

In-Class Problems / Self-study Problems / Test Preparation: Lecture 6

- **In-Class P1** Form the e' MOs for planar NH_3

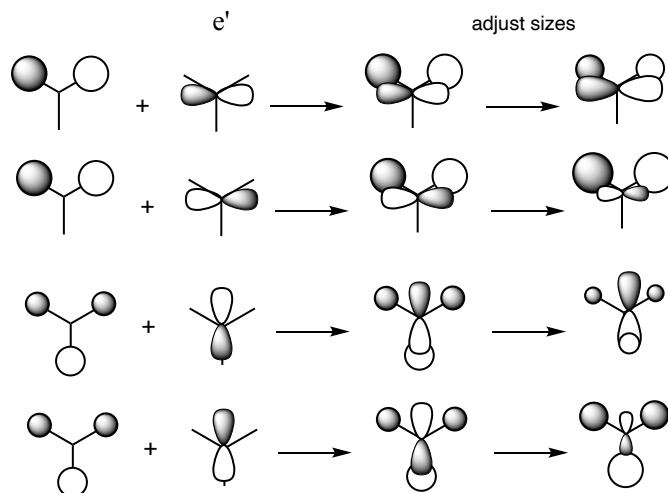


Figure 1 forming e' MOs for planar NH_3 .

- **In-Class P2** What are the main reasons the $2e'$ antibonding MOs go *down in energy*?
 - the $2e'$ antibonding MOs are stabilised due to a dominating reduction in the antibonding overlap of the central element pAO with the H sAOs,
 - there is also an increase in the through space H sAO antibonding interaction, but this is less than the NpAO-HsAO stabilisation which dominates
- **In-Class P3** Following the format of the diagram in Error! Reference source not found., determine the other mixed orbital by forming $-\psi(3a_1) + 4\psi(a_1)$, note that the first orbital is the negative of $\psi(3a_1)$

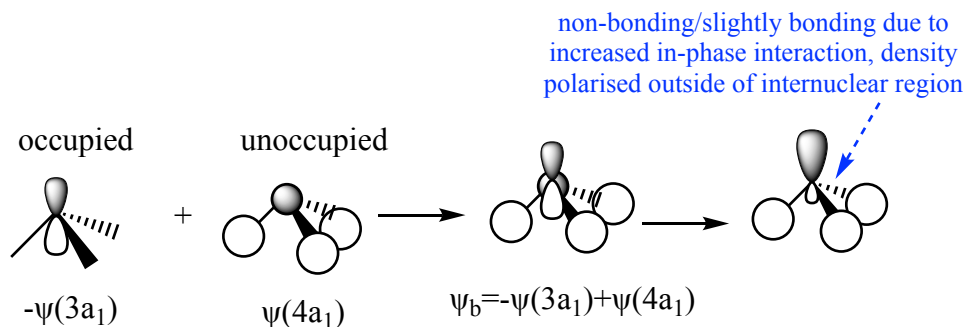


Figure 2 Mixing MOs (once with phase of one MO reversed)

- **Q1** draw and annotate the MO diagram for linear water HOH, this is shown on the left hand side of **Figure 3**
- **Q2** Use your MO diagram from Q1 as a starting point to explain if the linear CH_2 fragment is expected to be diamagnetic or paramagnetic
 - the MO diagram needs to be modified as C is less electronegative than O, the corresponding CH_2 fragment MO diagram shown on the right hand side of **Figure 3**
 - in linear CH_2 the last two electrons go into a degenerate set of π orbitals, these electrons will remain un-paired and thus linear CH_2 , if it existed, would be paramagnetic

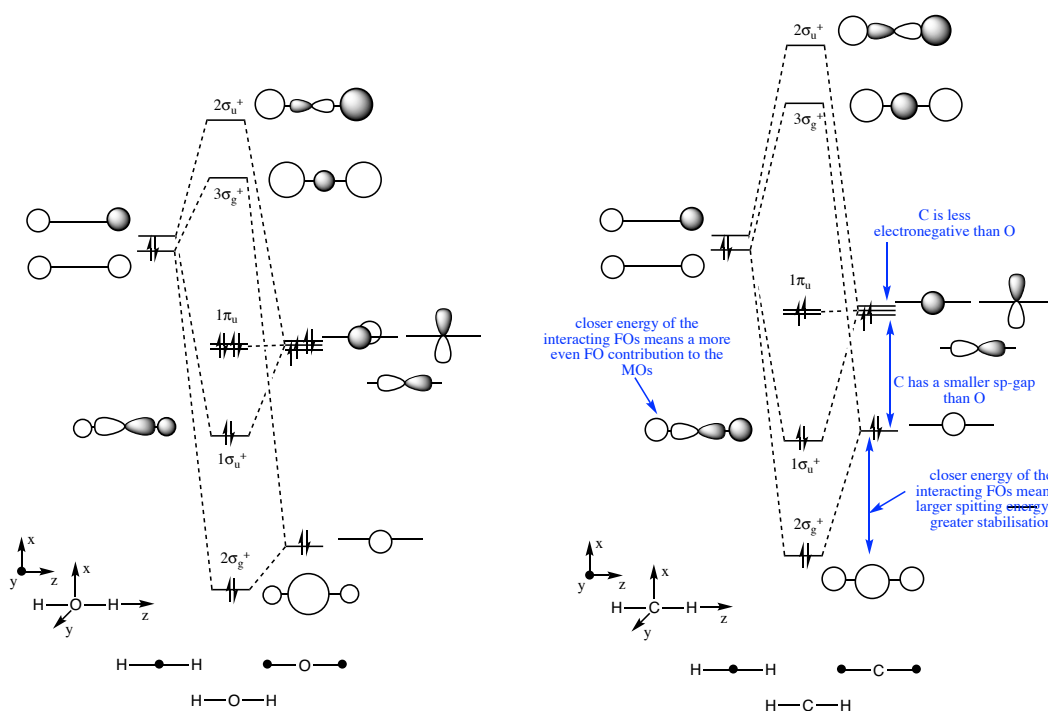


Figure 3 MO diagram comparing linear H₂O and CH₂.

- **Q3** Create the correlation diagram by reducing the H-O-H angle, and forming bent H₂O, see Figure 4, and write a short description of what is happening for each MO under the deformation

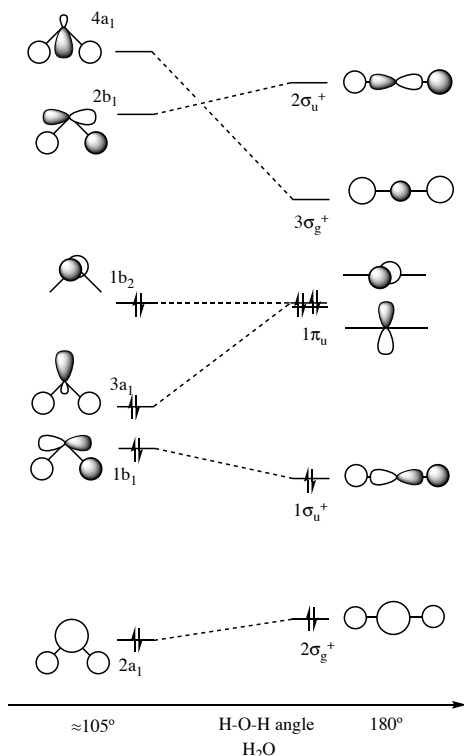


Figure 4 Correlation diagram for water

- by examining the "bonding" vs "antibonding" character of orbitals we can determine if they are stabilised or destabilised on the drop in symmetry.
- the $2\sigma_g^+$ (goes to $2a_1$) MO is stabilised due to an increase in the (through space) H-H sAO bonding overlap, there is no change in the Os-Hs overlap
- the $1\sigma_u^+$ (goes to $1b_1$) MO is destabilised due to a reduction in the Op-Hs bonding interaction, and an increase H-H antibonding interaction

- one of the $1\pi_u$ MOs (goes to $1b_2$) is non-bonding and thus has no change in energy
- the $2\sigma_u^+$ (goes to $2b_1$) MO is stabilised (go down in energy) due to a dominant decrease in the O-H bond bonding orbital overlap, there is also a smaller increase in the antibonding H...H through space interaction which raises the energy
- the other $1\pi_u$ and the $3\sigma_g^+$ MOs are special (go to the $3a_1$ and $4a_1$ MOs), in the linear $D_{\infty h}$ molecule the Op_x MO has π_u symmetry and therefore cannot mix with the $3\sigma_g^+$ MO, and thus cannot be stabilised.
- as soon as the linear molecule is distorted slightly it takes on C_{2v} symmetry, the symmetry label of the Op FO changes from $Op_x \rightarrow Op_z$ and the MO changes from $1\pi_u \rightarrow 3a_1$, and the symmetry label of the $3\sigma_g^+$ MO changes to $4a_1$, these orbitals are now allowed to mix and the occupied $3a_1$ MO is substantially stabilised.
- watch that the axes they must **formally re-orientate** on the symmetry change!

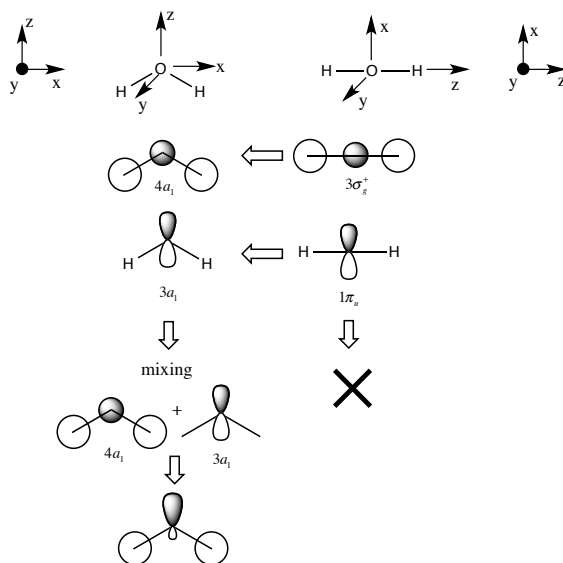


Figure 5 Mixing is “switched on” by the drop in symmetry

- **Q4** use qualitative MO theory to predict if BeH_2 will be bent or linear.
 - assume that we start from the same MO diagram as generated for H_2O
 - note that because Be is less electronegative than O the orbital coefficients for the MOs will change, **Figure 6**
 - the occupation is different!
 - BeH_2 will be linear
 - the stabilisation of the $3a_1$ MO which occurs in H_2O because of mixing does not occur in BeH_2 because the the $1\pi_u$ orbitals are not occupied and hence significant mixing cannot stabilise the molecule
 - thus it is the stability or instability of the $2a_1$ and $1b_1$ under the distortion which will determine the structure
 - in the diagram above I have shown a slight mixing of the $3a_1$ and $4a_1$, this is because all orbitals of the same symmetry actually interact slightly.
 - on moving away from linear the $2a_1$ is stabilised by overlap of the H $1s$ AO contributions, but the $1b_1$ is destabilised by more due to the antibonding overlap of the H $1s$ AO and reduction in overlap with the pAO on the Be.
 - the orbitals for the optimised linear structure are also shown on the MO diagram **Figure 6**

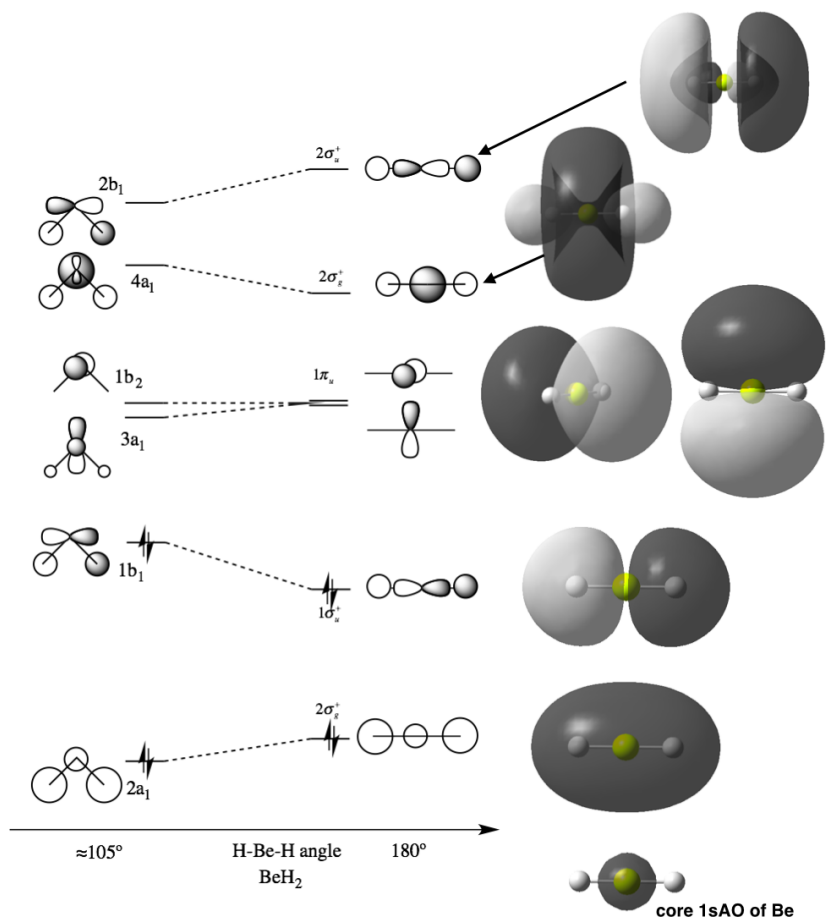


Figure 6 Correlation diagram for BeH₂