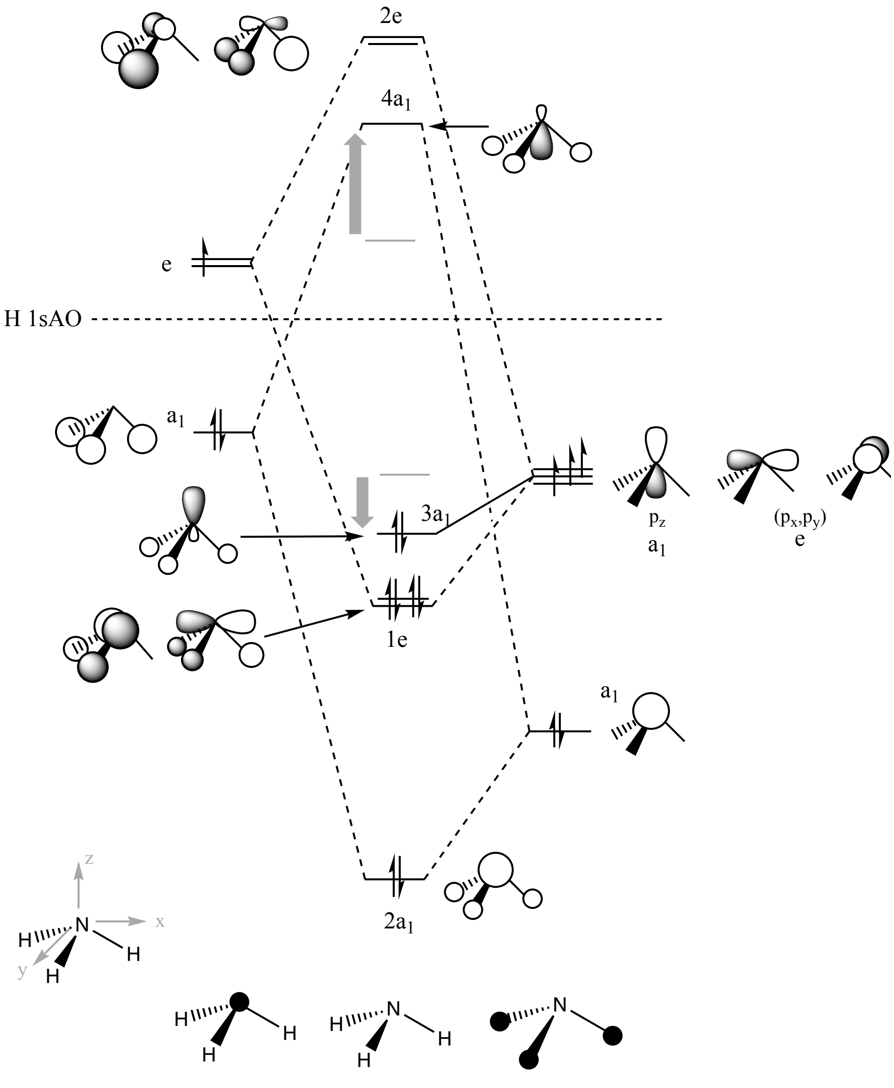


Figure 10 Final MO diagram

How realistic are the MOs?

- The computed MOs for ammonia are shown in **Figure 11**, our qualitative MOs are mostly correct!
    - notice the large diffuse ligand contributions to the unoccupied orbitals

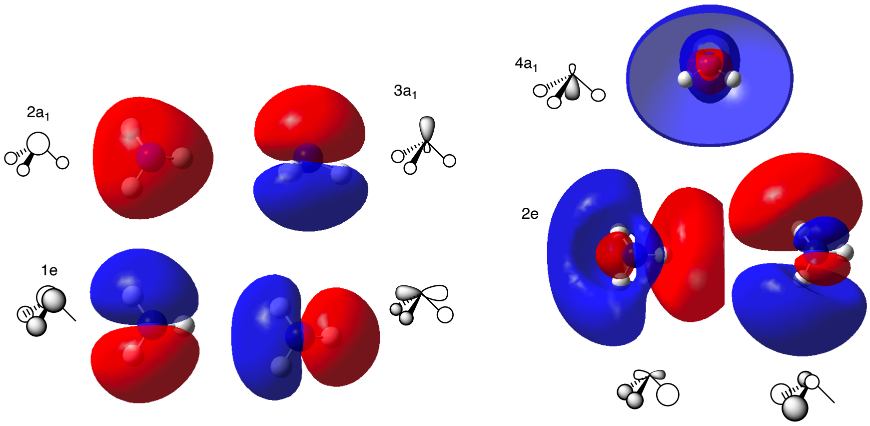


Figure 11 Real MOs

- What do we expect in a PES based on VSEPR?
    - Lewis structures predict three identical N-H bonds and one lone pair on the nitrogen atom (**Figure 12**)
    - the PES would therefore have two peaks, one for the degenerate bonds and one for the lone pair
- **Figure 13** is a photoelectron spectrum PES of ammonia

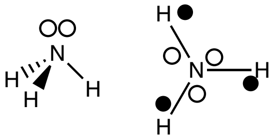


Figure 12 VSEPR prediction

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Figure 13 Photoelectron spectrum of ammonia

- The PES clearly shows 3 peaks in the positions we expect for the MOs we have derived!
- the peaks are broad and not "lines" because each individual ammonia molecule experiences a slightly different environment, and there is also extensive vibrational fine structure

- But if these MOs represent the **real** electronic structure, **where have the bonds gone???**
    - these MOs are **delocalised**, they bare little relationship to the familiar 2-center 2-electron (2c-2e) bonds we are used to
    - almost ALL the MOs all have contributions from all 4 atoms, they are 4 centre 2 electron MOs.

  - bonds (Lewis structures) however can be thought of as representing a build up of the *total* electron density
  - the MOs give the underlying electronic distribution, the *total of all the orbital contributions* gives the total electron density
  - we keep the ideas of (sp) hybridisation and 2c-2e bonds because they are historical and useful NOT because they represent reality
  - MO theory shows us that the electronic structure of something as simple as ammonia (or water) is far more complex than has traditionally been recognised.

Interpreting the EH_3 MO diagram

- why is BH_3 planar and NH_3 pyramidal?
  - the MO diagram for BH_3 is slightly different because B is less electronegative than H, but the same principles apply
  - mixing will be small unless there are electrons in the $3a_1$ MO, since it is the occupied orbitals that dominate the stability of these molecules
  - BH_3 has 6e (3 from B and 3 from H_3) which fill this diagram only up to the 1e' (or 1e) level. On distortion the 1e' level is destabilised, more than the $2a_1$' is stabilised and hence BH_3 prefers to remain planar.
  - NH_3 has 8e (5 from N and 3 from H_3) which fill this diagram to the $3a_1$ level. Vibronic coupling and the drop in symmetry means that mixing occurs between the occupied $3a_1$ and unoccupied $4a_1$ MO. This mixing is very strong and stabilises the $3a_1$ MO substantially and hence NH_3 is trigonal pyramidal and not planar.
- What can these MO diagrams tell us about the reactivity of BH_3 and NH_3?
- we know that BH_3 is a good Lewis acid
  - the LUMO of BH_3 is a non-bonding p_z orbital (a_2" symmetry) on the B.
  - the relatively low energy (not antibonding!) means that BH_3 will be accept electrons from species with higher energy HOMOs.
  - the non-bonding character also means donation of electrons from another molecule into this LUMO will not affect the overall bonding.
- we know that NH_3 is a good Lewis base
  - the HOMO of NH_3 is the non-bonding p_z orbital (a_1) on the N.
  - mixing has generated a MO with a strongly polarised "lone pair" like orbital which can interact with other molecules, but don't forget in reality there are also small H-atom contributions!
- What happens when BH_3 and NH_3 form a Lewis acid-base aduct?
  - in the new environment the symmetry is reduced to C_{3v}. Under the C_{3v} point group the pz AO and the $3a_1$' MO of BH_3 both move to a_1, and mixing is allowed, this lowers the energy of the "filling" orbital!
  - an empirical measure of this is the bond angle N-B-R for substituted BR_3 molecules, the more the Lewis base donates the stronger the distortion and larger the N-B-R bond angle
  - of course the MOs are not the only impact on bonding, there are steric, ionic, correlation and exchange influences as well!

Key Points

- be able to form a MO diagram for molecules of formula AH_2 and AH_3
- be able to discuss symmetry breaking and vibronic coupling
- be able to explain and illustrate MO mixing for these molecules
- be able to critically evaluate VSEPR theory, localised 2c-2e bonding and the delocalised MO pictures of bonding
- be able to form correlation diagrams and explain why a particular geometry is more stable than another with reference to the stability of its MOs

Self-Study Problems / Test Preparation

- **Q1** draw and annotate the MO diagram for linear water HOH
- **Q2** Use your MO diagram from Q1 as a starting point to explain if the linear CH_2 fragment is expected to be diagmagnetic or paramagnetic
- **Q3** Create the correlation diagram by reducing the H-O-H angle, and forming bent H_2O and write a short description of what is happening for each MO under the deformation.
- **Q4** Use qualitative MO theory to predict if BeH_2 will be bent or linear.