Symmetry Operations and Elements

- The goal for this section of the course is to understand how symmetry arguments can be applied to solve physical problems of chemical interest.

- To achieve this goal we must identify and catalogue the complete symmetry of a system and subsequently employ the mathematics of groups to simplify and solve the physical problem in question.

- A **symmetry element** is an imaginary geometrical construct about which a symmetry operation is performed.

- A **symmetry operation** is a movement of an object about a symmetry element such that the object's orientation and position before and after the operation are indistinguishable.

- A symmetry operation carries every point in the object into an **equivalent point or the identical point**.
The Electronic Structure of Ferrocene

- The two cyclopentadienyl (Cp) rings of ferrocene may be orientated in the two extremes of either an eclipsed ($D_{5h}$) or staggered ($D_{5d}$) conformation.

- The energy of rotation about the Fe-Cp axis is very small ($\sim 4 \text{ kJmol}^{-1}$) and ground state structures of ferrocene may show either of these conformations.

- There is also very little difference in electronic states between the $D_{5h}$ and $D_{5d}$ symmetries however the $D_{5d}$ point group irreducible representations are used here in the description of the electronic structure of ferrocene as they simplify the symmetry matching of ligand molecular orbitals (SALCs) and metal atomic orbitals.

- The primary orbital interactions that form the metal-ligand bonds in ferrocene occur between the Fe $d$ orbitals and the $\pi$-orbitals of the Cp ligand.

- If $D_{5d}$ symmetry is assumed, so that there is a centre of symmetry in the ferrocene molecule through the Fe atom there will be centro-symmetric ($g$) and anti-symmetric ($u$) combinations.
$\pi$ MOs of Cyclopentadienyl, $\text{C}_5\text{H}_5^-$

- $\text{C}_5\text{H}_5^-$, has three pairs of electrons delocalized in a $\pi$ system extending around the pentagonal ring.

- The five $2p$ orbitals perpendicular to the ring on the five carbon atoms combine to form three bonding ($\pi^1$, $\pi^2$, $\pi^3$) and three antibonding ($\pi^4^*$, $\pi^5^*$, $\pi^6^*$) MOs.

- The symmetries and forms of these MOs can be deduced by applying the operations of the point group $D_{5h}$ to a set of five vectors perpendicular to the ring, one at each carbon, to generate a reducible representation $\Gamma_\pi$. 

![Diagram showing the delocalization of electrons in a π system](image-url)
\[ \pi \text{ MOs of Cyclopentadienyl, } \text{C}_5\text{H}_5^- \]

\[
\begin{array}{|c|c|c|c|c|c|c|c|c|c|}
\hline
D_{5h} & E & 2C_5 & 2C_5^2 & 5C_2 & \sigma_h & 2S_5 & 2S_3^5 & 5\sigma_v & \Sigma & \Sigma/h \\
\hline
\Gamma_\pi & & & & & & & & & & \\
\hline
A_1' & & & & & & & & & & \\
A_2' & & & & & & & & & & \\
E_1' & & & & & & & & & & \\
E_2' & & & & & & & & & & \\
A_1'' & & & & & & & & & & \\
A_2'' & & & & & & & & & & \\
E_1'' & & & & & & & & & & \\
E_2'' & & & & & & & & & & \\
\hline
\end{array}
\]

\[ \Gamma_\pi = \quad d_{\Gamma} = \]
\[ \pi \text{ MOs of Cyclopentadienyl, } C_5H_5^- \]

\[
\begin{array}{|c|c|c|c|c|c|c|c|c|c|}
\hline
D_{5h} & E & 2C_5 & 2C_5^2 & 5C_2 & \sigma_h & 2S_5 & 2S_3^5 & 5\sigma_v & \Sigma & \Sigma/h & h = 20 \\
\hline
\Gamma_\pi & 5 & 0 & 0 & -1 & -5 & 0 & 0 & 1 & & & \\
\hline
A_1' & 5 & 0 & 0 & -5 & -5 & 0 & 0 & 5 & 0 & 0 & \\
A_2' & 5 & 0 & 0 & 5 & -5 & 0 & 0 & -5 & 0 & 0 & \\
E_1' & 10 & 0 & 0 & 0 & -10 & 0 & 0 & 0 & 0 & 0 & \\
E_2' & 10 & 0 & 0 & 0 & -10 & 0 & 0 & 0 & 0 & 0 & \\
A_1'' & 5 & 0 & 0 & -5 & 5 & 0 & 0 & -5 & 0 & 0 & \\
A_2'' & 5 & 0 & 0 & 5 & 5 & 0 & 0 & 5 & 20 & 1 & \\
E_1'' & 10 & 0 & 0 & 0 & 10 & 0 & 0 & 0 & 20 & 1 & \\
E_2'' & 10 & 0 & 0 & 0 & 10 & 0 & 0 & 0 & 20 & 1 & \\
\hline
\end{array}
\]

\[ \Gamma_\pi = A_2'' + E_1'' + E_2'' \quad \quad d_{\Gamma} = 1 + 2 + 2 = 5 \]
• The five p-orbitals on the planar Cp ring ($D_{5h}$ symmetry) can be combined to produce five molecular orbitals according to the reducible representation:

$$\Gamma_\pi = A_2'' + E_1'' + E_2''$$

• One combination has the full symmetry of the ring ($a_2''$)

• There are two doubly degenerate combinations ($e_1''$ and $e_2''$) having one and two planar nodes at right angles to the plane of the ring.

• The relative energies of these orbitals increase as the number of nodes increases.

• The $a_2''$ and $e_1''$ orbitals are both fully occupied in the electronic configuration of the Cp$^-$ anion whereas the $e_2''$ orbitals are net anti-bonding and are unfilled.
The π-molecular orbitals of the cyclopentadienyl ring ($D_{5h}$)

- $E_2''$ (4 nodes)
  - anti-bonding

- $E_1''$ (2 nodes)
  - weakly bonding

- $A_2''$ (0 nodes)
  - bonding

- The five $p$-orbitals on the planar Cp ring ($D_{5h}$ symmetry) can be combined to produce five molecular orbitals.
For a bis-cyclopentadienyl metal complex \((\eta^5\text{-Cp})_2M\), such as ferrocene, the \(\pi\)-orbitals of the two \(\text{Cp}\) ligands are combined pairwise to form the symmetry-adapted linear combination of molecular orbitals (SALC’s) which are described by the irreducible representations of the \(D_{5d}\) point group.

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<th>(E)</th>
<th>(2C_5)</th>
<th>(2C_5^2)</th>
<th>(5C_2)</th>
<th>(i)</th>
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</table>

\(\Gamma_\pi = \)  
\(d_{\Gamma} = \)
For a bis-cyclopentadienyl metal complex \((\eta^5\text{-Cp})_2M\), such as ferrocene, the \(\pi\)-orbitals of the two Cp ligands are combined pairwise to form the symmetry-adapted linear combination of molecular orbitals (SALC’s) which are described by the irreducible representations of the \(D_{5d}\) point group.

\[
\begin{array}{c|cccccccccc}
D_{5d} & E & 2C_5 & 2C_5^2 & 5C_2 & i & 2S_{10}^3 & 2S_{10} & 5\sigma_d & \Sigma & \Sigma/h \\
\hline
\Gamma_\pi & 10 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2 & \\
A_{1g} & 10 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 10 & 20 & 1 \\
A_{2g} & 10 & 0 & 0 & 0 & 0 & 0 & 0 & -10 & 0 & 0 & \\
E_{1g} & 20 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 20 & 1 \\
E_{2g} & 20 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 20 & 1 \\
A_{1u} & 10 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 20 & 1 \\
A_{2u} & 10 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 20 & 1 \\
E_{1u} & 20 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 20 & 1 \\
E_{2u} & 20 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 20 & 1 \\
\end{array}
\]

\[
\Gamma_\pi = A_{1g} + E_{1g} + E_{2g} + A_{2u} + E_{1u} + E_{2u}
\]

\[
d_\Gamma = 1 + 2 + 2 + 1 + 2 + 2 = 10
\]
• The $\Gamma_\pi$ SALCs of the (Cp)$_2$ framework are also defined by the sum and difference of SALCs from the two contributing Cp ligands whose results must correspond to the irreducible components of $\Gamma_\pi$ (Cp)$_2$, i.e.

\[(\psi_1 + \psi_1), (\psi_1 - \psi_1); (\psi_2 + \psi_2), (\psi_2 - \psi_2) \ldots \text{etc.}\]

where, for example, '$\psi_1 + \psi_1$' gives rise to a molecular orbital of $A_{1g}$ symmetry.

• This gives rise to three sets of ligand molecular orbitals of gerade ($g$) and ungerade ($u$) symmetry with respect to the centre of inversion;
  
  ➢ a low lying filled bonding pair of $A_{1g}$ and $A_{2u}$ symmetry
  ➢ a filled weakly bonding pair of $E_{1g}$ and $E_{1u}$ symmetry
  ➢ an unfilled anti-bonding pair of $E_{2g}$ and $E_{2u}$ symmetry.
SALCs for a (η⁵-Cp)₂M complex

\[ \Gamma_\pi = A_{1g} + E_{1g} + E_{2g} + A_{2u} + E_{1u} + E_{2u} \]
• Using the reducible representation of SALCs the corresponding metal AOs are found

\[ \Gamma_\pi = A_{1g} + E_{1g} + E_{2g} + A_{2u} + E_{1u} + E_{2u} \]

• Thus, in \( D_{5d} \) the bonding metal orbitals transform as

\[
\begin{align*}
A_{1g} & : (s, d_z^2) \\
E_{1g} & : (d_{yz}, d_{xz}) \\
E_{2g} & : (d_x^2 - d_y^2, d_{xy}) \\
A_{2u} & : (p_z) \\
E_{1u} & : (p_x, p_y)
\end{align*}
\]

• By considering the AO and SALC symmetries and how overlap can be affected the MO bonding picture of ferrocene can be constructed.

• Each combination of AOs and SALCs leads to a bonding molecular orbital \( [ (\psi_{\text{ligand molecular orbital}}) + (\psi_{\text{metal atomic orbital}}) ] \) and a corresponding anti-bonding molecular orbital \( [ (\psi_{\text{ligand molecular orbital}}) - (\psi_{\text{metal atomic orbital}}) ] \) providing that the energies of the two component sets are sufficiently close for overlap.
Symmetry matching of the SALC’s with the metal atomic orbitals

- $e_{2g}$
  - $d_{xy}$
  - $d_{x^2-y^2}$

- $e_{2u}$
  - No metal orbital of appropriate symmetry available

- $e_{1g}$
  - $d_{yz}$
  - $d_{xz}$

- $e_{1u}$
  - $p_y$
  - $p_x$

- $a_{1g}$
  - $s$
  - $d_{z^2}$

- $a_{1u}$
  - $p_z$
A qualitative molecular orbital diagram for ferrocene ($D_{5d}$)

$\text{Fe}^{II}$

$\text{SALC}$'s

$p_z$
$p_y$
$p_x$

$a_{1u}$
$e_{1u}$

$a_{2u}$, $e_{1u}$

$s$

$a_{1g}$

$a_{1g}$

$d_{xy}$
$d_{x^2-y^2}$

$a_{1g}$, $e_{1g}$, $e_{2g}$

$e_{2g}$

$e_{2u}$

$d_{z^2}$
$d_{yz}$
$d_{xz}$

$a_{1g}$
$e_{1g}$

$a_{1g}$, $a_{2u}$

$e_{1g}$

$a_{1g}$

$a_{2u}$
A qualitative molecular orbital diagram for ferrocene ($D_{5d}$)

Fe$^{II}$

SALC's

$p_z$

$a_{1u}$

$p_y$

$e_{1u}$

$p_x$

$e_{2g}, e_{2u}$

$s$

$a_{1g}$

$a_{1g}, e_{1g}, e_{2g}$

$d_{xy}$

$e_{2g}$

$d_{xz}$

$e_{1u}$

$d_{yz}$

$a_{1g}$

$a_{2u}$

$a_{1g}, a_{2u}$
A qualitative molecular orbital diagram for ferrocene ($D_{5d}$)

Fe$^{II}$

SALC’s

$p_z$
$p_y$
$p_x$

$a_{1u}$

$e_{1u}$

$a_{2u}$, $e_{1u}$

$d_{xy}$
$d_{x^2-y^2}$

$a_{1g}$

$a_{1g}$

$s$

$a_{1g}$

$a_{1g}$

$a_{1g}$

$a_{1g}$

$e_{1g}$

$e_{1g}$

$e_{2g}$, $e_{2u}$

$e_{1g}$, $e_{1u}$

$e_{1g}$

$e_{1u}$

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$e_{1u}$
A qualitative molecular orbital diagram for ferrocene ($D_{5d}$)

Fe$^{III}$

SALC's

$p_z$
$a_{1u}$

$p_y$
$e_{1u}$

$p_x$

$a_{2u}$, $e_{1u}$

$s$
$a_{1g}$

$d_{xy}$
$a_{1g}$, $e_{1g}$, $e_{2g}$

$d_{x^2-y^2}$

$e_{2g}$

$d_{z^2}$
$a_{1g'}$

$d_{yz}$
$e_{1g}$

$d_{xz}$

$a_{1g}$, $a_{2u}$

$e_{1g}$, $e_{1u}$

$e_{2g}$, $e_{2u}$
A qualitative molecular orbital diagram for ferrocene ($D_{5d}$)

Fe$^{II}$

SALC's

$p_z$
$a_{1u}$

$p_y$
$e_{1u}$

$p_x$

$s$
$a_{1g}$

$d_{xy}$
$a_{1g}$, $e_{1g}$, $e_{2g}$

$d_{xz}$
$d_{yz}$
$e_{2g}$

$a_{1u}'$
$e_{1g}$

$d_{x^2-y^2}$

$a_{2u}$

$a_{1g}^*$

$a_{1g}$

$a_{1g}$

$e_{2g}$, $e_{2u}$

$e_{1g}$, $e_{1u}$

$a_{1g}$, $a_{2u}$

$a_{1g}$, $a_{2u}$

$a_{1g}$
A qualitative molecular orbital diagram for ferrocene ($D_{5d}$)
A qualitative molecular orbital diagram for ferrocene ($D_{5d}$)
A qualitative molecular orbital diagram for ferrocene ($D_{5d}$)

Fe$^{II}$

Fe

SALC's

$e_{1u}$

$p_z$

$p_y$

$p_x$

$a_{1u}$

$e_{1u}$

$a_{2u}$

$a_{2u}^*$

$a_{1g}$

$a_{1g}^*$

$e_{2g}$

$e_{2g}^*$

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$e_{1g}$

$a_{2u}$

$a_{2u}$

$a_{2u}$
A qualitative molecular orbital diagram for ferrocene ($D_{5d}$)

Fe$^{II}$

SALC's

$p_z$

$p_y$

$p_x$

$s$

$a_{1g}$

$d_{xy}$

$d_{xz}$

$d_{yz}$

$e_{1g}$

$e_{1u}$

$a_{1u}$

$e_{1u}$

$a_{2u}$

$e_{1g}$

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$e_{1u}$
A qualitative molecular orbital diagram for ferrocene ($D_{5d}$)

- $p_z$ and $p_y$
- $e_{1u}$
- $a_{1u}$
- $e_{1u}^*$
- $a_{2u}$
- $e_{2u}$
- $e_{2g}^*$
- $e_{1g}^*$
- $a_{1g}$
- $e_{1g}$
- $e_{1u}$
- $a_{1u}$
- $e_{1g}$
- $a_{2u}$
- $a_{1g}$
- LUMO
- HOMO
• Due to a difference in energies the lowest energy $a_{1g}$ molecular orbital is mainly ligand based with a slight admixture of the Fe 4s and 3dz$^2$ orbitals.

• Similarly the $a_{2u}$ level has little if any metal character due to higher lying Fe 4pz orbital with which it is formally able to combine.

• The $e_{1g}$ molecular orbital arises from the bonding combination of the ligand $e_{1g}$ orbitals with the Fe 3dxz and 3dyz orbitals. This is the only symmetry combination of orbitals in the two Cp rings that has appreciable overlap with the metal 3d orbitals to act as an efficient donor and it is thus this interaction which is mainly responsible for the stability of the complex.

• The corresponding anti-bonding orbitals, $e_{1g}^*$, are unfilled in the ground state of ferrocene but they are involved in excited state transitions.

• The $e_{1u}$ bonding molecular orbitals are again mainly ligand based but with a small contribution from the higher energy Fe 3 $p_x, p_y$ orbitals.

• The $a_{1g}$ HOMO mostly consists of the Fe 3dz$^2$ orbital as the $a_{1g}$ SALC and the metal dz$^2$ orbital result in little or no overlap.

• The $e_{2g}$ ($d_{x^2-y^2}$, $d_{xy}$) metal orbitals are considered weakly-bonding due to poor overlap with the $e_{2g}$ SALC orbitals.
Since the occupied orbitals are of either \( \sigma_{1g}\), \( e_{1g}\) or \( e_{2g}\) type symmetry no intrinsic barrier to internal rotation is predicted as each of these molecular orbitals are symmetric about the axis of rotation.

The very low values observed for this rotation (~ 4 kJmol\(^{-1}\)) may be attributed to van der Waals forces between the two Cp rings.

The attachment of additional groups or ligands destroys the \( D_{5d}/D_{5h}\) symmetry of ferrocene thus significantly altering the MO diagram.


Example: Constructing a MO for Platinum Tetrachloride, [PtCl$_4$]$^{2-}$

point group = $D_{4h}$

\[ \Gamma_{\sigma} = A_{1g} + B_{1g} + E_u \]

\[ d_{\Gamma} = 1 + 1 + 2 = 4 \]

Pt bonding AOs

$A_{1g} : \quad 6s, \ 5d_{z^2}$

$E_u : (6p_x, \ 6p_y)$

$B_{1g} : \quad 5d_{x^2-y^2}$

Pt non-bonding AOs

$A_{2u} : \quad 6p_z$

$B_{2g} : \quad 5d_{xy}$

$E_g : \quad (5dxz, \ 5dyz)$
Symmetry  | bonding MOs | anti-bonding MOs
---|---|---
$B_{1g}$ | ![Bonding MOs](image1) | ![Anti-bonding MOs](image2)
$E_{u}$ | ![Bonding MOs](image3) | ![Anti-bonding MOs](image4)
$A_{1g}$ | ![Bonding MOs](image5) | ![Anti-bonding MOs](image6)

non-bonding AOs

$p_{z}$ | $d_{xy}$ | $d_{xz}$ | $d_{yz}$

$A_{2u}$ | $B_{2g}$ | $E_{g}$
\[ \text{Pt}^{2+} \]

- \( 6p (a_{2u}, e_u) \)
- \( 6s (a_{1g}) \)
- \( 5d (a_{1g}, b_{1g}, b_{2g}, e_g) \)
- \( dx^2-y^2 \)
- \( dxy \)
- \( dbz \)
- \( dz^2 \)

\[ \text{Cl}^{-2} \text{Pt}^{3+} \text{Cl}^{-1} \]

\[ 4\text{Cl}^- \]

\( B_{1g} \)

\( E_u \)

\( A_{1g} \)

- \( b_{1g} \)
- \( e_u \)
- \( a_{1g} \)
Example: Constructing a MO for Tetrakis(triphenylphosphine)Palladium, Pd(PPh₃)₄

\[
\Gamma_\sigma = A_1 + T_2
\]

\[
d_{\Gamma} = 1 + 3 = 4
\]

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<th>(E)</th>
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<td>12</td>
<td>24</td>
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Pd bonding AOs

\(A_1: 5s\)

\(T_2: (5p_x, 5p_y, 5p_z)\)

\((4dxy, 4dxz, 4dyz)\)

Pd non-bonding AOs

\(E: (4dx^2-y^2, 4dz^2)\)
Construction of SALCs for \( \sigma \) bonding in \( T_d \) complexes

- Consider first the \( A_1 \) SALC. It must have the same symmetry of the \( s \) orbital on the central metal atom. This requires that it be everywhere positive and unchanged by all symmetry operations.

\[
\Gamma_\sigma = A_1 + T_2 \quad A_1 \rightarrow \sigma_1 + \sigma_2 + \sigma_3 + \sigma_4
\]
Construction of SALCs for σ bonding in $T_d$ complexes

- The $T_2$ SALC’s must match the symmetries of the $(p_x, p_y, p_z)$ and $(d_{xy}, d_{xz}, d_{yz})$ orbitals, e.g. must have positive amplitude where the $p$ orbital is positive and negative amplitude where the $p$ orbitals are negative.

$$\Gamma_\sigma = A_1 + T_2$$

$$T_2 = \begin{cases} 
\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4 \\
\sigma_1 - \sigma_2 - \sigma_3 + \sigma_4 \\
\sigma_1 + \sigma_2 - \sigma_3 - \sigma_4 
\end{cases}$$
Construction of SALCs for \( \sigma \) bonding in \( T_d \) complexes

\[ \Gamma_\sigma = A_1 + T_2 \]

\( A_1 \) (0 nodes)

\( T_2 \) (1 node)

\( P_z \)

\( P_x \)

\( P_y \)
\[ \Gamma_\sigma = A_1 + T_2 \]
\begin{align*}
\text{Pd}^0 & \quad \text{5p \,(t_2)} \\
& \quad \text{5s \,(a_1)} \\
& \quad \text{4d \,(t_2, e)} \\
\end{align*}

4 \text{ PPh}_3
The tetrahedral geometry is electronically favored by $d^4$ or $d^{10}$ metal complexes where the non-bonding orbitals are either $1/2$ or entirely filled, respectively.
The tetrahedral geometry is electronically favored by d⁴ or d¹⁰ metal complexes where the non-bonding orbitals are either 1/2 or entirely filled, respectively.
The Electronic Structure of bisbenzenechromium
\[ \text{Cr}(\eta^6-\text{C}_6\text{H}_6)_2 \]

- Similar to ferrocene, primary orbital interactions that form the metal-ligand bonds in occur between the Cr \( d \) orbitals and the \( \pi \)-orbitals of the benzene ligand.

- The two benzene rings of \( \text{Cr}(\eta^6-\text{C}_6\text{H}_6)_2 \) are ideally orientated in an eclipsed \( (D_{6h}) \) conformation.

Homework – generate an MO diagram for the \( \text{Cr}(\eta^6-\text{C}_6\text{H}_6)_2 \) molecule