Improper Rotations S_6 for O_h

- there are $6S_4$ operations in the O_h point group
  - each pair of C_4 axis and σ_d mirror plane has an associated improper rotation, the S_4 axis is coincident with the C_4 axis.
  - phase changes are important for improper rotations and it is best to work with pAOs rather than sAO when drawing out these operations. There are two sets of symmetry related orbitals; the equatorial and axial p_π orbitals. These subsets only transform amongst themselves under the S_4, **Figure 1**

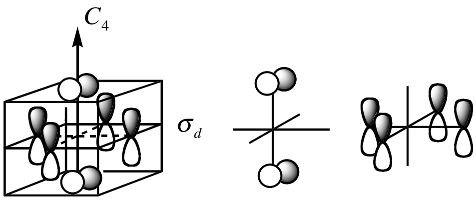

Figure 1 Sets of symmetry related orbitals

  - Consider a S_4^1 operation which consists of a rotation of 90º around a C_4 axis and then reflection in the associated σ_h plane. An example of the S_4^1 operation is given in **Figure 2**. For simplicity the effect of the S_4^1 operation has been shown for a single equatorial and axial p_π orbital. Notice that if you considered only the equatorial p_π orbitals you might conclude that $S_4^1 = C_2''$, which would be incorrect.

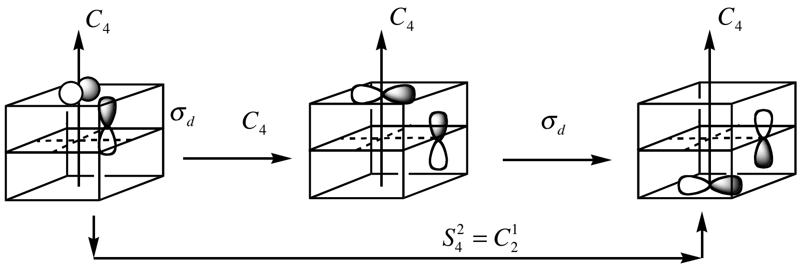

Figure 2 S_4^1 operation

  - working through the various improper rotation symmetry operations results in identifying that $S_4^2 = C_2$ and $S_4^4 = E$, **Figure 3**, thus for each C_4 axis (of which there are three) there are two unique S_4 operations (S_4^1 $S_4^3 = S_4^{-1}$) and hence there are $6S_4$ operations in O_h.

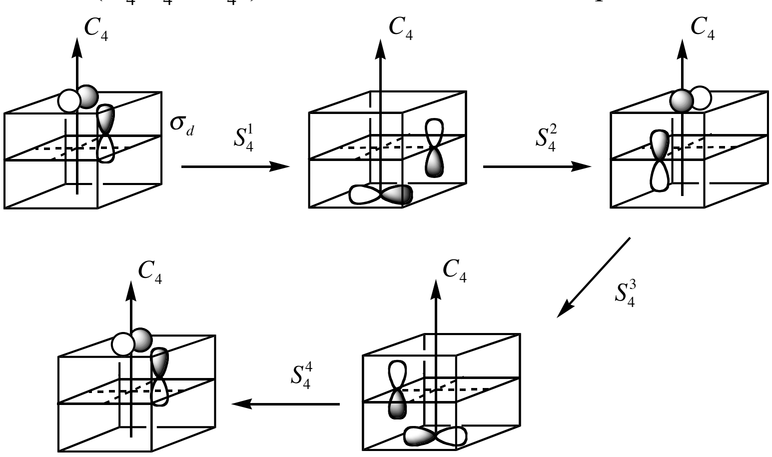

Figure 3 All S_4 operations

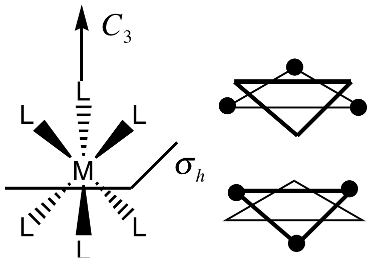

Figure 4 simplified model for octahedral complex emphasising the C_3 axis

- there are $8S_6$ operations
  - 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
  - in **Figure 4**, a simplified model is shown with has black dots on the sites that are occupied by ligands
  - consider S_6^1, a rotation of 60° and then reflection in the associated σ_h plane perpendicular to the axis, **Figure 5**
  - all of the S_6 operations are shown in **Figure 6**, only two are unique S_6^1 and $S_6^5 = S_6^{-1}$.
  - thus for each C_3 axis (of which there are four) there are two associated S_6 operations and hence there are $8S_6$ operations in O_h

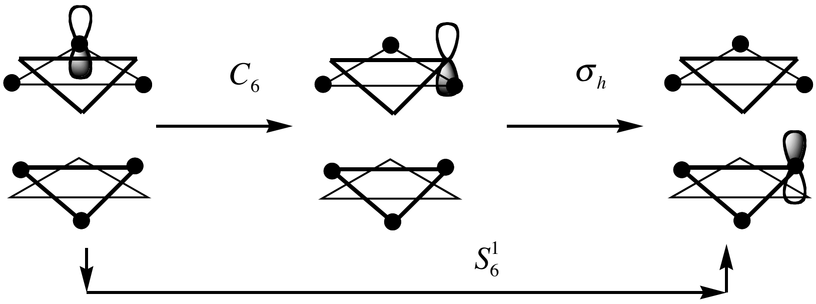

Figure 5 Components of the S_6^1 operation

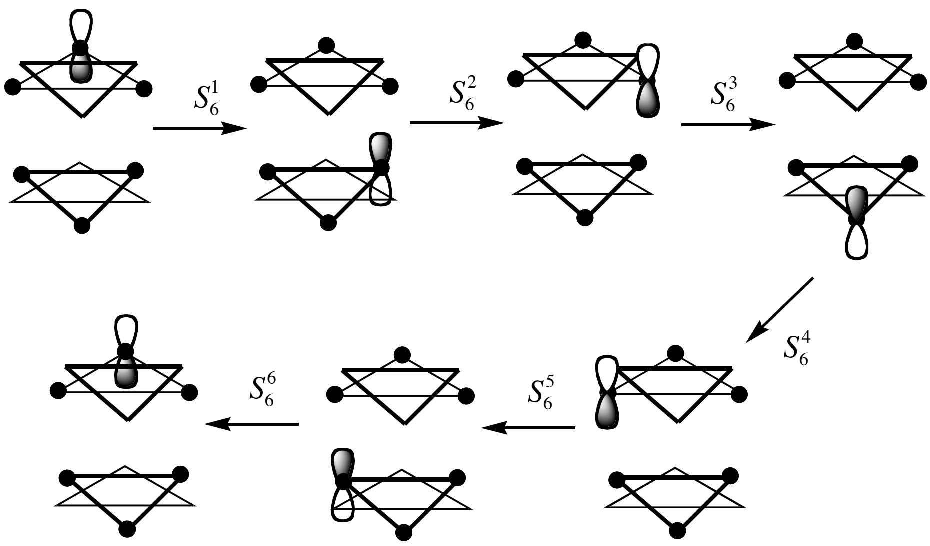

Figure 6 The S_6 operations