Construct and annotate a valence molecular orbital diagram for the linear molecule $MgCl_2$. Assume the Cl 3pAOs lie deeper in energy than the Mg 3sAO and that the Mg and Cl orbitals interact only slightly. Mg is a main group metal so the *valence* AOs are included in the MO diagram are the 3s and 3p AOs.

Extension (very advanced!)

Experimentally it has been found that the heavier group II (Ca, Mg, Ba) halides deviate from linear, and are increasingly bent. A number of theoretical models have been proposed to account for this behaviour, one of them suggests that occupied dAOs on the heavier group II element can participate in bonding via mixing with the HOMO region MOs. Another suggests that π-bonding interactions are enhanced on bending. Consider only the HOMO region occupied MOs, distort the molecule by reducing the L-M-L angle and analyse the resulting changes in these MOs, does the molecule appear overall stabilised or destabilised? Introduce dAO contributions on the central element, and evaluate their effect on the stability of the distorted molecule. (*I will be happy to look at and discuss your answers to this question with you*)

Forming a MO diagram

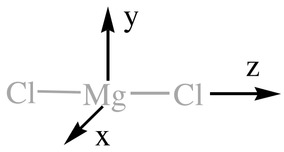
1. determine the molecular shape and identify the point group of the molecule
2. define the axial system find all of the symmetry operations on the molecule
3. identify the chemical fragments, and put them along the bottom of the diagram
4. determine the energy levels and symmetry labels of the fragment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

1. Determine the molecular shape and identify the point group of the molecule

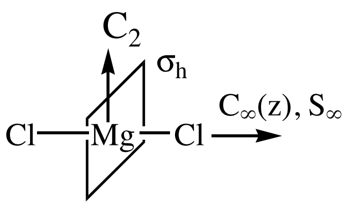
- shape has been given: linear
- point group: $D_{\infty h}$

2. Define the axial system find all of the symmetry operations on the molecule

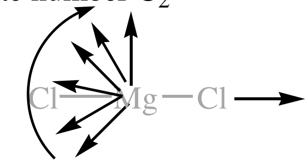
- define axial system: z-axis aligns along the principle axis (highest symmetry axis) C_∞



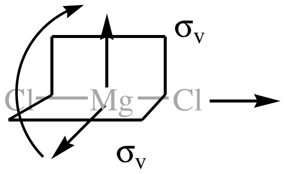
- find all of the symmetry operations/elements:
  - character table headings: E, $2C_\infty^\phi$ $\infty\sigma_v$, i, S_∞^ϕ …∞C_2
  - the C_∞ axis is also a C_2, C_3, C_4, C_5 ... up to C_∞ axis, this is represented by the angle ϕ in C_∞^ϕ
  - symmetry elements



infinte number C_2



each C_2 has an associated σ_v plane therefore an infinite number σ_v



3. Identify the chemical fragments, and put them along the bottom of the diagram

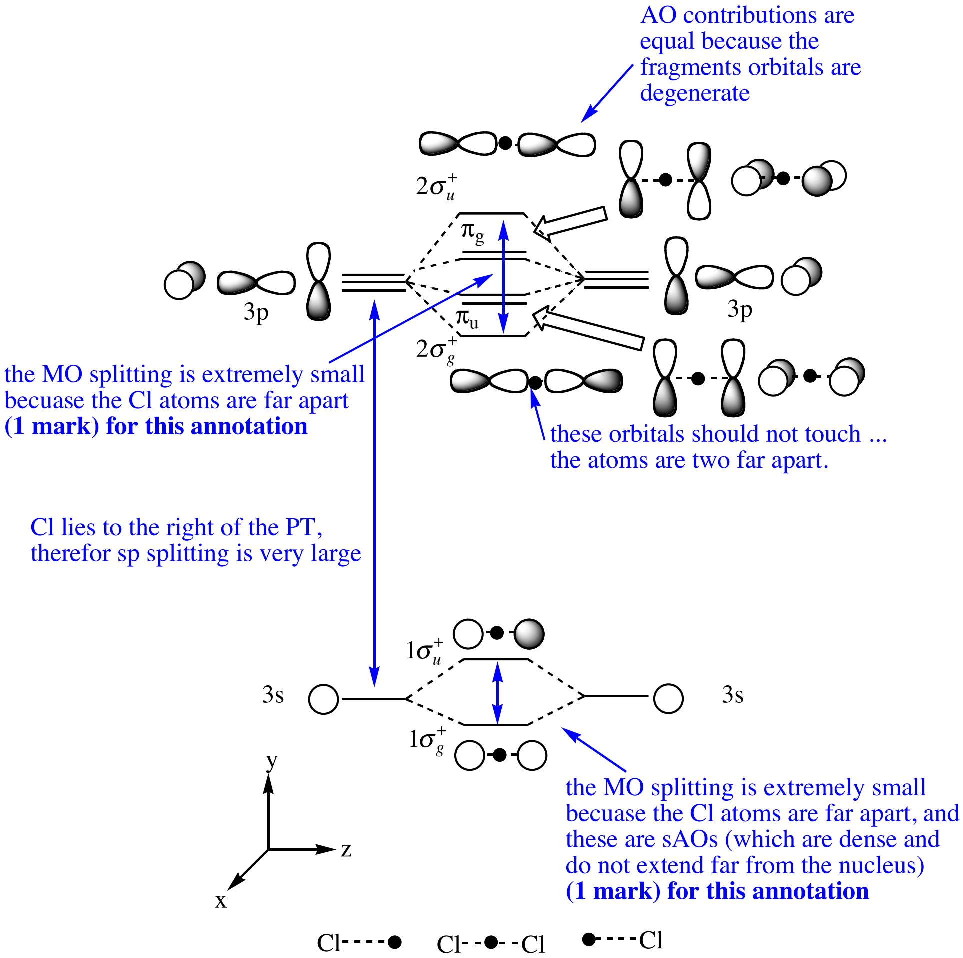
- Chemical fragments as Cl–•–Cl, with Cl atoms far apart and •–Mg–• a central Mg atom. First we need to construct an intermediate diagram for the Cl_2 unit, Cl–•–Cl, this is shown below. Then we will add the Mg cation fragment.

4. Determine the energy levels and symmetry labels of the fragment orbitals

Intermediate diagram for Cl–•–Cl fragment

- this is not Cl_2 so looking for
  - good separation between atoms
  - orbitals that do not touch
  - almost degenerate energy levels in both 3s and 3p manifolds, the 3p π split less than the 3p σ
- because the individual Cl are not symmetry fragments we combine FOs of the same symmetry (s, p_x, p_y and p_z) and then we have to determine the symmetry of the resultant MO under the point group of the molecule
  - $1\sigma_g+$ totally symmetric is easy
  - the $1\sigma_u+$ has the same symmetry as the z-axis

  - the $2\sigma_g+$ has the same phase pattern as a dz^2 AO
  - the π bonding MOs (π_u) formed from the p_x and p_y AOs have the same symmetry as the x and y axes
  - the π anti-bonding MOs (π_g) formed from the p_x and p_y AOs have the same symmetry as the dxz and dyz AOs
  - the $2\sigma_u+$ MO maps onto itself under rotation about the z-axis, so must be of σ type. It inverts under i so must be un-gerade (u) and is anti-symmetric under C_2 rotation so must be "plus" (+). Thus this is a σ_u+ MO.
- symmetry labels for MOs are ALWAYS small letters, not capitals **(important point!)** (from talking with students it appears many of you do not know the Greek letters, these can be found in the front of Atkins physical chemistry (or look them up on-line). Greek letters are used commonly in equations in physical chemistry and you should know them (both capitols and normal)!
- looking for a large sp gap, the $1\sigma_u$ and $2\sigma_g$ should not be close, ideally a written comment on this either in text or as an annotation
- there will be no s-p mixing because (a) the large sp gap (cf O_2 and F_2) and (b) there are two bonds between the atoms. Thus the σ and π interactions will not split enough to drive the orbitals into a region where they can mix.



AO contributions are equal because the fragments orbitals are degenerate

the MO splitting is extremely small becuase the Cl atoms are far apart **(1 mark) for this annotation**

these orbitals should not touch ... the atoms are two far apart.

Cl lies to the right of the PT, therefor sp splitting is very large

the MO splitting is extremely small becuase the Cl atoms are far apart, and these are sAOs (which are dense and do not extend far from the nucleus) **(1 mark) for this annotation**

Figure 1 Intermediate diagram

Then for the full MO diagram

- the question states that "*the Cl 3pAOs lie deeper in energy than the Mg 3sAO*"
  - thus the Mg 3sAO must lie above the 3pAOs (the Cl fragment barely interacts and so the Mg 3s will lie above the $2\sigma_u$ Cl fragment FO)
- the question states "*a valence molecular orbital diagram*" this implies:

  - the use of all and only the last shell principle quantum number orbitals, for Cl this will be the 3s and 3p, for Mg this will be the 3s and 3p ONLY
  - Mg lies to the left of the PT, the sp gap is very small, thus both the 3s and 3p AOs should be shown
  - Mg is a main group metal so we do not show the dAOs
- the question states "*Construct and annotate* "
  - 5 out of 20 marks were assigned for key annotations
  - *for example* from Lecture 3: I have **annotated** this MO diagram (the grey bits). I expect you to annotate your MO diagrams, explaining key features.

IMPORTANT

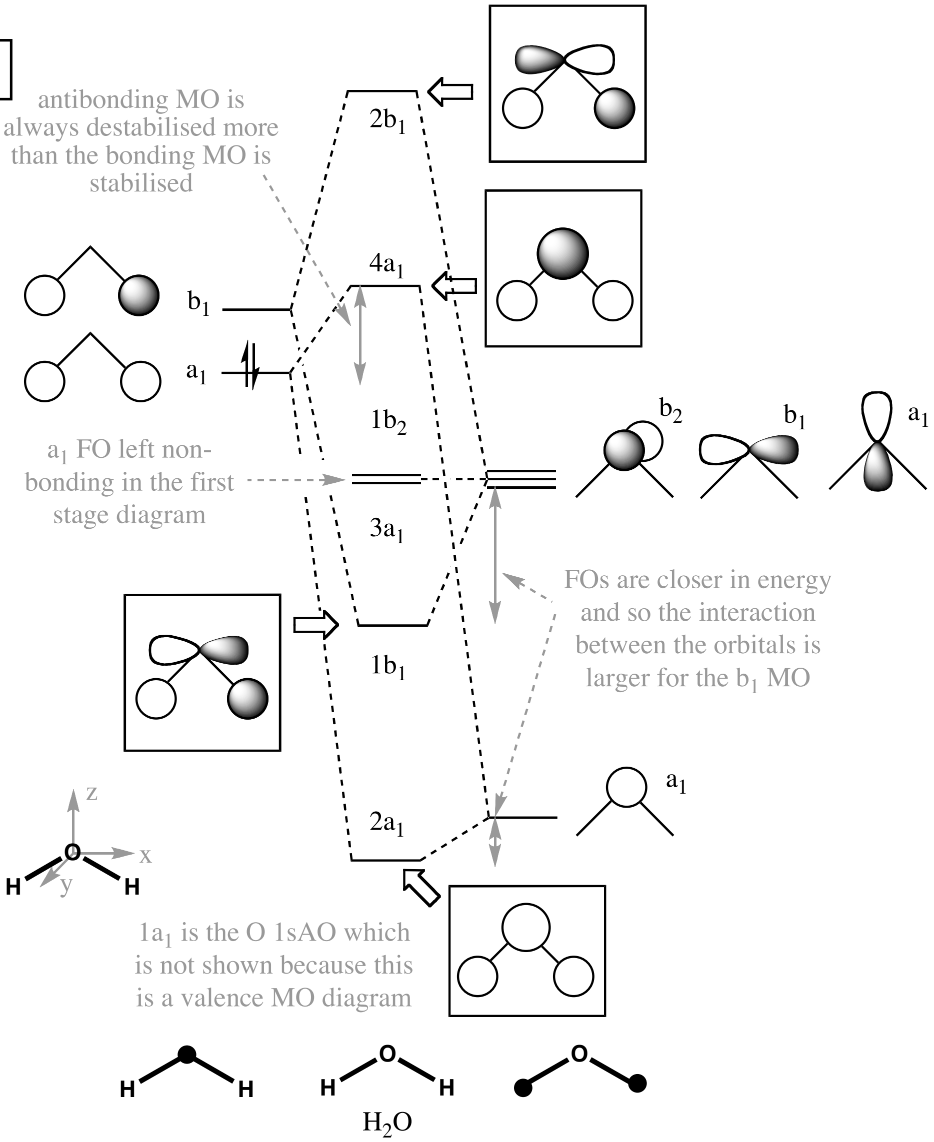


Figure 2 Figure 8 from Lecture 3 showing annotations

- use same molecular structure for all orbitals **(important point!)**
  - the nuclei are assumed stationary re the Born-Oppenheimer approximation UNLESS doing a correlation diagram. You cannot have nuclei in one position for one MO and then bonds stretched, contracted or moved out-of-plane for other MOs. Be consistent!
  - use place holders in the fragments and in the MOs this will stop you from making mistakes when you add FOs to form the full MO

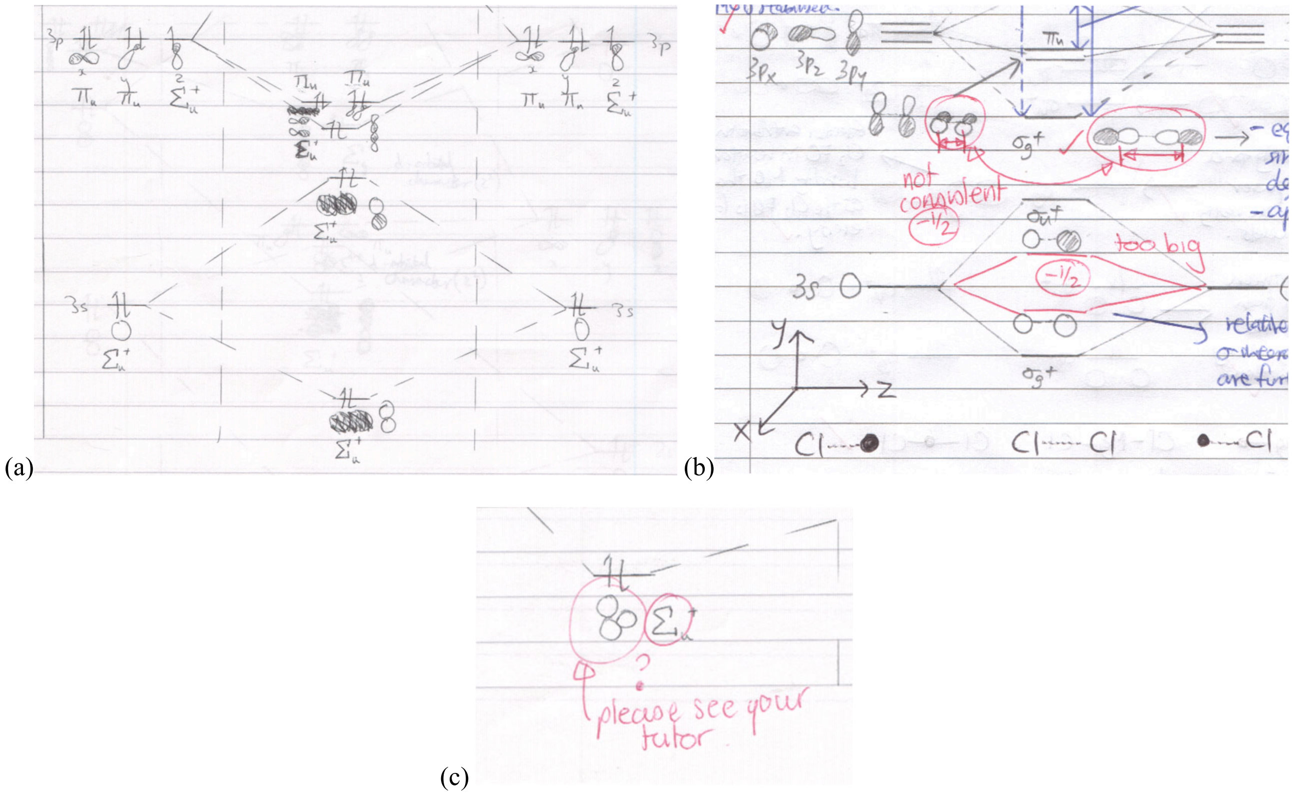
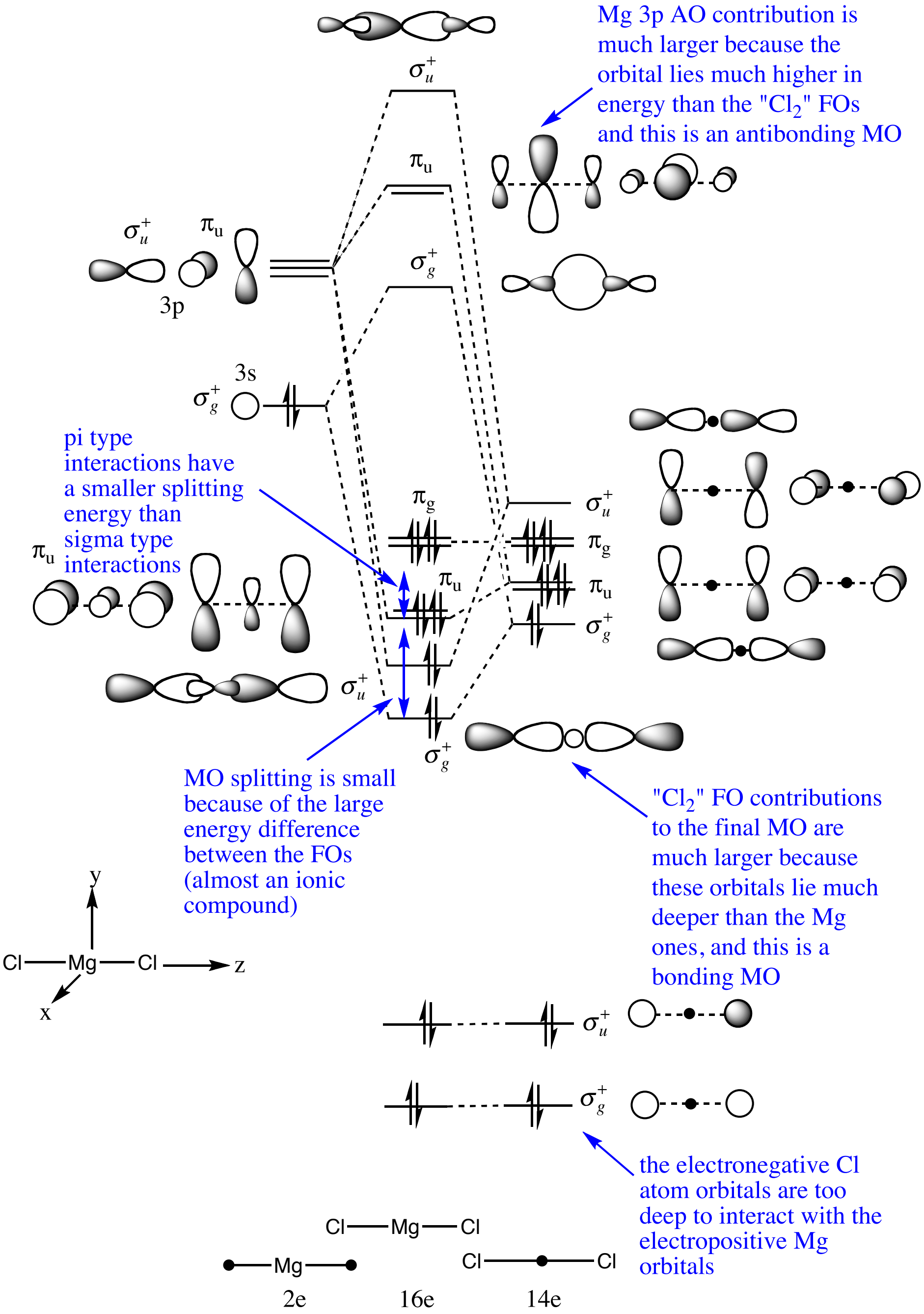


Figure 3 (a) show change of alignment of molecule between MOs, (b) showing significant increase in atomic positions between MOs, (c) showing combination of AOs that is not linear

5. combine fragment orbitals of the same symmetry, estimate the splitting energy and draw in the MO energy levels and MOs (in pencil!)



Mg 3p AO contribution is much larger because the orbital lies much higher in energy than the "Cl$_2$" FOs and this is an antibonding MO

pi type interactions have a smaller splitting energy than sigma type interactions

MO splitting is small because of the large energy difference between the FOs (almost an ionic compound)

"Cl$_2$" FO contributions to the final MO are much larger because these orbitals lie much deeper than the Mg ones, and this is a bonding MO

the electronegative Cl atom orbitals are too deep to interact with the electropositive Mg orbitals

Figure 4 Annotated MO diagram

6. determine the number of electrons in each fragment and hence the central MO region

- Cl_2 fragment has 14e
- Mg fragment has 2e
- total is 16e

7. identify if any MO mixing occurs, and redraw the MO diagram with the mixed MOs

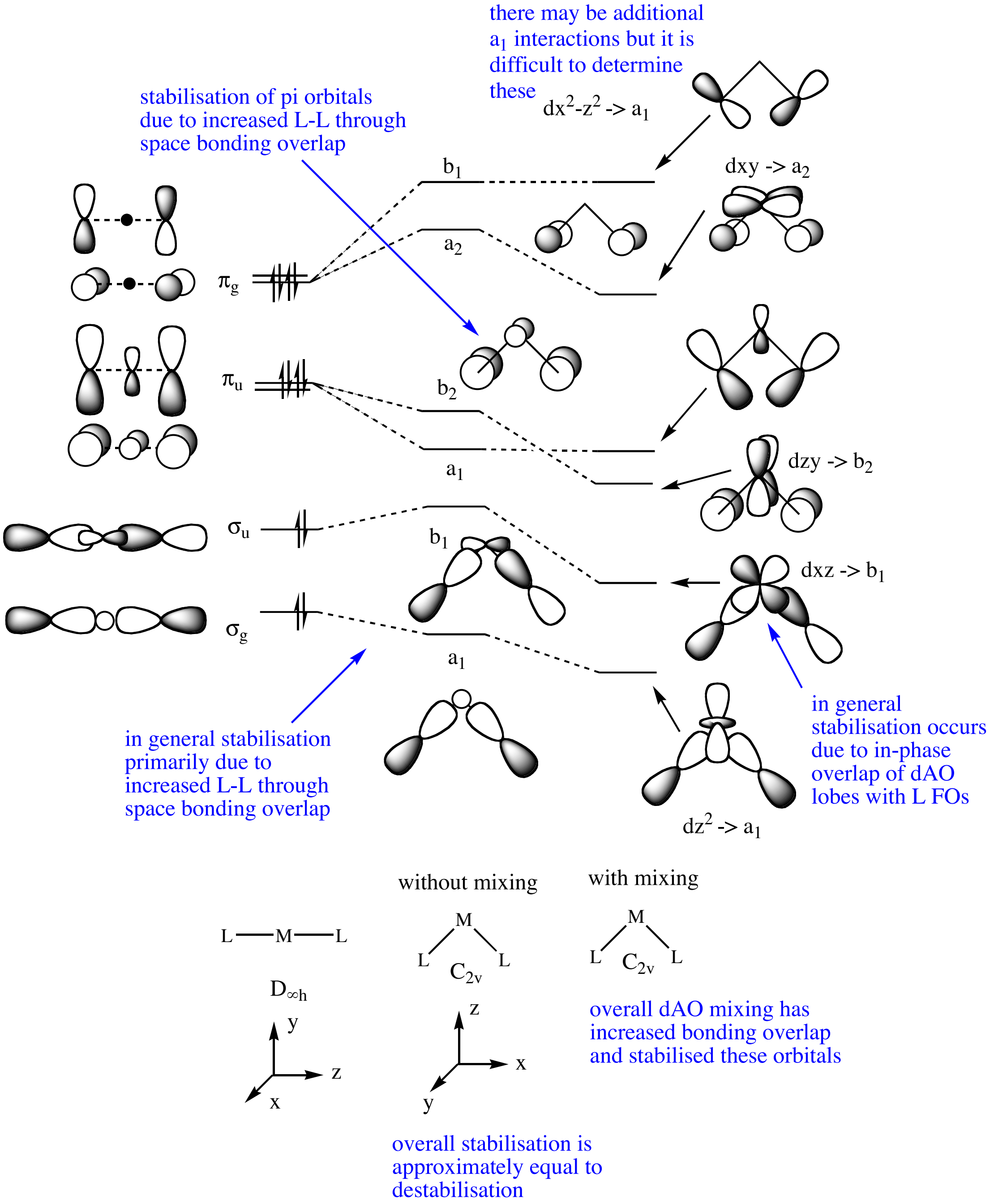
- mixing must be between orbitals of the same symmetry that are not part of the same bonding-antibonding pair, and is largest when the orbitals are close in energy, in the HOMO-LUMO region, and when one of the MOs is non-bonding or unoccupied.
- The π_g MO could mix (occupied, non-bonding, in HOMO-LUMO region), but there is no unoccupied MO orbital of the correct symmetry to mix with this MO -> no mixing

Marking Scheme

- Setup
  - **1 mark** for point group
  - **1 mark** for symmetry elements
  - **1 mark** for define axial system and molecule orientation with respect to the axial system (**0.5** if only axial system is shown)
  - **1 mark** for chemical fragments (**0.5** if place-holders are not shown)
- Fragment Orbitals
  - **1 mark** for Cl_2 fragment energies (-0.5 if no sAOs or if sAOs are not deep, -0.5 splitting too large)
  - **1 mark** for explaining why the splitting is so small, preferably as an annotation
  - **1 mark** for Cl_2 FOs (-0.5 AOs too close or if orientation changes, -1 if LCAOs not used)
  - **1 mark** for Mg fragment energies and FOs
  - **1 mark** symmetry labels (-0.5 if capitols used, -0.5 for simple mistakes like missing u or g)
- Molecular Orbitals
  - **0.5 marks** for σ_g interaction
  - **0.5 marks** for π_u interaction
  - **0.5 marks** for σ_u interaction
  - **0.5 marks** for rest
  - **1 mark** for altering the AO size to reflect expected coefficient size
  - **1 mark** for an annotation explaining that the bonding MO has a larger contribution from the lower energy FO and the antibonding MO has a larger contribution from the higher energy FO
  - **1 mark** symmetry labels (-0.5 if capitols used, -0.5 for simple mistakes like missing u or g)
  - **1 mark** MO energies (-1 if the interaction is not small, -0.5 for using deep ClsAOs, -0.5 for not using Mg pAOs, or using Mg 2pAOs, -0.5 for only using Mg 2p(σ) and not 2p(π), maximum loss is 1 mark)
  - **1 mark** MO for explaining, ideally as an annotation, why there is only a slight stabilisation, that is the MOs are far apart in energy
  - **1 mark** for explaining, ideally as an annotation, that the Cl sAOs are too deep in energy to interact with the Mg FOs
  - **1 mark** for explaining, ideally as an annotation, that there is no mixing because mixing must be between orbitals of the same symmetry that are not part of the same bonding-antibonding pair, and is largest when the orbitals are close in energy, in the HOMO-LUMO region, and when one of the MOs is non-bonding or unoccupied. None of these conditions are satisfied for $MgCl_2$ MOs. (Lecture 3)
  - **1 mark** for correct electronic configuration
  - **1 mark** for a diagram I could read that was relatively neat and tidy
- Feedback given to students last year which may be helpful for you.
  - The MO diagrams we create are based on the "linear combination of atomic orbitals (LCAOs) so you should not combine the orbitals from different centers, see Lecture 4 Figure 7. If you do this you cannot accurately determine bonding and antibonding interactions, and if forming intermediate diagrams you will run into problems.
  - Deep AOs lead to a large electronegativity, the orbitals are deep and so it is hard to remove the electrons from the atom, the electronegativity is a result of orbital stability
  - Mixing only occurs between MOs, MOs do not mix with FOs
  - Use each FO ONLY ONCE, then invoke mixing
  - It is excellent that many students tried to interpret their diagram, however it is not appropriate to try and work out the bond order for anything other than a diatomic.

Extension for experts! (voluntary).

Experimentally it has been found that the heavier group II (Ca, Mg, Ba) halides deviate from linear, and are increasingly bent. A number of theoretical models have been proposed to account for this behaviour, one of them suggests that occupied dAOs on the heavier group II element can participate in bonding via mixing with the HOMO region MOs. Another suggests that π-bonding interactions are enhanced on bending. Consider only the HOMO region occupied MOs, distort the molecule by reducing the L-M-L angle and analyse the resulting changes in these MOs, does the molecule appear overall stabilised or destabilised? Introduce dAO contributions on the central element, and evaluate their effect on the stability of the distorted molecule. (*I will be happy to look at and discuss your answers to this question with you*)



there may be additional a_1 interactions but it is difficult to determine these

stabilisation of pi orbitals due to increased L-L through space bonding overlap

in general stabilisation primarily due to increased L-L through space bonding overlap

in general stabilisation occurs due to in-phase overlap of dAO lobes with L FOs

overall dAO mixing has increased bonding overlap and stabilised these orbitals

overall stabilisation is approximately equal to destabilisation

Figure 5 Correlation MO diagram