Self-Study Problems / Exam Preparation

- Draw the MO diagram for Mo_2 and show that a sextuple bond order is potentially possible.
  - Cr, has the valence configuration $[Ar]3d^4 4s^2$ Mo and W are similar with higher principle quantum number 5s and 6s respectively, the metals are more stable with half filled shells $[Ar]nd^5(n+1)s^1$, **Figure 1**

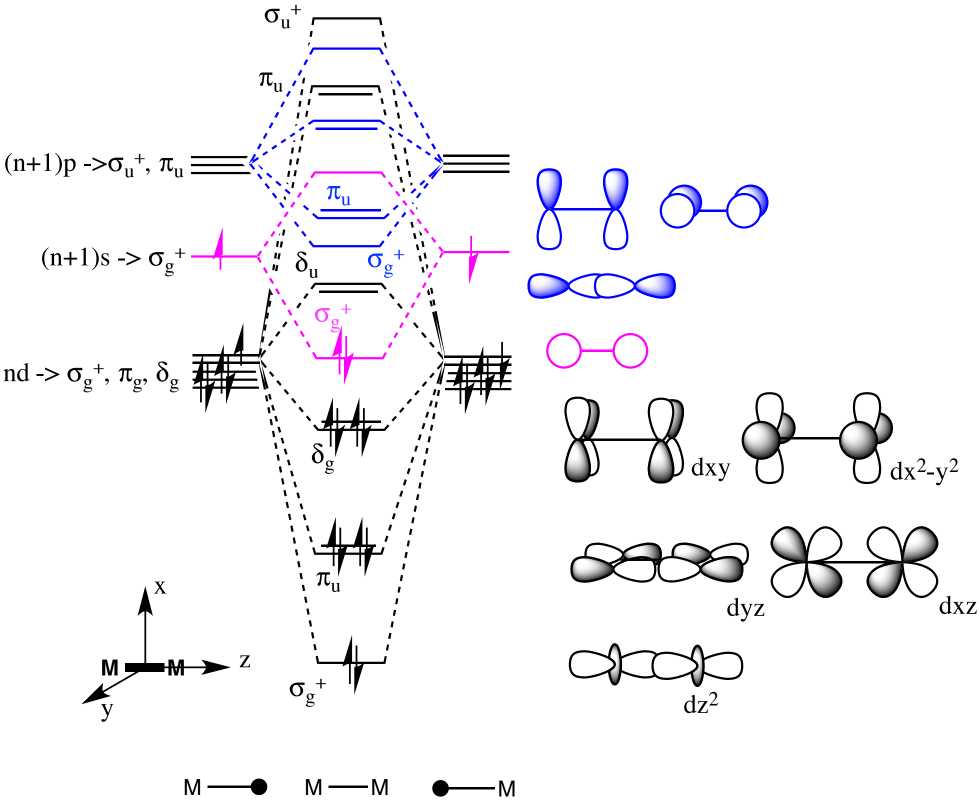


Figure 1 M_2 showing sextuple bonding

- Use the long method to show that the M_2 dimer dxz/dyz combination of AOs has π_u symmetry.
  - remember the $D_{\infty h}$ symmetry elements, **Figure 2**

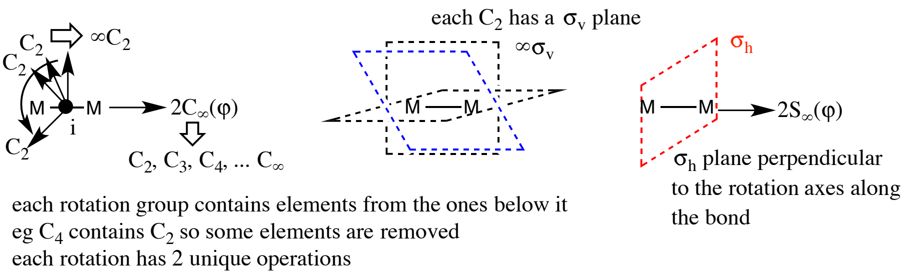


Figure 2 $D_{\infty h}$ symmetry elements

  - start building a representation table, **Figure 3**

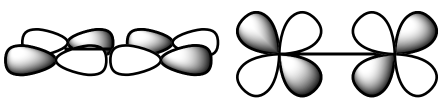
$D_{\infty h}$	E	$2C_x(\varphi)$	$\infty\sigma_v$	i	$2S_x(\varphi)$	∞C_2
						

Figure 3 $D_{\infty h}$ empty representation table

- work out how the degenerate orbitals transform under each symmetry element, **Figure 4**

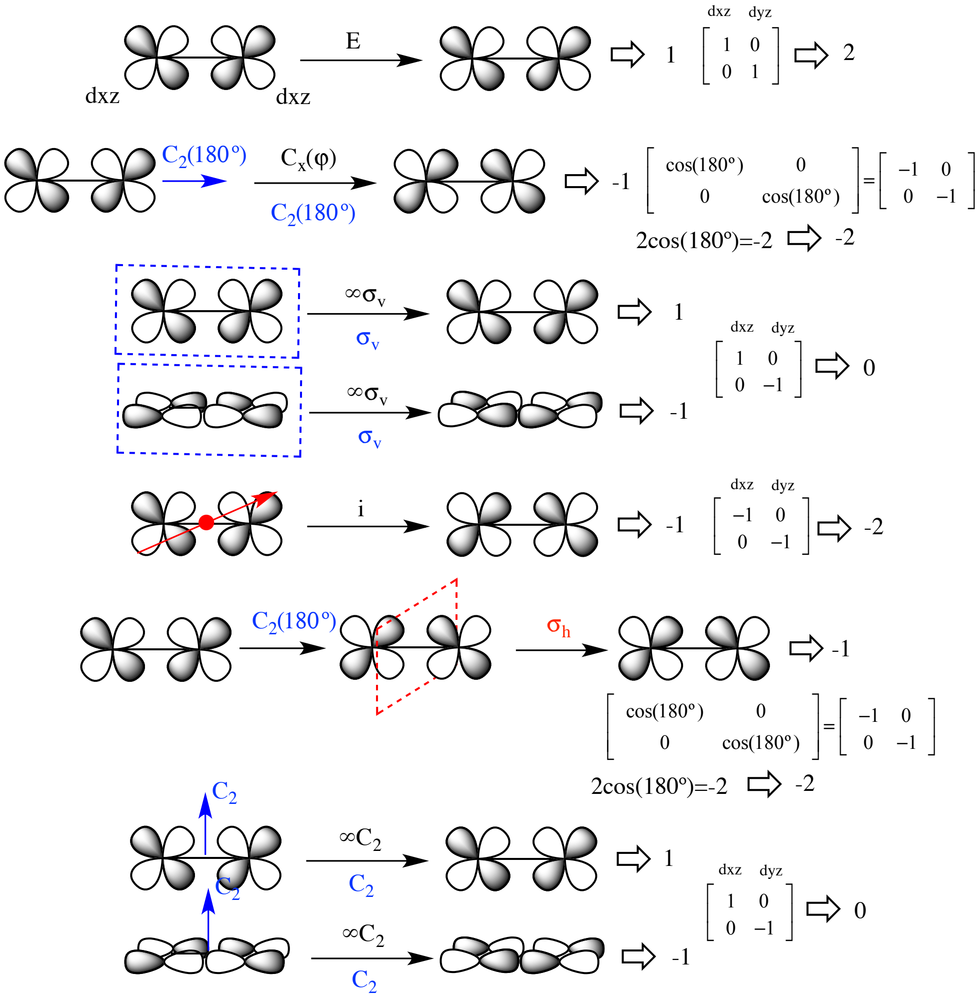
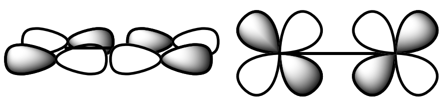


Figure 4 working out the characters

- and fill in the representation table, **Figure 5**



$D_{\infty h}$	E	$2C_x(\varphi)$	$\infty\sigma_v$	i	$2S_x(\varphi)$	∞C_2	
	2	0	2	-2	-2	0	⇨ π_u

Figure 5 $D_{\infty h}$ filled representation table

- Clearly show using diagrams that $S_4^2 = C_2$ and $S_4^4 = E$ Thus, showing that there are 2 unique operations per S_4 axis in the O_h point group.
  - using one pAO from each of the two sets of symmetry related pAOs for C_4 and σ_h **Figure 6**

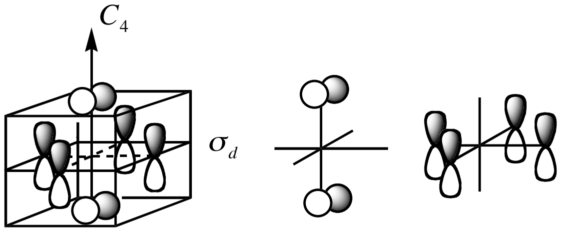


Figure 6 Sets of symmetry related orbitals

  - show the effect of two sequential S_4 operations, this is the same as $1C_2$ rotation which is also the same as $2C_4$ rotations, **Figure 7**

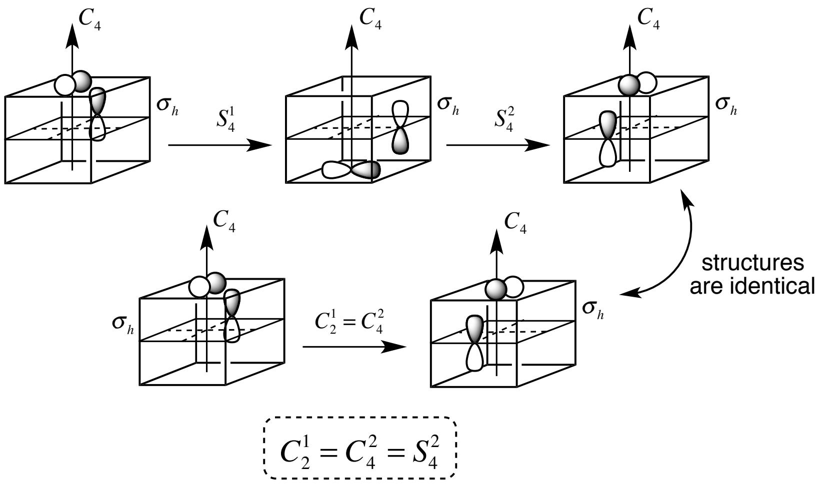


Figure 7 $2S_4$ operations under the O_h point group

  - show the effect of four sequential S_4 operations, this is the same as E, ie the starting structure, **Figure 8**

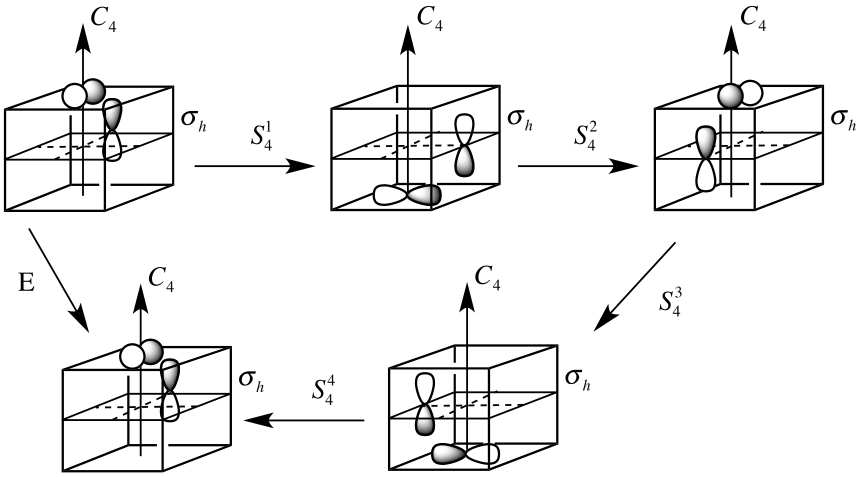


Figure 8 $4S_4$ operations under the O_h point group

  - (S_4^1 $S_4^3 = S_4^{-1}$) are the unique operations (ie a forward and a backward rotation)

- Clearly show using diagrams that S_6^1 and $S_6^5 = S_6^{-1}$ are the only unique operations for each S_6 axis in the O_h point group.
  - there are $8S_6$ operations in O_h, each C_3 axis can also be thought of as having a coincident C_6 and σ_h mirror plane perpendicular to this axis. these are not symmetry elements of O_h because of the staggered arrangement of the three ligands
  - all of the S_6 operations are shown in **Figure 9**, only two are unique S_6^1 and $S_6^5 = S_6^{-1}$. $S_6^2 = C_3^1$, $S_6^3 = i$, $S_6^4 = C_3^2$ and $S_6^6 = E$ here I show explicitly that $S_6^2 = C_3^1$ in **Figure 10**

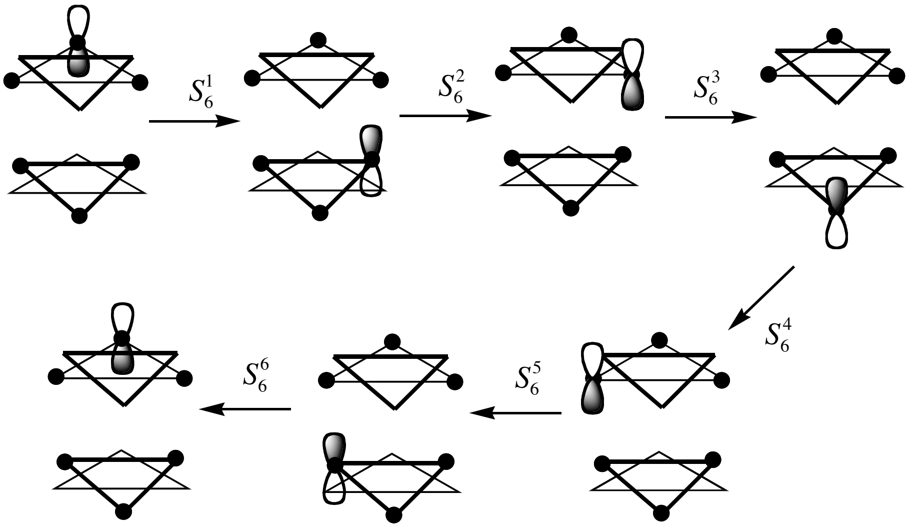


Figure 9 The S_6 operations

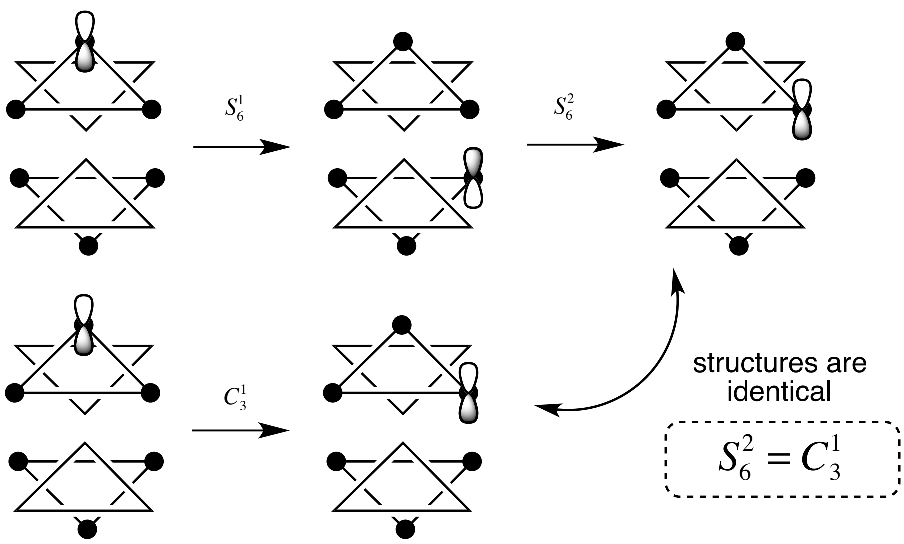


Figure 10 $2S_6$ operations under the O_h point group