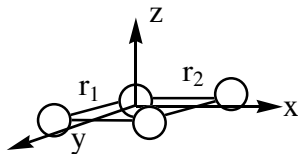


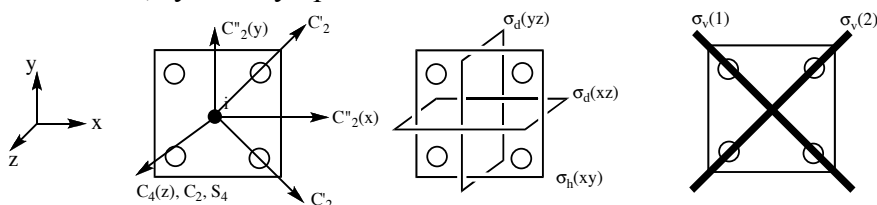
Construct the valence molecular orbital diagram for four H atoms arranged in a square as shown below. Then construct a correlation diagram by stretching r_2 . Indicate if the MOs go up or down in energy and explain why. Discuss when a square or a rectangular structure will be more stable.



Forming a MO diagram

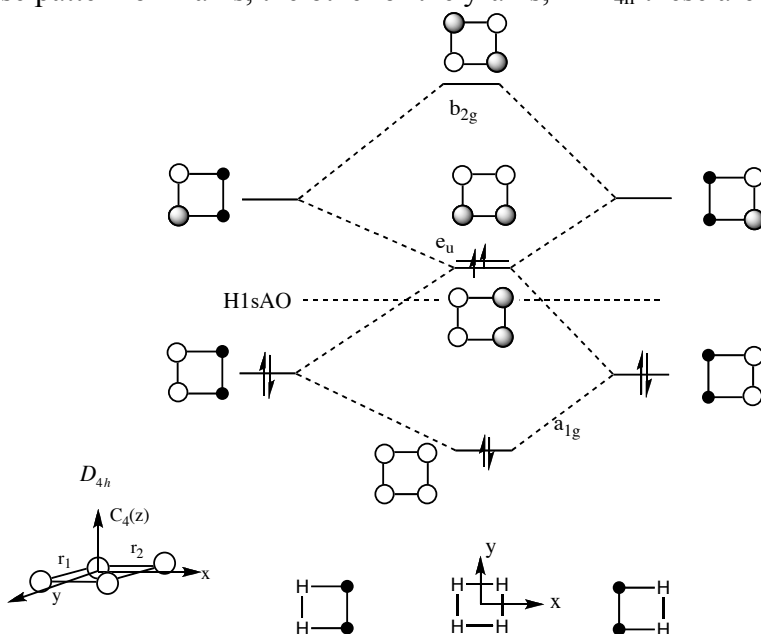
1. determine the molecular shape and identify the point group of the molecule
2. define the axial system find all of the symmetry operations on the molecule
3. identify the chemical fragments, and put them along the bottom of the diagram
4. determine the energy levels and symmetry labels of the fragment 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
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 the MO diagram check-list!
9. analyse the MO diagram

shape has been given, but start with the high symmetry structure point group is D_{4h}
axial system has been defined, symmetry operations

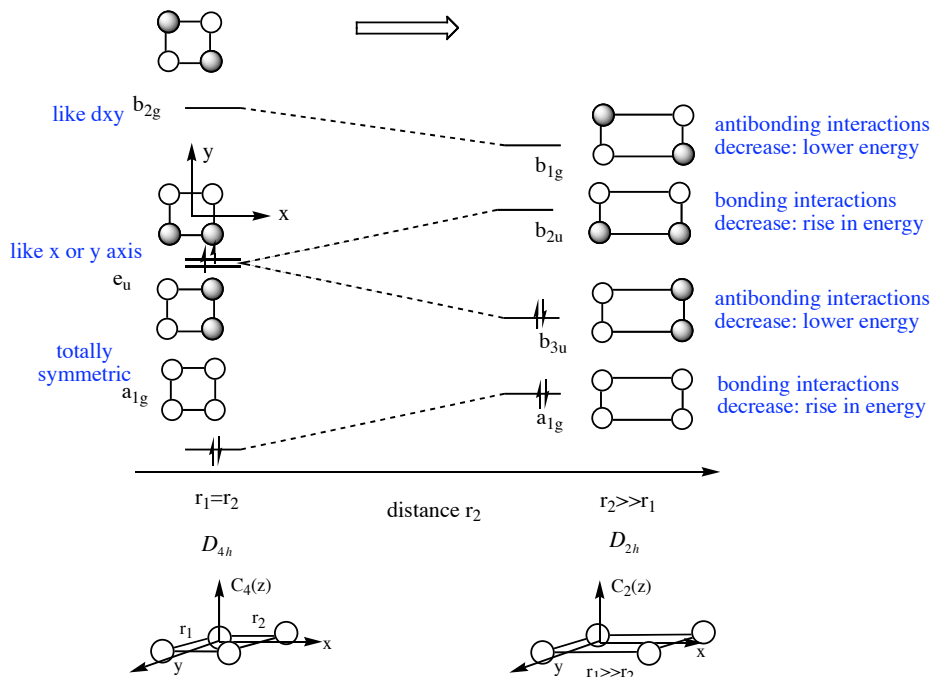


this is pretty easy to construct from two H_2 molecules interacting side on
how do you know the middle two are degenerate?

1. they have the same phase pattern
2. one has the phase pattern of x-axis, the other of the y-axis, in D_{4h} these are degenerate and e_u



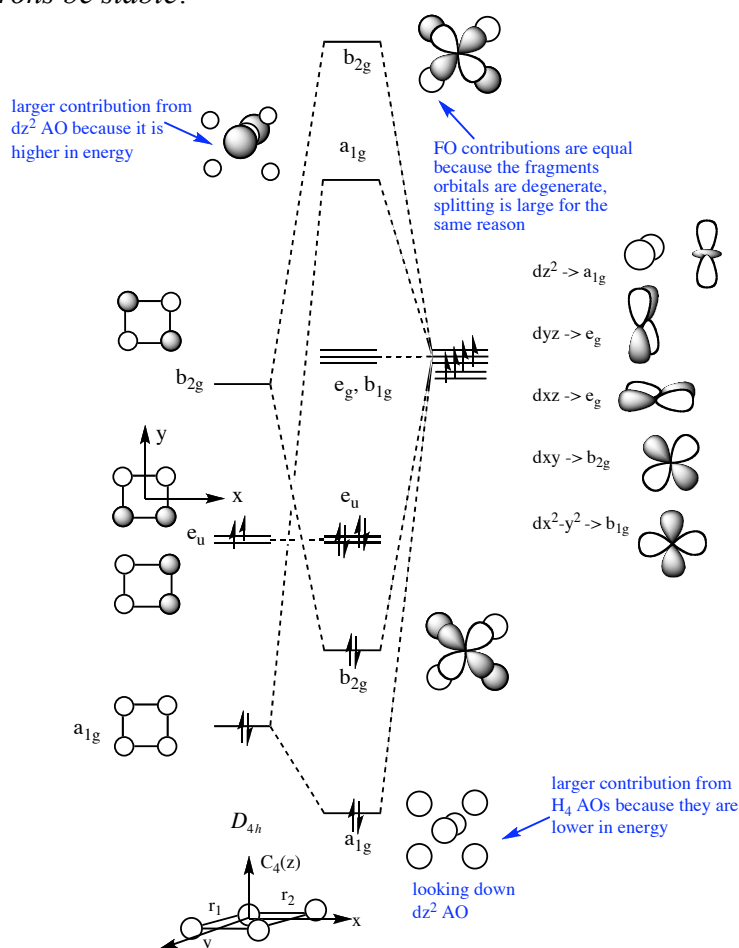
start with the high symmetry geometry and then distort looking at what happens to the overlap of the orbitals.



rectangular structure is likely to be more stable if the stabilisation of the b_{3u} orbital exceeds the destabilisation of the a_{1g} orbital. H_4^- (anion) however could be expected to be more stable as a square structure due to destabilisation of the b_{2u} orbital.

Extension.

Determine the MO diagram if a TM is placed in the center of the square formed by the four H atoms. The dAO fragment orbitals will be nearly degenerate with the antibonding FO from the H_4 fragment. Will a TM with 4d electrons be stable?



Yes a square planar species with 4 electrons in the dAOs will be stable. In addition, since the LUMO is the non-bonding dAOs more electrons can be added without substantially destabilising the molecule.