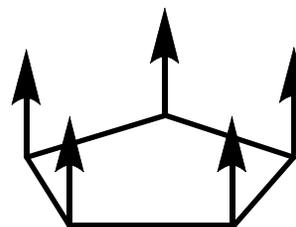
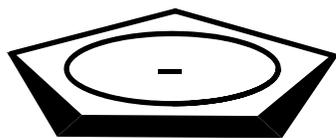


The Electronic Structure of Ferrocene

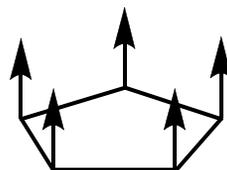
- The two cyclopentadienyl (Cp) rings of ferrocene may be orientated in the two extremes of either an eclipsed (D_{5h}) or staggered (D_{5d}) conformation.
- The energy of rotation about the Fe-Cp axis is very small ($\sim 4 \text{ kJmol}^{-1}$) and ground state structures of ferrocene may show either 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 π -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.

π MOs of Cyclopentadienyl, $C_5H_5^-$

- $C_5H_5^-$, has three pairs of electrons delocalized in a π system extending around the pentagonal ring.
- The five $2p$ orbitals perpendicular to the ring on the five carbon atoms combine to form three bonding (π^1, π^2, π^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 Γ_π .



π MOs of Cyclopentadienyl, $C_5H_5^-$



D_{5h}	E	$2C_5$	$2C_5^2$	$5C_2$	σ_h	$2S_5$	$2S_3^5$	$5\sigma_v$	Σ	Σ/h	$h = 20$
Γ_π	5	0	0	-1	-5	0	0	1			
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	

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

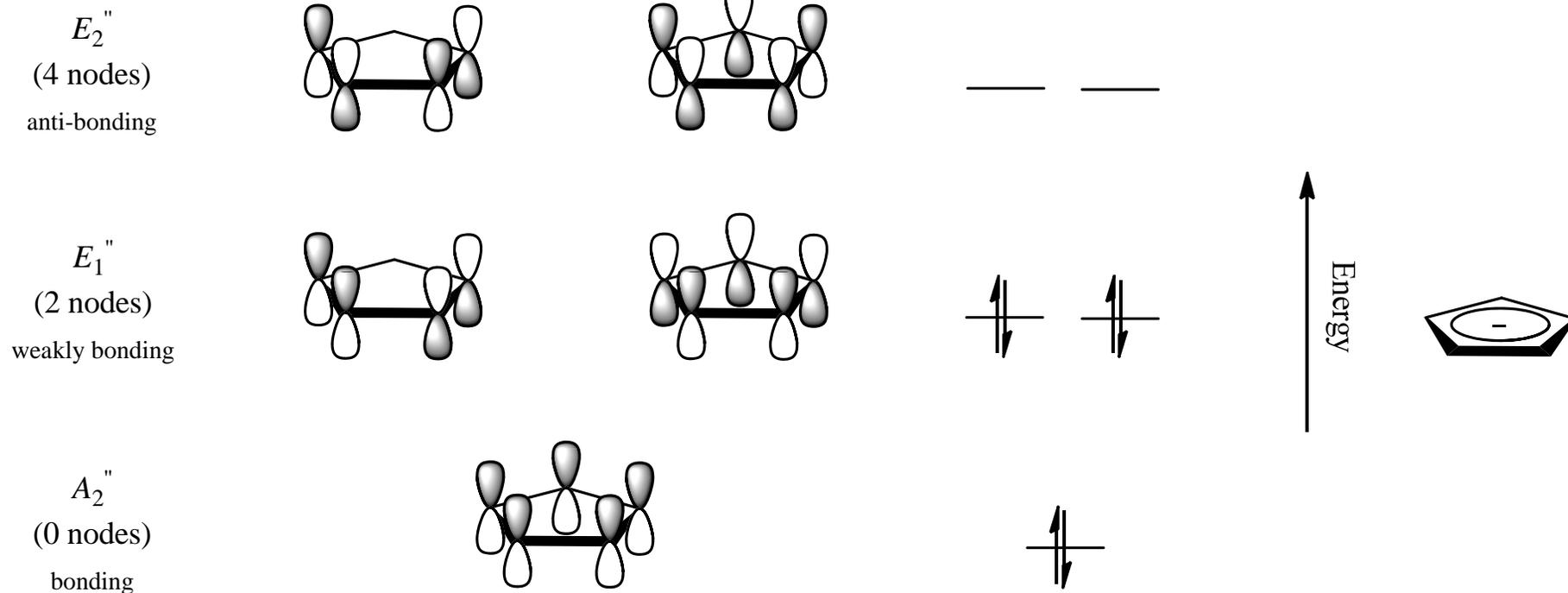
$$d_\Gamma = 1 + 2 + 2 = 5$$

- 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.

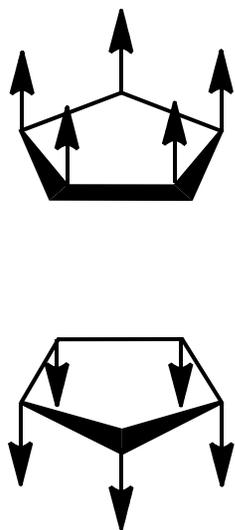
The π -molecular orbitals of the cyclopentadienyl ring (D_{5h})



- 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 $(\eta^5\text{-Cp})_2\text{M}$, such as ferrocene, the π -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.

$h = 20$



D_{5d}	E	$2C_5$	$2C_5^2$	$5C_2$	i	$2S_{10}^3$	$2S_{10}$	$5\sigma_d$	Σ	Σ/h
Γ_π	10	0	0	0	0	0	0	2		
A_{1g}	10	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	20	1
E_{2g}	20	0	0	0	0	0	0	0	20	1
A_{1u}	10	0	0	0	0	0	0	-10	0	0
A_{2u}	10	0	0	0	0	0	0	10	20	1
E_{1u}	20	0	0	0	0	0	0	0	20	1
E_{2u}	20	0	0	0	0	0	0	0	20	1

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

$$d_\Gamma = 1 + 2 + 2 + 1 + 2 + 2 = 10$$

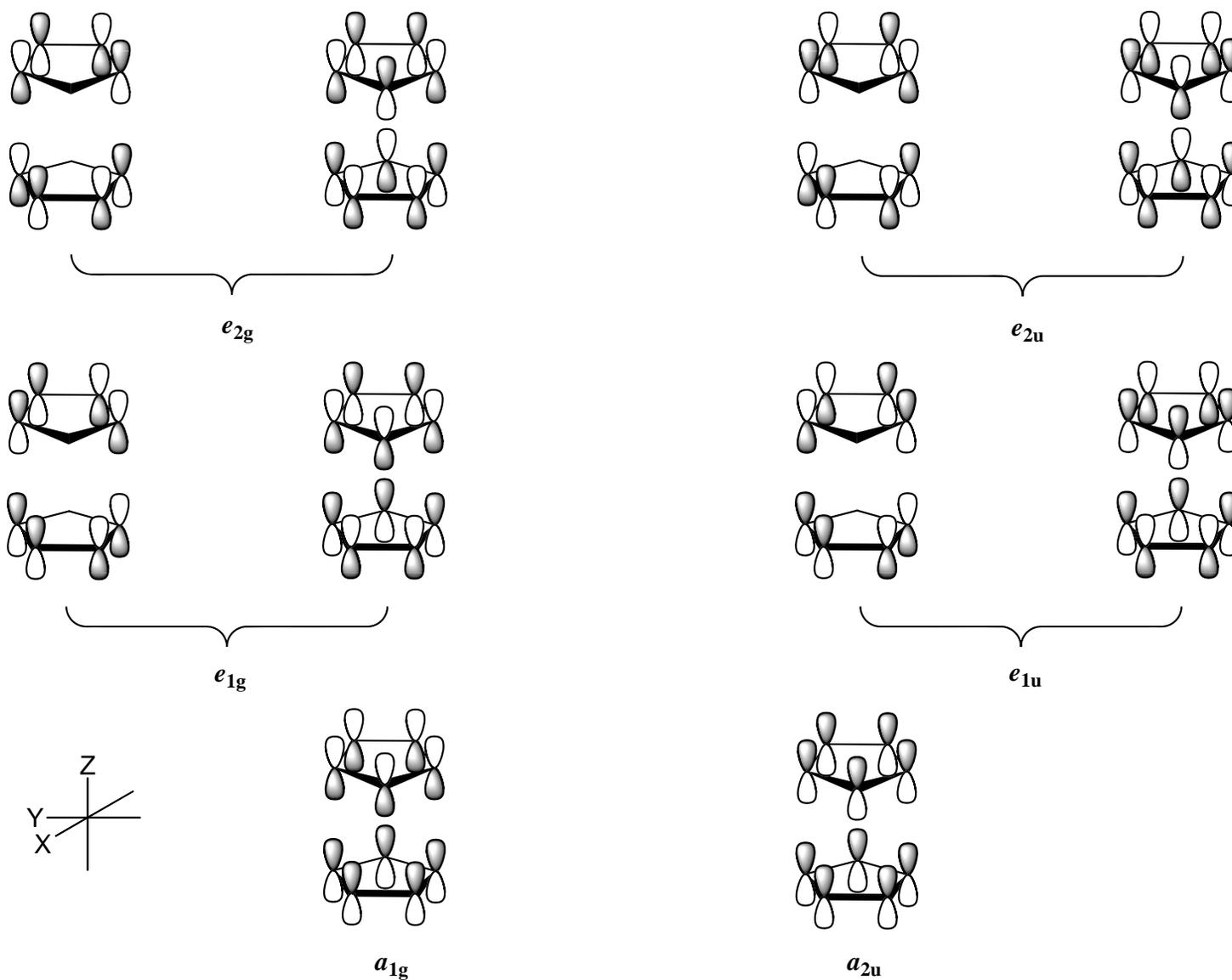
- The Γ_{π} SALCs of the $(\text{Cp})_2$ framework are also defined by the sum and difference of SALCs from the two contributing Cp ligands whose results must correspond to the irreducible components of $\Gamma_{\pi}(\text{Cp})_2$, i.e.

$$(\psi_1 + \psi_1), (\psi_1 - \psi_1); (\psi_2 + \psi_2), (\psi_2 - \psi_2) \dots \text{etc.}$$

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 $(\eta^5\text{-Cp})_2\text{M}$ 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

$$A_{1g} : (s, d_z^2)$$

$$E_{1g} : (d_{yz}, d_{xz})$$

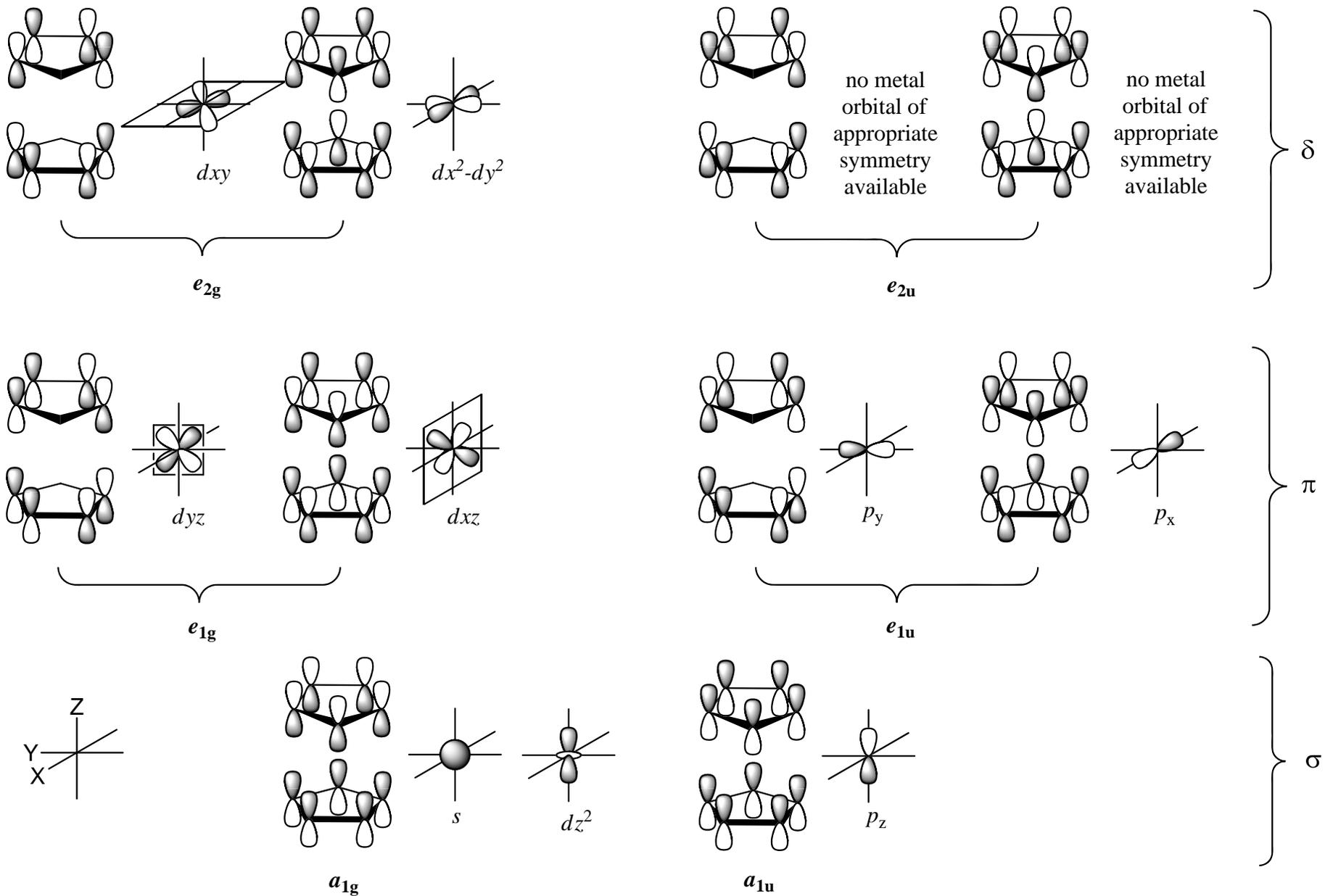
$$E_{2g} : (d_x^2 - d_y^2, d_{xy})$$

$$A_{2u} : (p_z)$$

$$E_{1u} : (p_x, p_y)$$

- 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

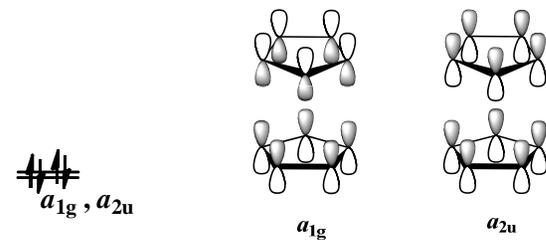
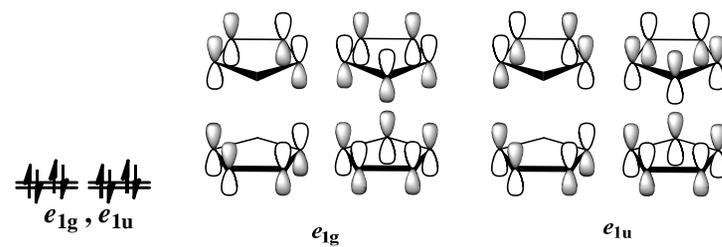
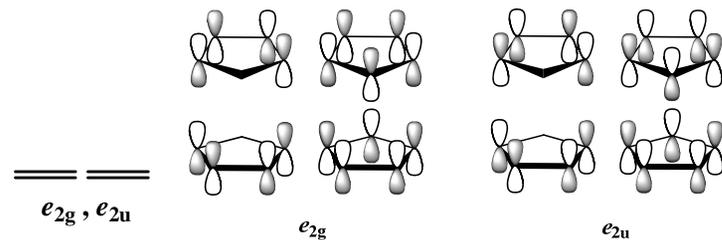
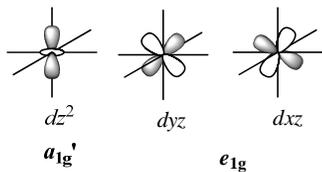
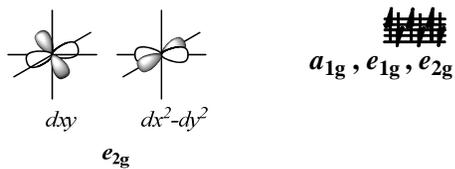
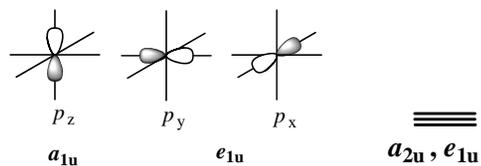


A qualitative molecular orbital diagram for ferrocene (D_{5d})

Fe^{II}



SALC's

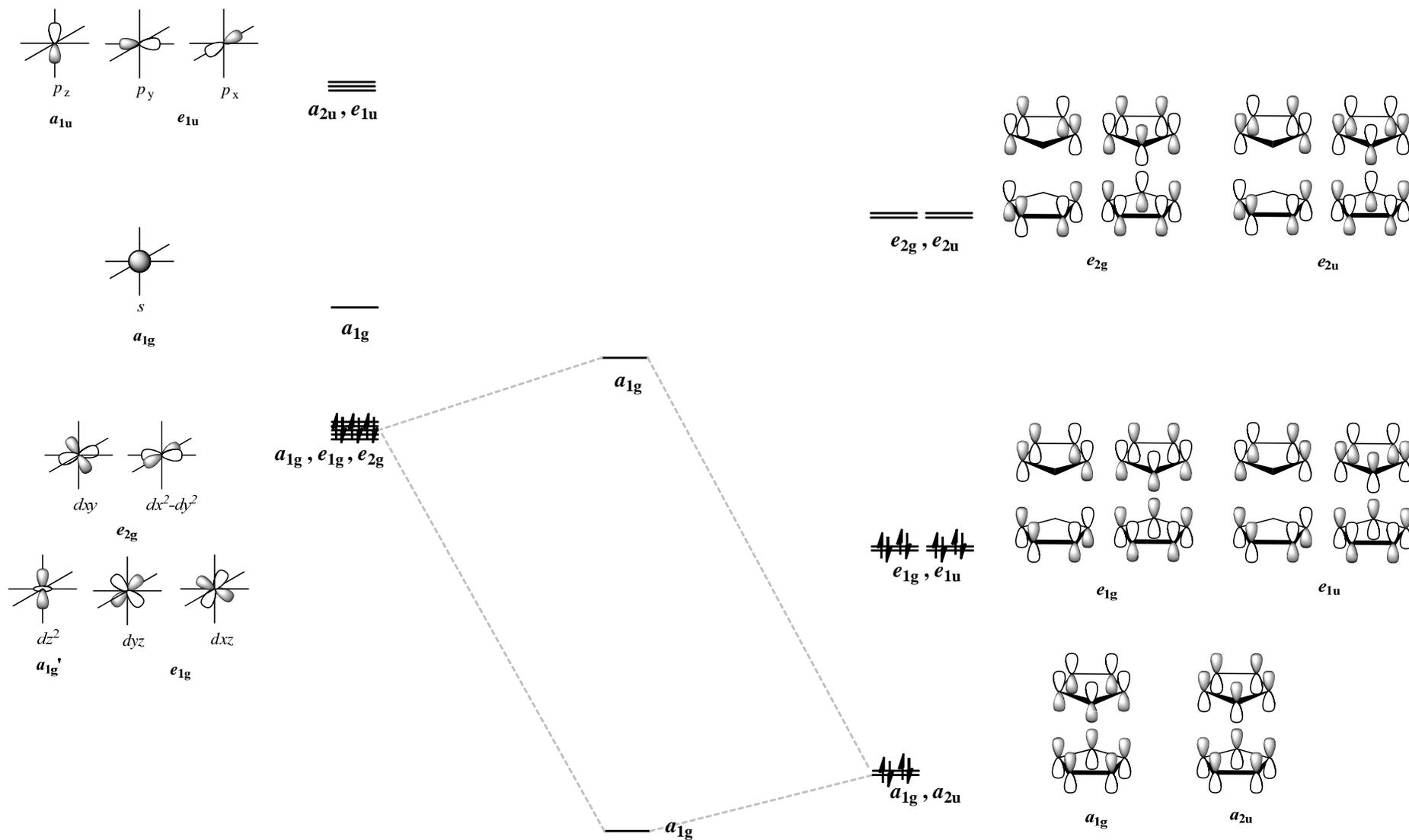


A qualitative molecular orbital diagram for ferrocene (D_{5d})

Fe^{II}

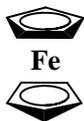


SALC's

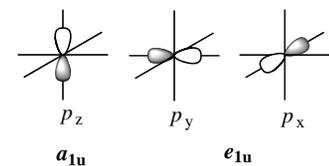


A qualitative molecular orbital diagram for ferrocene (D_{5d})

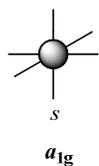
Fe^{II}



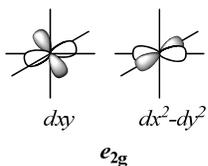
SALC's



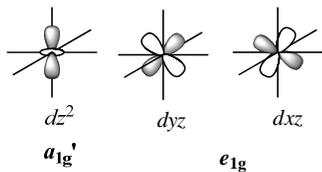
a_{2u}, e_{1u}



a_{1g}



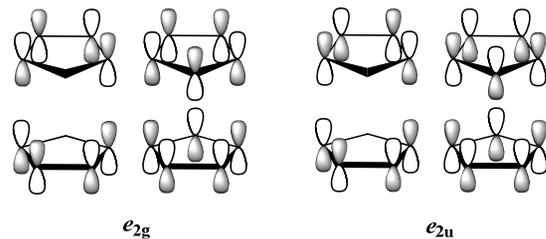
a_{1g}, e_{1g}, e_{2g}



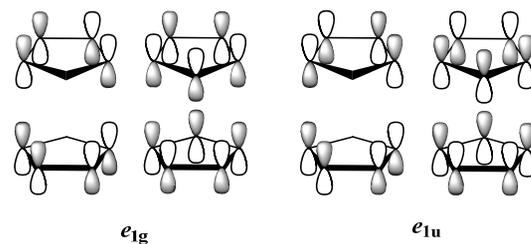
a_{1g}



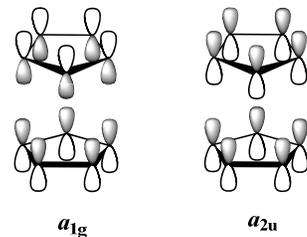
e_{2g}, e_{2u}



e_{1g}, e_{1u}

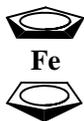


a_{1g}, a_{2u}

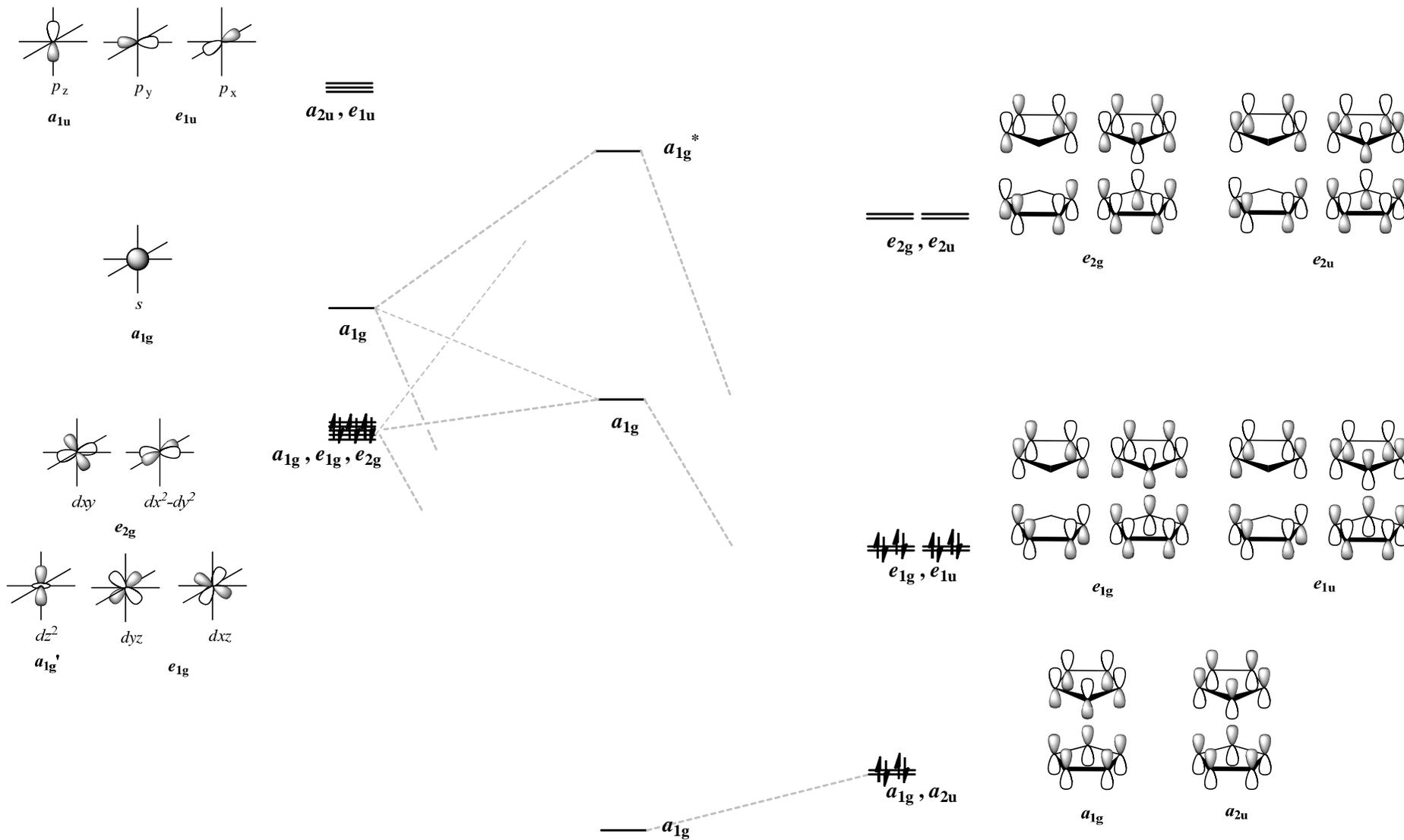


A qualitative molecular orbital diagram for ferrocene (D_{5d})

Fe^{II}

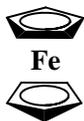


SALC's

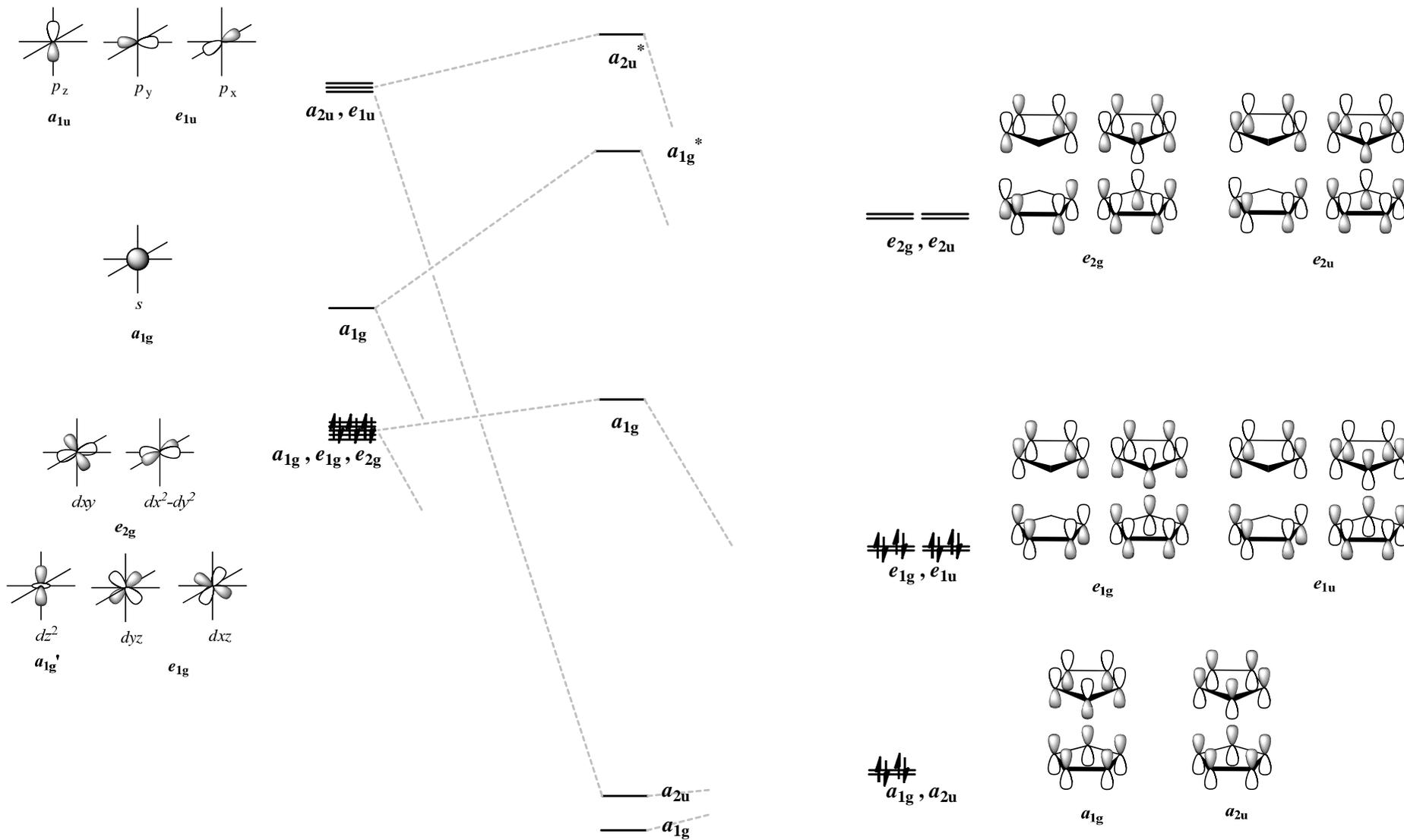


A qualitative molecular orbital diagram for ferrocene (D_{5d})

Fe^{II}



SALC's

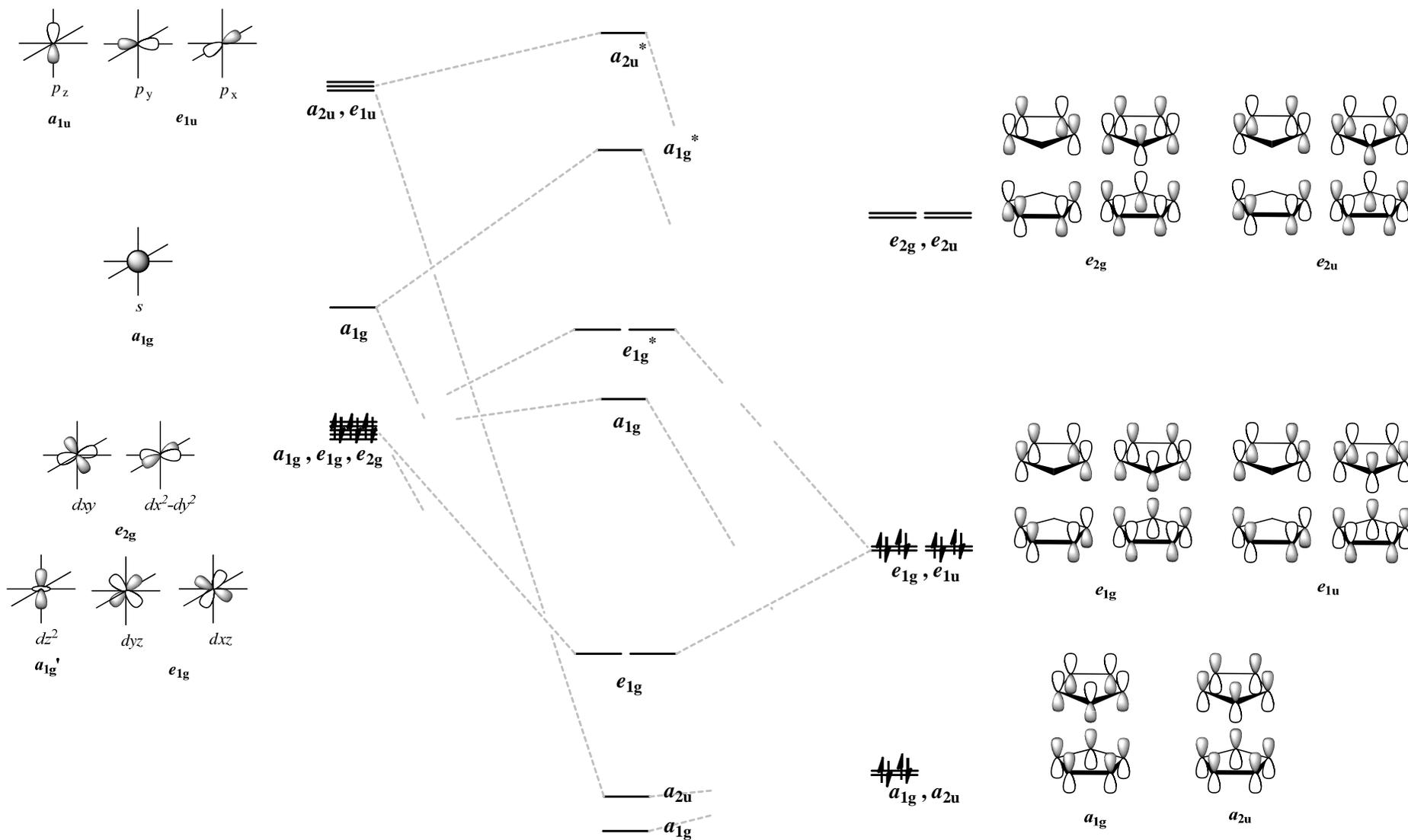


A qualitative molecular orbital diagram for ferrocene (D_{5d})

Fe^{II}



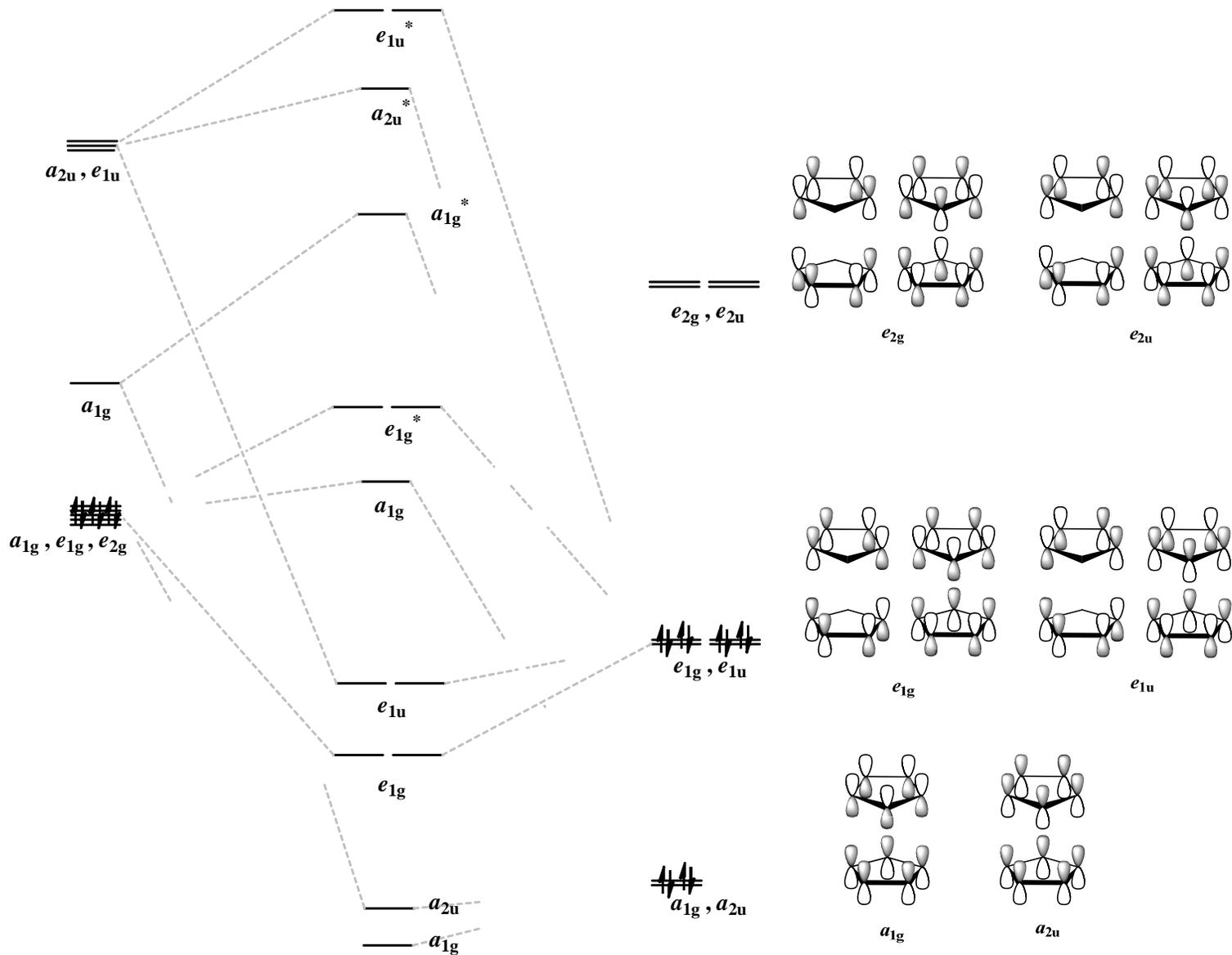
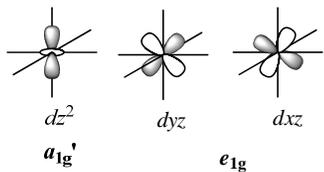
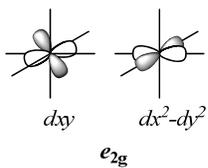
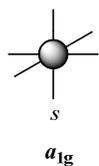
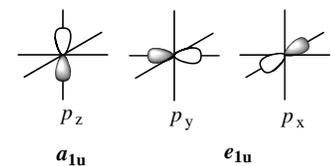
SALC's



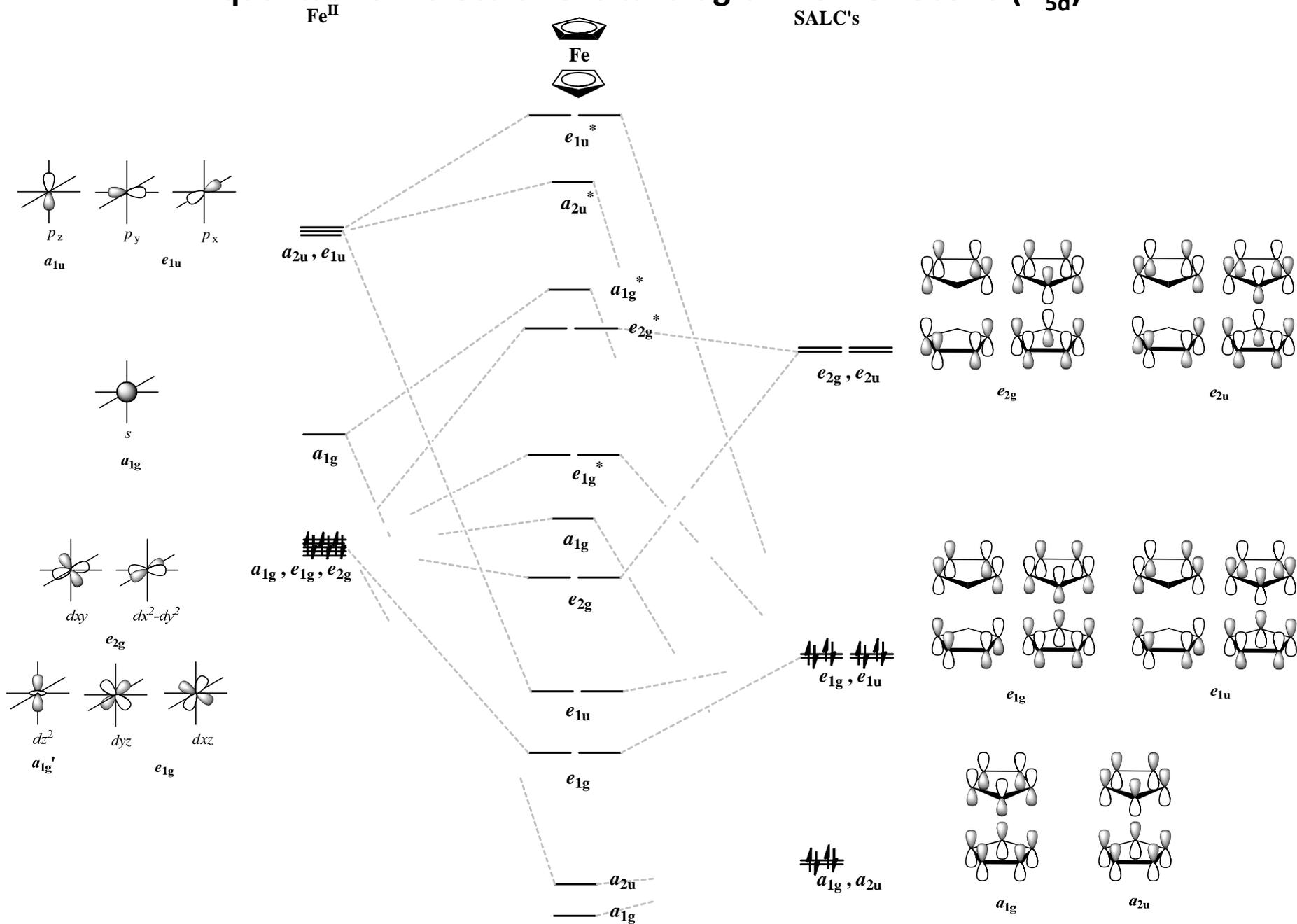
A qualitative molecular orbital diagram for ferrocene (D_{5d})

Fe^{II}

SALC's



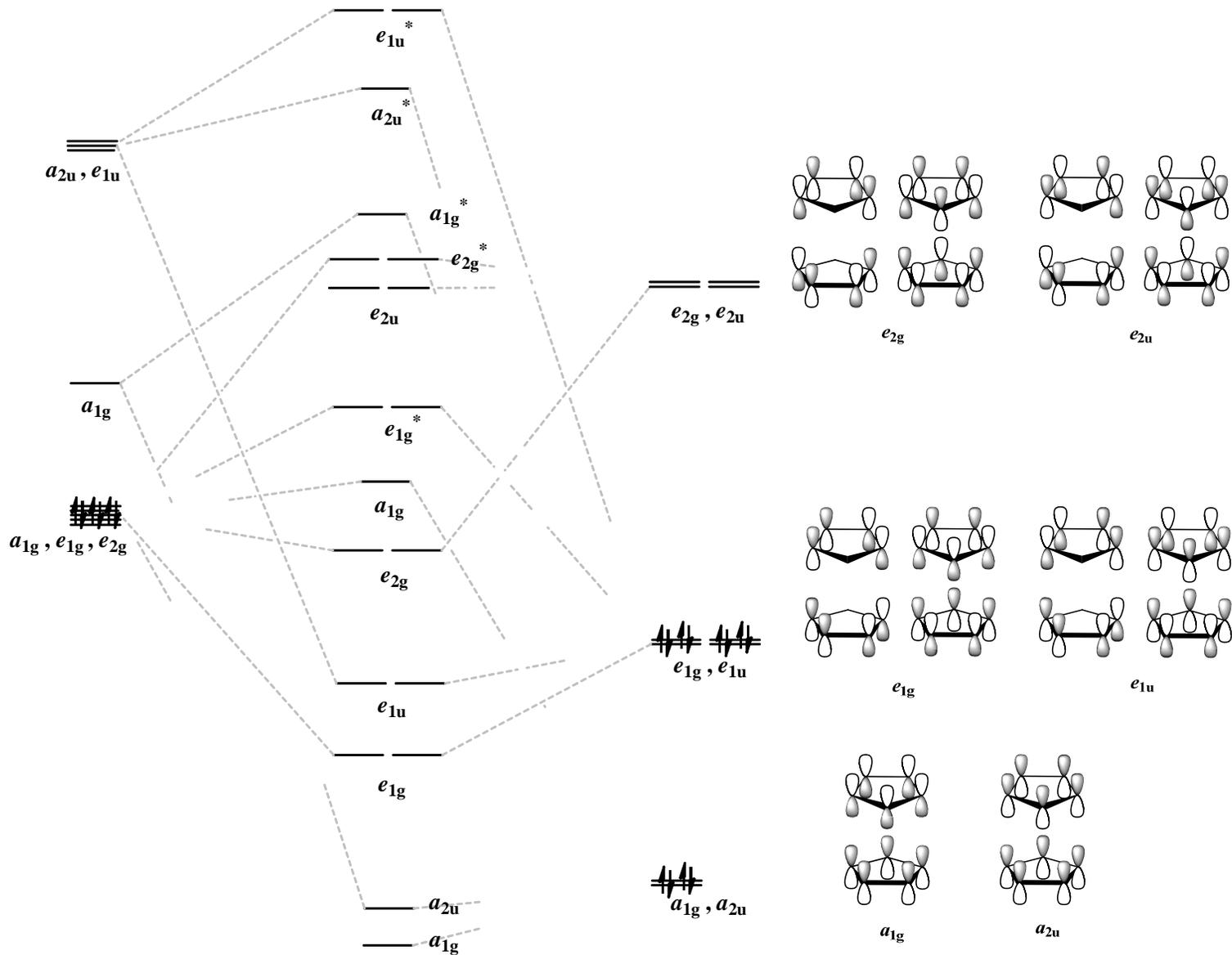
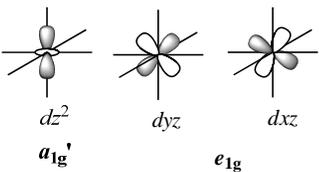
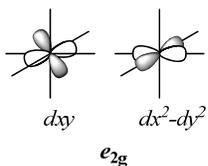
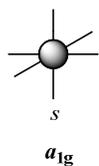
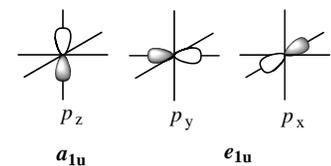
A qualitative molecular orbital diagram for ferrocene (D_{5d})



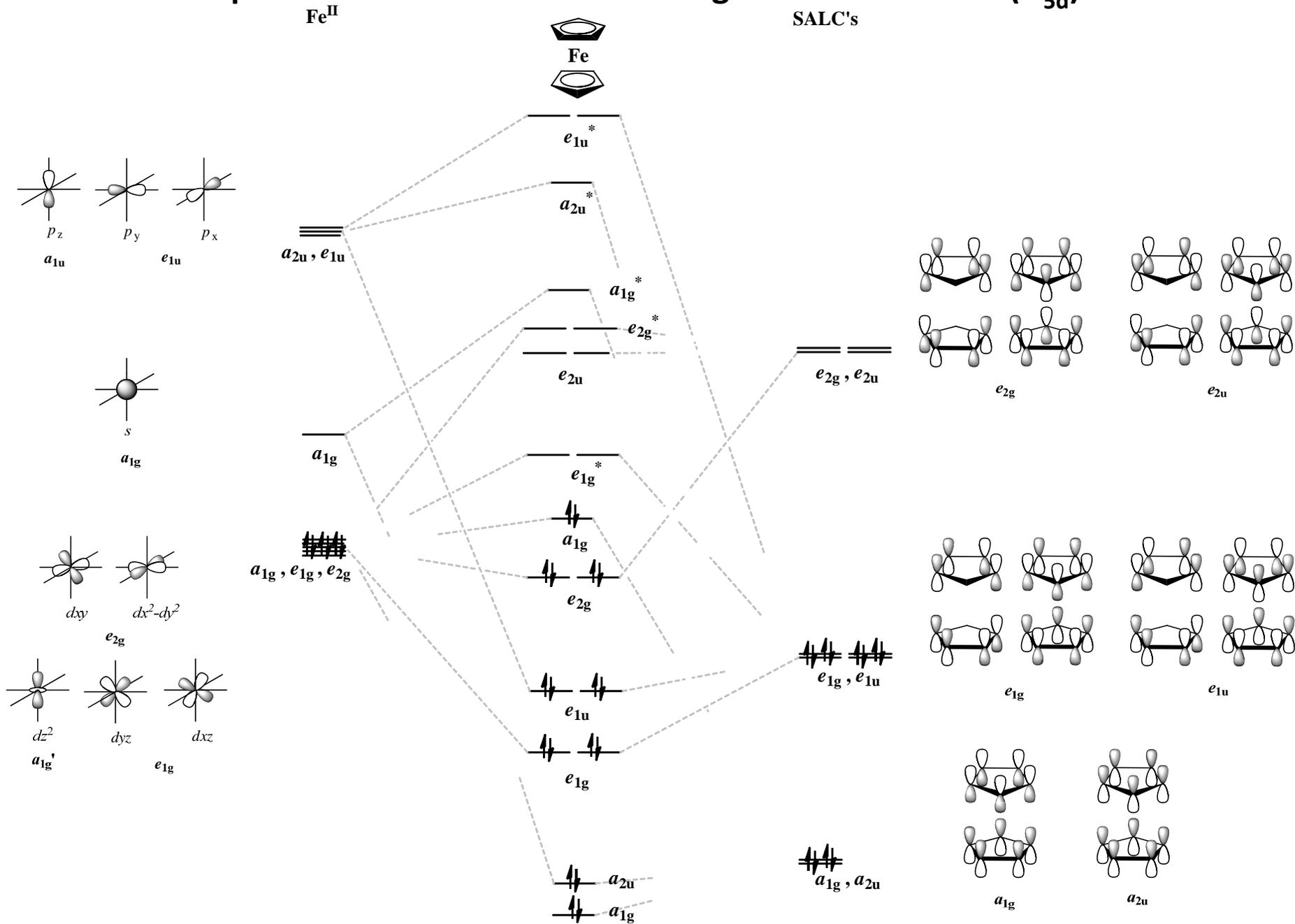
A qualitative molecular orbital diagram for ferrocene (D_{5d})

Fe^{II}

SALC's



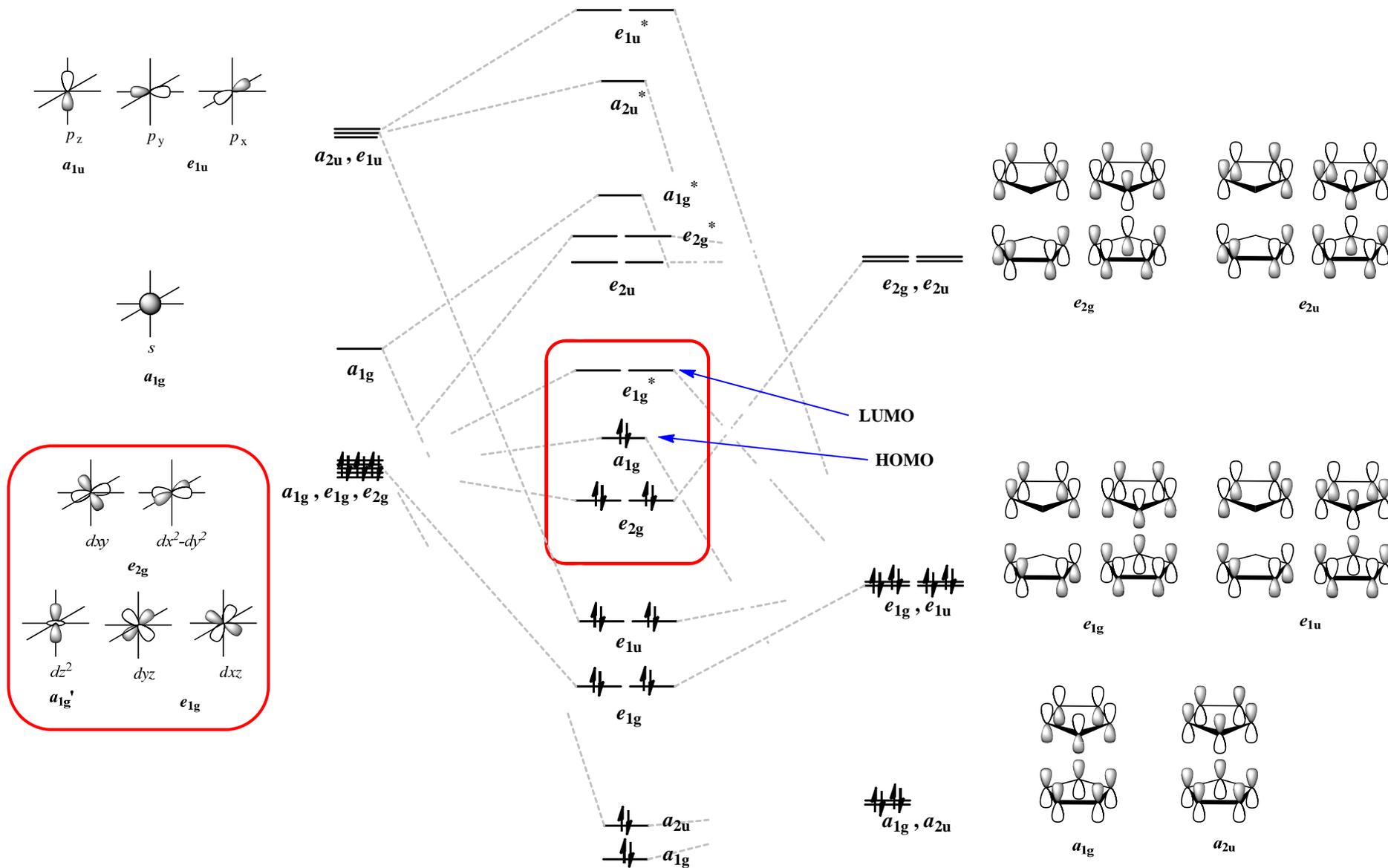
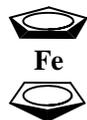
A qualitative molecular orbital diagram for ferrocene (D_{5d})



A qualitative molecular orbital diagram for ferrocene (D_{5d})

Fe^{II}

SALC's



- 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 $4p_z$ 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 $3p_x, p_y$ 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} (dx^2-y^2, dxy) metal orbitals are considered weakly-bonding due to poor overlap with the e_{2g} SALC orbitals.

- Since the occupied orbitals are of either a_{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 ($\sim 4 \text{ kJmol}^{-1}$) 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.

1. S. Barlow, H. E. Bunting, C. Ringham, J. C. Green, G. U. Bublitz, S. G. Boxer, J. W. Perry, S. R. Marder, *J. Amer. Chem. Soc.* 1999, 121, 3715-3723.

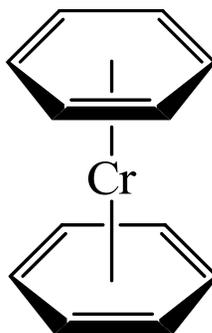
2. J. C. Calabrese, L. T. Cheng, J. C. Green, S. R. Marder, W. Tam, *J. Amer. Chem. Soc.* 1991, 113, 7227-7232.

3. D. R. Kanis, M. A. Ratner, T. J. Marks, *Chem. Rev.* 1994, 94, 195-242.

The Electronic Structure of bisbenzenechromium



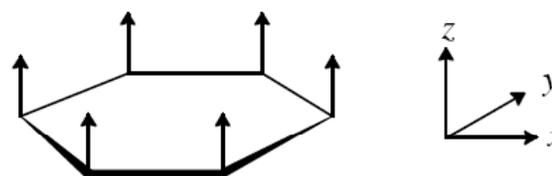
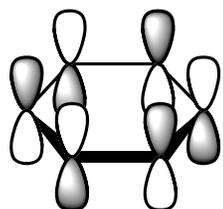
- Similar to ferrocene, primary orbital interactions that form the metal-ligand bonds in occur between the Cr *d* orbitals and the π -orbitals of the benzene ligand.
- The two benzene rings of $\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2$ are ideally orientated in an eclipsed (D_{6h}) conformation.



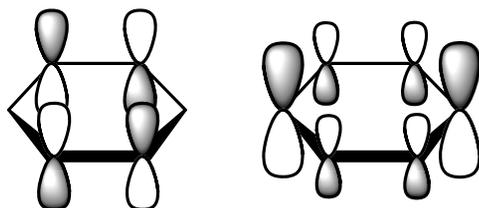
π MOs of Benzene, C₆H₆

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
Γ_π	6	0	0	0	-2	0	0	0	0	-6	0	2

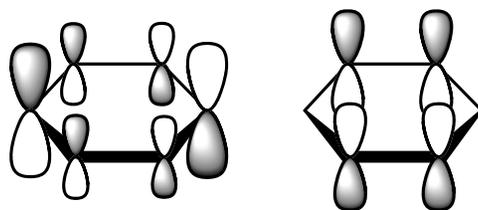
B_{2g}
(6 nodes)
anti-bonding



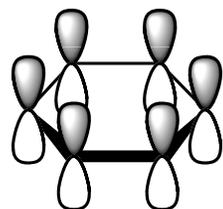
E_{2u}
(4 nodes)
anti-bonding



E_{1g}
(2 nodes)
bonding

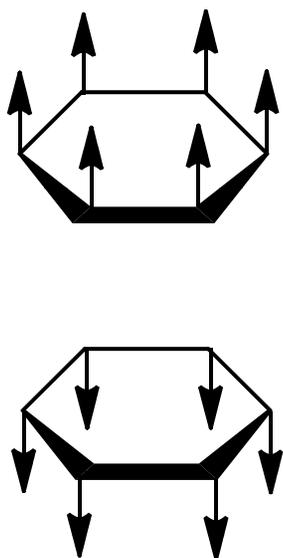


A_{2u}
(0 nodes)
bonding



$$\Gamma_\pi = B_{2g} + E_{1g} + A_{2u} + E_{2u}$$

- For $(\eta^6\text{-C}_6\text{H}_6)_2\text{M}$ the π -orbitals of the two benzene ligands are combined pairwise to form the SALCs which are described by the irreducible representations of the D_{6h} point group.

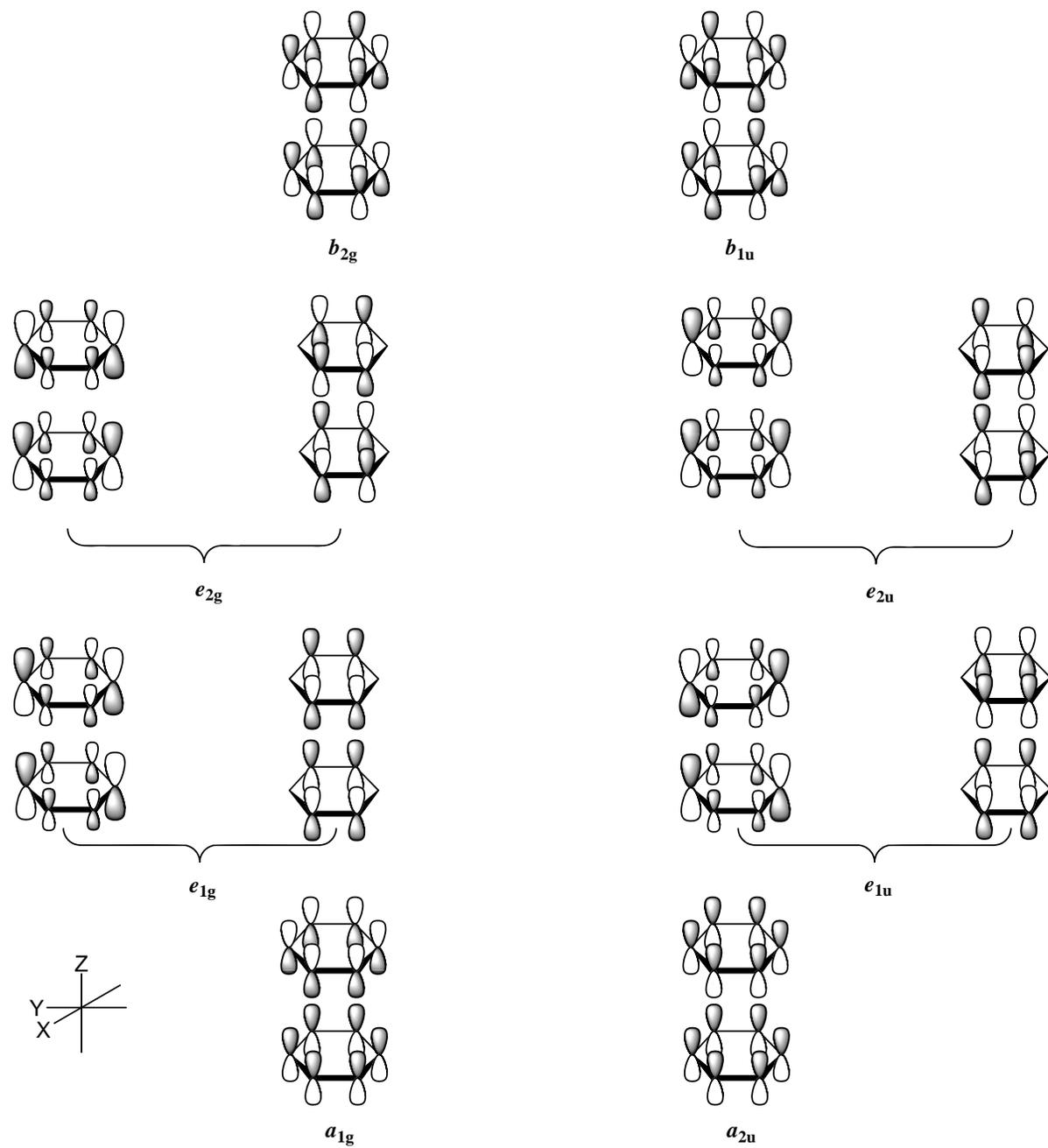


D_{6h}	$h = 24$												Σ	Σ/h
	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$		
Γ_π	12	0	0	0	0	0	0	0	0	0	0	4		
A_{1g}	12	0	0	0	0	0	0	0	0	0	0	12	24	1
A_{2g}	12	0	0	0	0	0	0	0	0	0	0	-12	0	0
B_{1g}	12	0	0	0	0	0	0	0	0	0	0	-12	0	0
B_{2g}	12	0	0	0	0	0	0	0	0	0	0	12	24	1
E_{1g}	24	0	0	0	0	0	0	0	0	0	0	0	24	1
E_{2g}	24	0	0	0	0	0	0	0	0	0	0	0	24	1
A_{1u}	12	0	0	0	0	0	0	0	0	0	0	-12	0	0
A_{2u}	12	0	0	0	0	0	0	0	0	0	0	12	24	1
B_{1u}	12	0	0	0	0	0	0	0	0	0	0	12	24	1
B_{2u}	12	0	0	0	0	0	0	0	0	0	0	-12	0	0
E_{1u}	24	0	0	0	0	0	0	0	0	0	0	0	24	1
E_{2u}	24	0	0	0	0	0	0	0	0	0	0	0	24	1

$$\Gamma_\pi = A_{1g} + B_{2g} + E_{1g} + E_{2g} + A_{2u} + B_{1u} + E_{1u} + E_{2u}$$

$$d_\Gamma = 1 + 1 + 2 + 2 + 1 + 1 + 2 + 2 = 12$$

SALCs for a $(\eta^5\text{-Cp})_2\text{M}$ complex $\Gamma_\pi = A_{1g} + B_{2g} + E_{1g} + E_{2g} + A_{2u} + B_{1u} + E_{1u} + E_{2u}$



- Using the reducible representation of SALCs the corresponding metal AOs are found

$$\Gamma_{\pi} = A_{1g} + B_{2g} + E_{1g} + E_{2g} + A_{2u} + B_{1u} + E_{1u} + E_{2u}$$

- In D_{6h} the bonding metal orbitals transform as

$$A_{1g} : (s, d_z^2)$$

$$E_{1g} : (d_{yz}, d_{xz})$$

$$E_{2g} : (d_x^2 - d_y^2, d_{xy})$$

$$A_{2u} : (p_z)$$

$$E_{1u} : (p_x, p_y)$$

- The metal s , p and d orbitals all transform in D_{6h} in a similar manner as found for the D_{4d} ferrocene metal AOs, thus a similar LCAO can be carried out.

Symmetry matching of the SALC's with the metal atomic orbitals

