

Quantum Chemistry

Lecture 24

Orbital Interactions

Tetrahedral molecules

Trigonalbipyramidal molecules

Octahedral molecules

NC State University

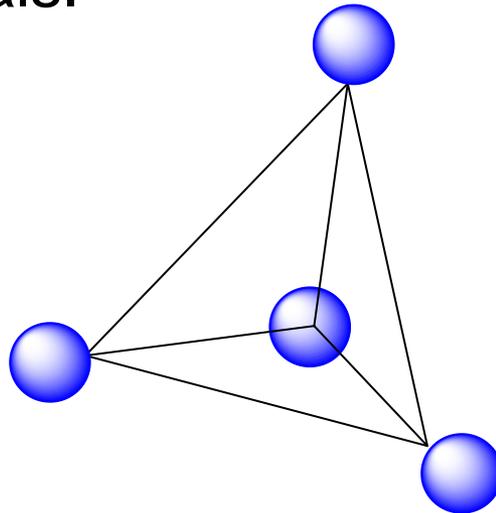
Molecules with tetrahedral symmetry

There are few organic molecules with tetrahedral symmetry, such as CH_4 and CCl_4 . Si and Ge also provide a few examples. However, inorganic complexes comprise the largest class of molecules having T_d symmetry. Thus, we will consider an example from both organic and inorganic chemistry in order to understand the application of MO theory to the tetrahedral geometry.

We can employ the same methods used previously for H_2O , NH_3 , C_2H_4 etc. to generate SALCs. We consider the four $1s$ orbitals of the H atoms as a set.

Geometry of a tetrahedron

The arrangement of the ligands in the T_d point group is shown in the Figure below. For the approximation used here we will consider the ligands as spheres of charge at the apices of the tetrahedron. For example, this model is applicable for σ -dative bonding with metals.



Tetrahedral ligand field shown in idealized form.

Application to the T_d point group

We have used the character table as a multiplication table to calculate the irreducible representations. We see that the 1s orbitals can form two SALCs.

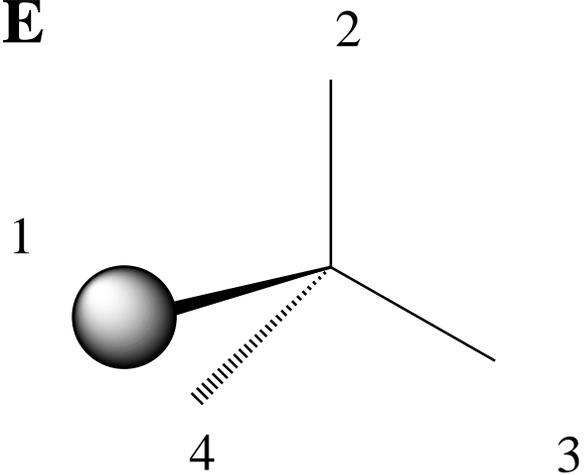
T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	Irreps
A_1	1	1	1	1	1	1
A_2	1	1	1	-1	-1	0
E	2	-1	2	0	0	0
T_1	3	0	-1	1	-1	0
T_2	3	0	-1	-1	1	1

$$\Gamma_{1s} = a_1 + t_2$$

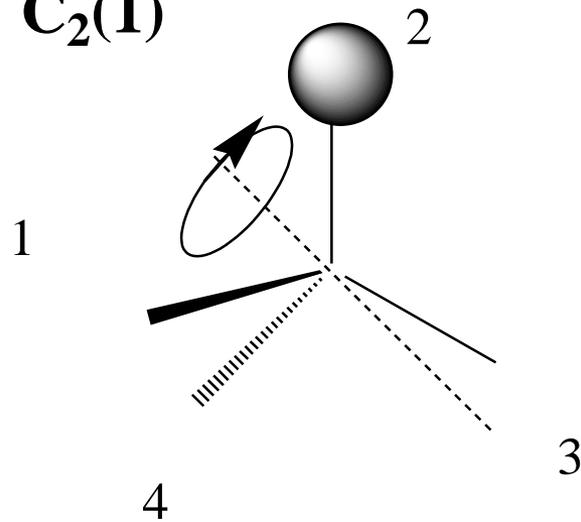
SALCs in the T_d point group

We can form the SALCs using the projection operator method. If we choose one member of the set we can see how that member is transformed by each operation in the group. Remember that in this case it is not the class that matters, but each operation. For example, there are 8 C_3 rotations about the four bonds of CH_4 (two for each bond as shown). We must use all of these rotations in the projection operator method. We can also include the identity, E and the 3 C_2 rotations. The C_2 rotations are about an axis that bisects the bonds as shown on the following slides. If we use only the E , 8 C_3 and 3 C_2 rotations shown the following two slides then we have a pure rotation subgroup for the T_d point group.

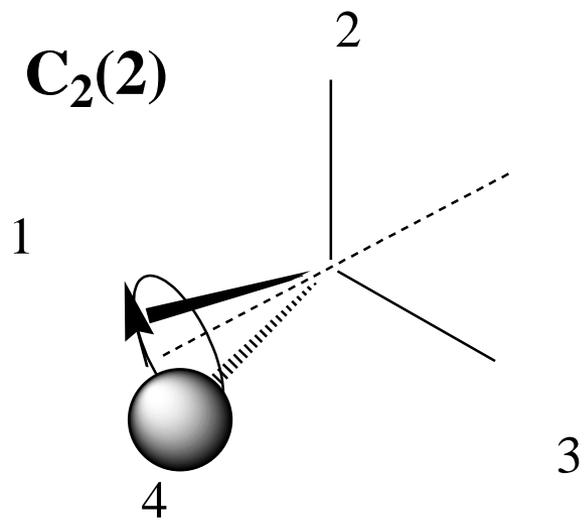
E



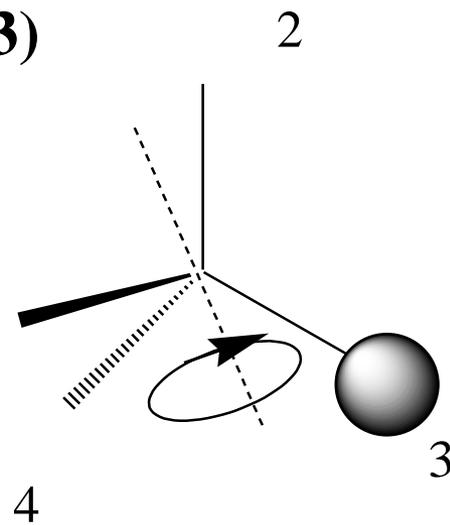
$C_2(1)$

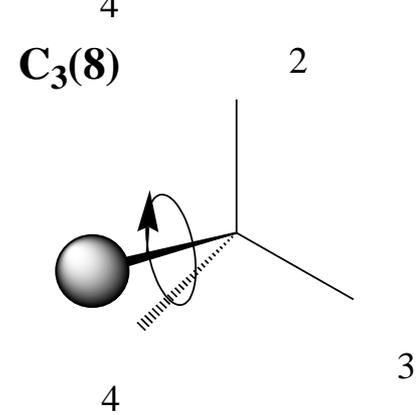
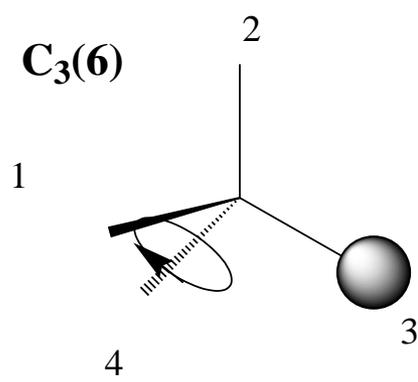
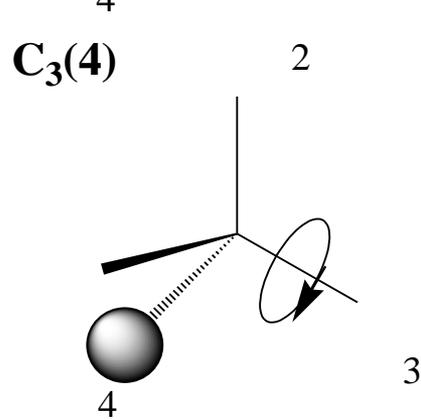
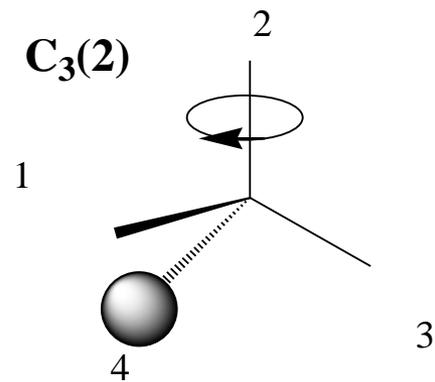
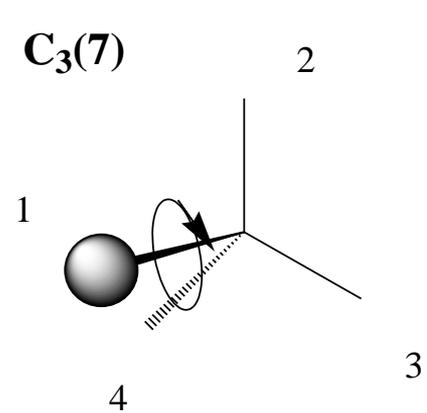
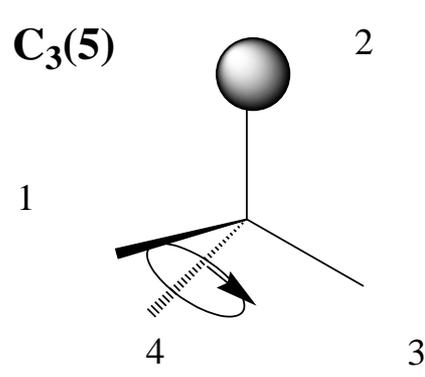
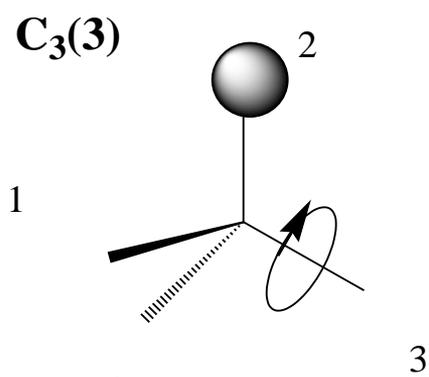
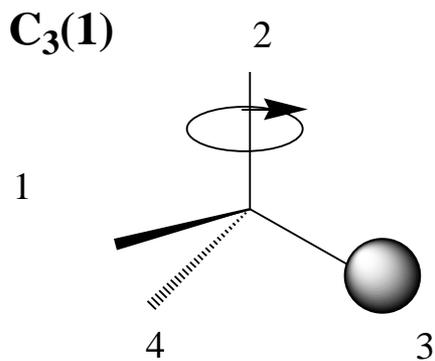


$C_2(2)$



$C_2(3)$





Inspection shows that each orbital appears three times. Since each has a character of 1 the total for a_1 is,

$$\psi_{a_1} = 3(\phi_1 + \phi_2 + \phi_3 + \phi_4)$$

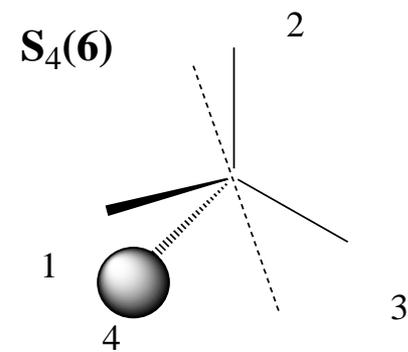
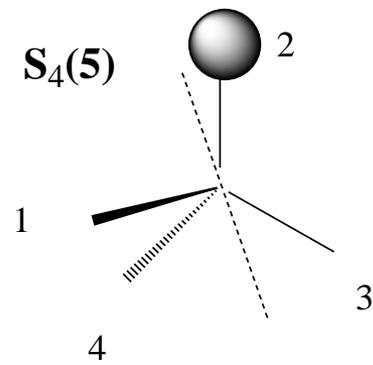
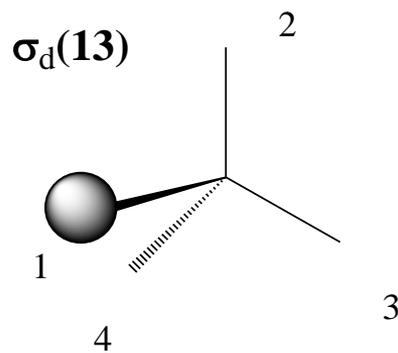
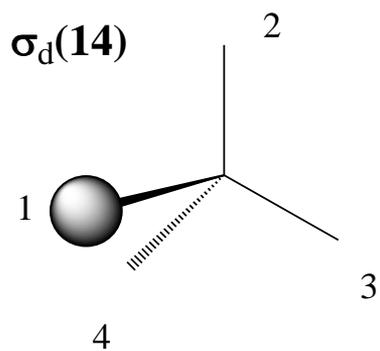
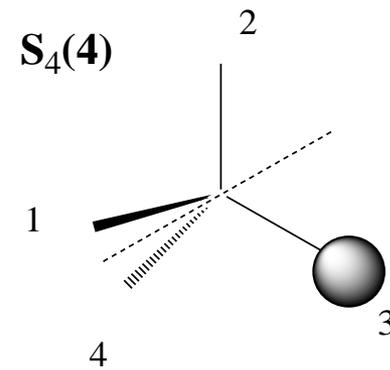
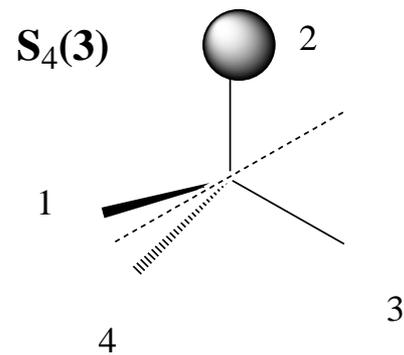
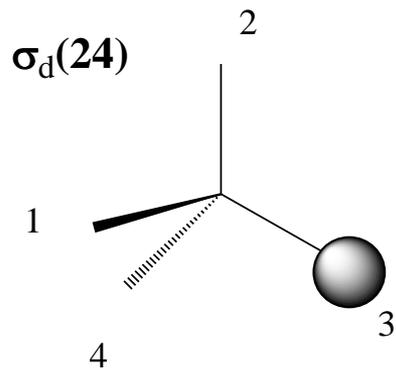
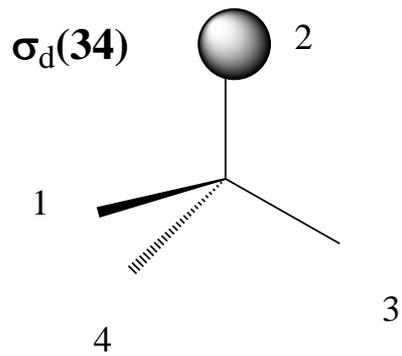
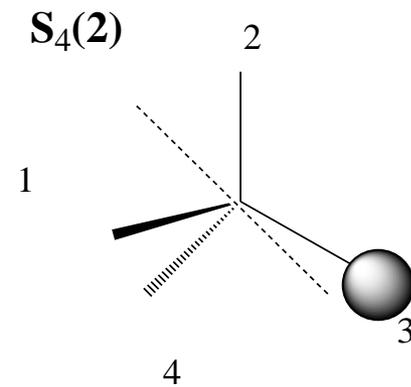
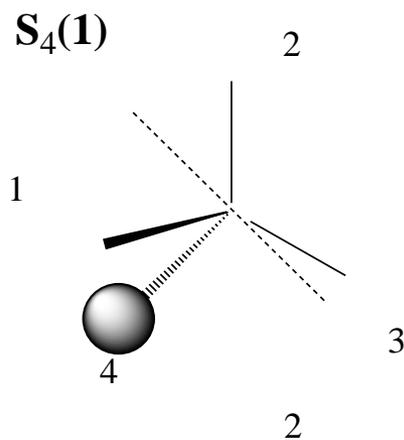
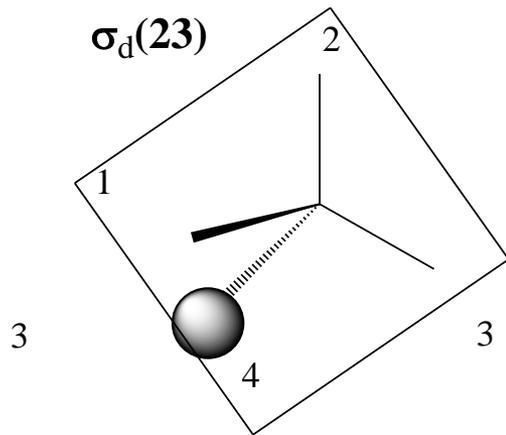
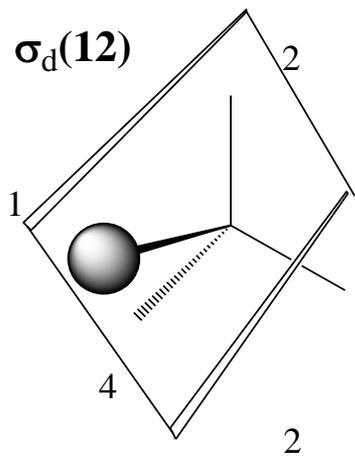
However, this SALC is not normalized. The normalized SALC is:

$$\psi_{a_1} = \frac{1}{\sqrt{3}}(\phi_1 + \phi_2 + \phi_3 + \phi_4)$$

If we assume that we can apply the pure rotation subgroup to the t_2 SALC we see that only the operations E and C_2 are non-zero. In this case one of the three possible the normalized SALCs is

$$\psi_{t_2,1} = \frac{1}{\sqrt{12}}(3\phi_1 - \phi_2 - \phi_3 - \phi_4)$$

We can check whether this result is sound by examining the projection operators for the remaining 12 symmetry operations in the T_d point group.



Projection operators in the T_d point group

$$P^E = \phi_1$$

$$P^{C_3} = 2\phi_1 + 2\phi_2 + 2\phi_3 + 2\phi_4$$

$$P^{C_2} = \phi_2 + \phi_3 + \phi_4$$

$$P^{S_4} = 2\phi_2 + 2\phi_3 + 2\phi_4$$

$$P^{\sigma_d} = 3\phi_1 + \phi_2 + \phi_3 + \phi_4$$

Thus, for T_2 we have

$$\psi_{t_2,1} = 3P^E - P^{C_2} - P^{S_4} + P^{\sigma_d}$$

$$\begin{aligned} \psi_{t_2,1} &= 3\phi_1 - (\phi_2 + \phi_3 + \phi_4) - (2\phi_2 + 2\phi_3 + 2\phi_4) \\ &\quad + 3\phi_1 + \phi_2 + \phi_3 + \phi_4 \end{aligned}$$

From this complete analysis we can see that the result using all of the symmetry operations is the same as we would have obtained using only the pure rotation subgroup.

Two orthogonal SALCs can be constructed to complete the three-dimensional irreducible representation

$$\psi_{t_2,2} = \frac{1}{\sqrt{2}}(\phi_3 - \phi_4)$$

$$\psi_{t_2,3} = \frac{1}{\sqrt{6}}(2\phi_2 - \phi_3 - \phi_4)$$

An alternative set of SALCs can be constructed in a rotated coordinate system

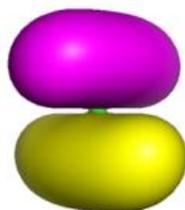
$$\psi_{t_2,1} = \frac{1}{2}(\phi_1 + \phi_2 - \phi_3 - \phi_4)$$

$$\psi_{t_2,2} = \frac{1}{2}(\phi_1 - \phi_2 - \phi_3 + \phi_4)$$

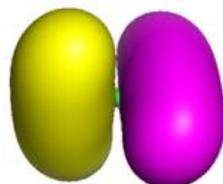
$$\psi_{t_2,3} = \frac{1}{2}(\phi_1 - \phi_2 + \phi_3 - \phi_4)$$

CH₄ as an example of an organic molecule in the T_d point group

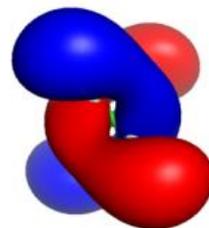
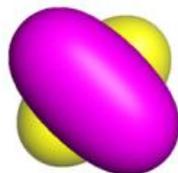
This is the representation that is manifest in the calculated t₂ MOs shown below for CH₄. Calculation using DMol3 yields the MOs for methane.



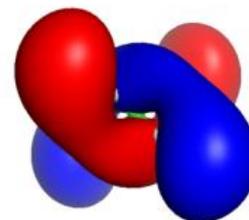
MO 2 A₁



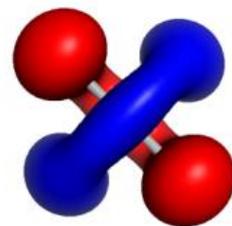
MO 3-5 T₂



MO 6 A₁



MO 7-9 T₂



MO Energies from a DFT calculation on CH₄

MO	Irrep	Hartrees	eV	Occup
1	a ₁	-9.85972	-268.297	2
2	a ₁	-0.62173	-16.918	2
3-5	t ₂	-0.34377	-9.354	6
6	a ₁	0.095791	2.607	0
7-9	t ₂	0.134068	3.648	0
10	e	0.772189	21.012	0

Crystal field theory

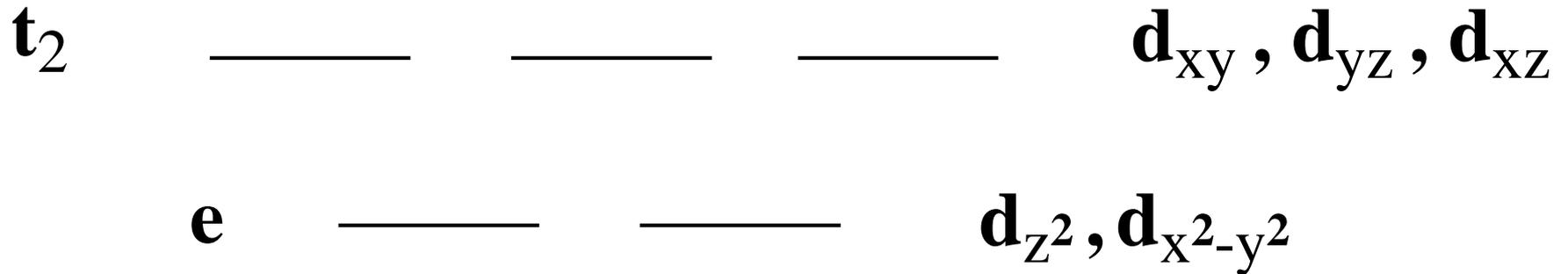
When considering the bonding of ligands to a metal one can begin with crystal field theory. The idea behind crystal field theory is that the metal is electron poor and the ligand is electron rich. Therefore, the ligand interacts with the metal by σ -donation of electron density. The d-electrons of the metal will have the lowest energy if they are not in the vicinity of the electron rich ligand. Thus, the d-electrons practice avoidance by first occupying the orbitals which point away from the direction of the ligand. To determine how the d-orbitals are affected by a given geometry, we can calculate the point group of the ligands. If the irrep of the ligands matches with a particular set of d-orbitals, then this set will be raised in energy.

Example of CuCl_4^{3-}

As a chemical example, we consider CuCl_4^{3-} . For simplicity we will consider only the σ -donation by the Cl^- ions. Thus, we consider them to be charged spheres surrounding the Cu^+ ion with a tetrahedral geometry. We have already determined the irreps for such a structure in the previous section. The irreps are $a_1 + t_2$. Next we consult the character table to determine the irreps for the d-orbitals. Examining the quadratic column we find that there are two sets. The d_{xy} , d_{yz} and d_{xz} transform as t_2 and the d_z^2 and $d_{x^2-y^2}$ transform as e . Thus the t_2 set is higher in energy since this set has the same symmetry as the ligand.

Energy level diagram

d-orbital energy diagram is:



Energy level splitting of the d-orbitals in a tetrahedral ligand field.

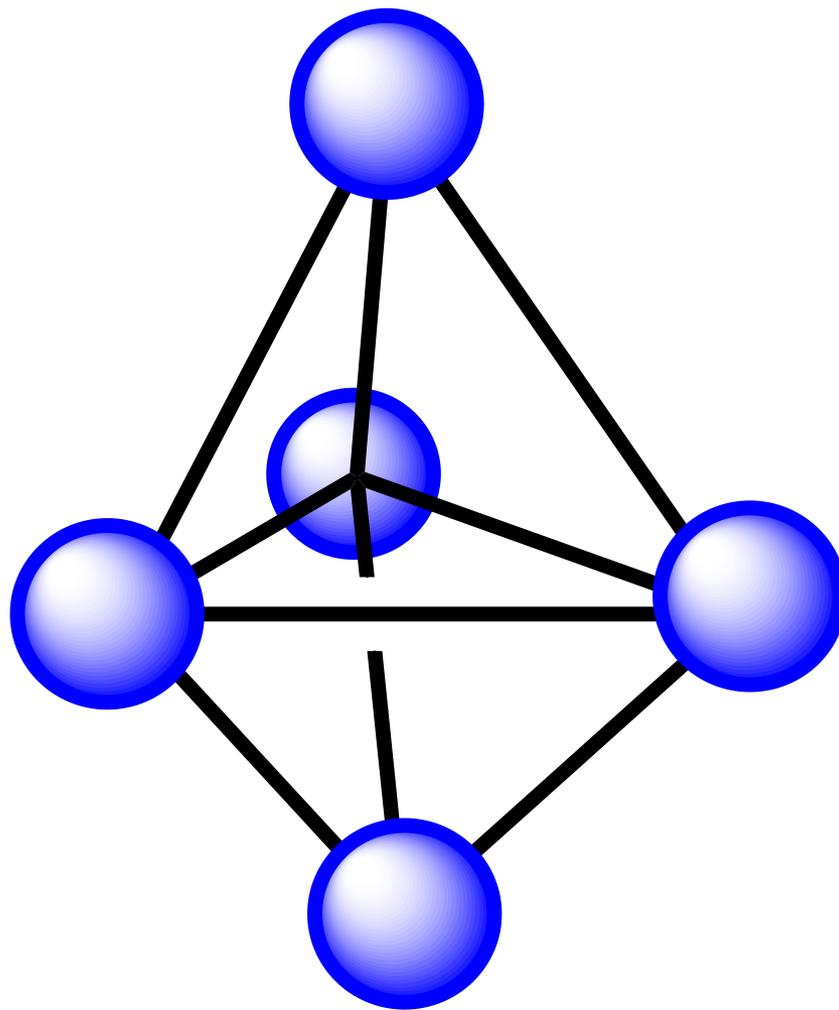
Trigonal Bipyramidal Molecules

The trigonal bipyramid is not as common as the other symmetries. It is a five-coordinate geometry in which there are three equatorial and two axial molecules. Examples include PF_5 , PCl_5 and $\text{Fe}(\text{CO})_5$. These molecule belong to the D_{3h} point group. As an example of the application of MO theory we can consider the crystal field due to the σ -bonding lone pairs of the CO molecules.

The reducible representation for the five sigma orbitals is:

D_{3h}	E	$2C_3$	$3C'_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_σ	5	2	1	3	0	3

Trigonal Bipyramidal Geometry



Decomposition into irreps

D_{3h}	E	$2C_3$	$3C'_2$	σ_h	$2S_3$	$3\sigma_v$	#lrr
A'_1	1	1	1	1	1	1	2
A'_2	1	1	-1	1	1	-1	0
E'	2	-1	0	2	-1	0	1
A''_1	1	1	1	-1	-1	-1	0
A''_2	1	1	-1	-1	-1	1	1
E''	2	-1	0	-2	1	0	0

Thus,

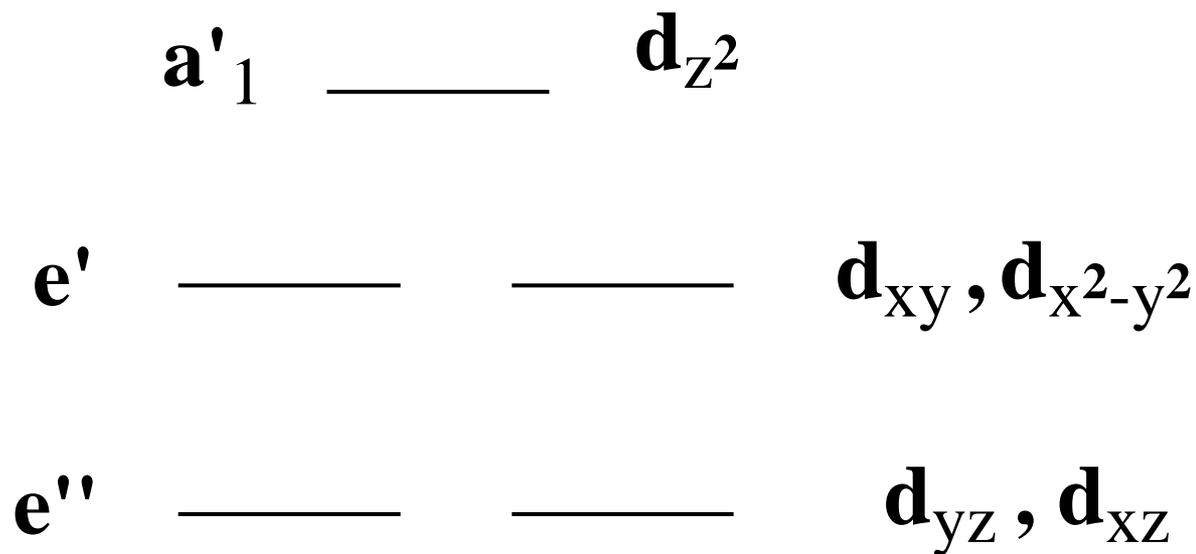
$$\Gamma_{\sigma} = 2a'_1 + e' + a''_2$$

From the D_{3h} character table we find that the d-orbitals have the irreps

$$\Gamma_{d\text{-orbital}} = 2a'_1 + e' + e''$$

Energy level diagram

Thus, the a'_1 and e' sets of ligand orbitals have the same symmetry as the d_{z^2} and the $d_{x^2-y^2}/d_{xy}$, respectively. This is shown in the energy level diagram for the d-orbitals.



Energy level splitting of the d-orbitals in a trigonal bipyramidal ligand field.

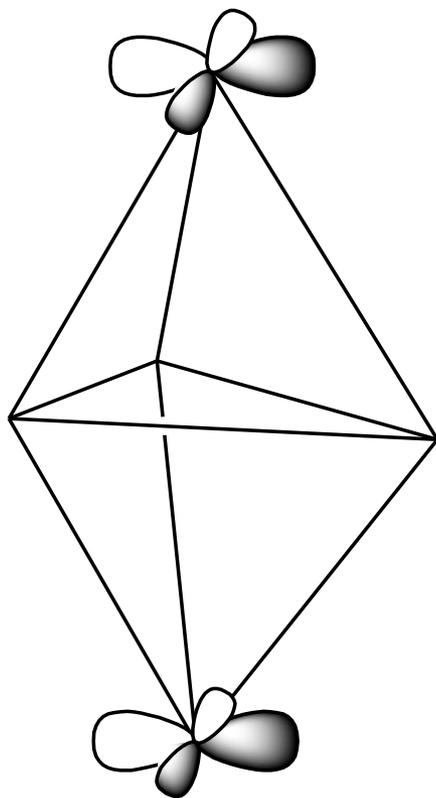
Sigma- and pi-bonding

Neutral Fe has 8 d-electrons and thus the d-orbital levels e'' and e' are filled in $\text{Fe}(\text{CO})_5$.

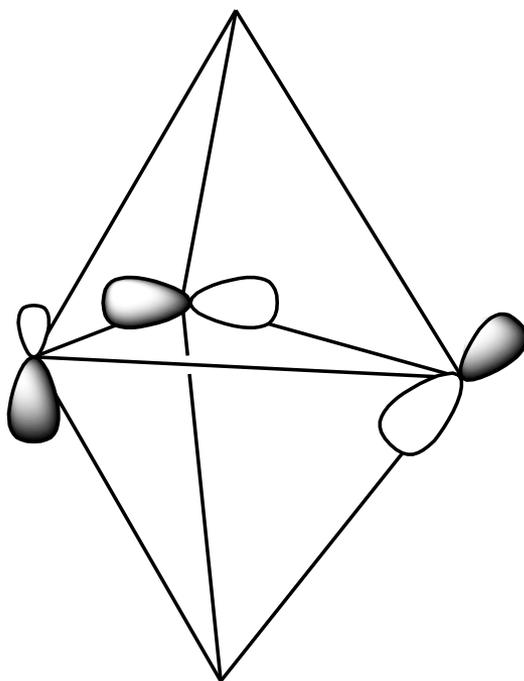
We can consider a more difficult application by thinking about the so-called π -backbonding from the metal to the ligand. CO is called a π -acid ligand since its unoccupied π^* orbital can accept electron density from the metal. We can ask which d orbitals can donate electron density to the axial and equatorial CO ligands. In this case we can model the basis as a set of p-orbitals that are perpendicular to the metal-ligand bond axis. Only filled metal d-orbitals are capable of interaction with the ligand. The donation of electron density to the ligand results in a shorter metal-CO bond and simultaneously a longer C-O bond because of the additional electron density in a π^* MO.

Symmetry-related sets

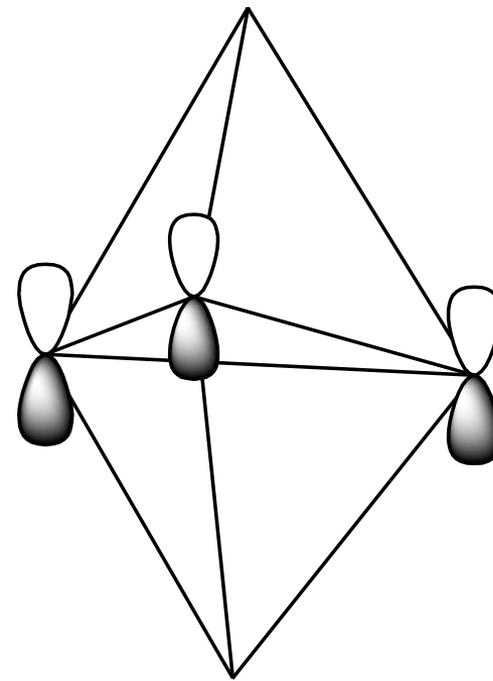
The possible sets of ligand π -symmetry orbitals are shown



Axial



**Equatorial
Parallel**



**Equatorial
Perpendicular**

Decomposition into irreps

Since the 3-fold axis inherently mixes the x- and y-coordinates, it is not possible to consider only one of the π -symmetry orbitals in the axial set. Physically this corresponds to the fact that the CO molecule could have any orientation in the axial position. However, the equatorial set of π -symmetry orbitals can be divided into parallel and perpendicular orientations as shown in the Figure. The sets transform as follows

D_{3h}	E	$2C_3$	$3C'_2$	σ_h	$2S_3$	$3\sigma_v$
Γ_{ax}	4	-2	0	0	0	0
Γ_{eq1}	3	0	-1	3	0	-1
Γ_{eq2}	3	0	-1	-3	0	1

D_{eh}	E	$2C_3$	$3C'_2$	σ_h	$2S_3$	$3\sigma_v$	# Γ_{eq}	# Γ_{ax1}	# Γ_{ax2}
A'_1	1	1	1	1	1	1	0	0	0
A'_2	1	1	-1	1	1	-1	1	1	0
E'	2	-1	0	2	-1	0	1	1	0
A''_1	1	1	1	-1	-1	-1	0	0	0
A''_2	1	1	-1	-1	-1	1	0	0	1
E''	2	-1	0	-2	1	0	0	0	1

The reducible representations are decomposed as follows:

$$\Gamma_{ax} = a'_2 + e'$$

$$\Gamma_{eq1} = a'_2 + e'$$

$$\Gamma_{eq2} = a''_2 + e''$$

Bonding and non-bonding sets

Both the parallel equatorial ligands and the axial transform as

$$a'_2 + e'$$

When we compare these irreps with the d-orbital irreps we see that e' corresponds to the $d_{x^2-y^2}/d_{xy}$ orbitals. This analysis shows us that the e' orbitals mix the axial and equatorial bonding.

The equatorial perpendicular bonding transforms as

$$a''_2 + e''$$

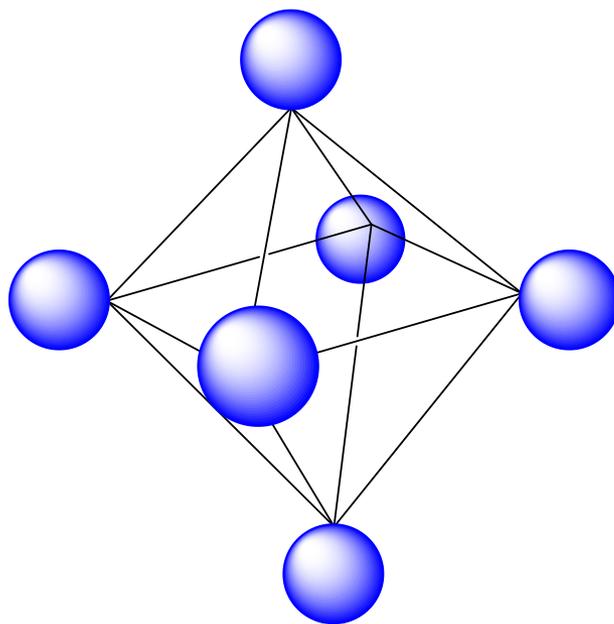
so that the d-orbitals that can donate electron density to the COs have e'' symmetry. These are the d_{xz} and d_{yz} . These are Bonding orbitals. However, the orbitals in the a'_2 and a''_2 sets Are non-bonding since there is no d-orbital with that irrep.

Octahedral molecules

Octahedral symmetry is found in a few small molecules, e.g. SF_6 , but is an extremely common coordination geometry for metals. There are carbonyl compounds such as $\text{Mn}(\text{CO})_6$, that is related in properties to $\text{Fe}(\text{CO})_5$ discussed in the previous section. However, 6 is a common coordination number so we can also consider compounds such as $\text{Co}(\text{NH}_3)_6^{2+}$ or $\text{Fe}(\text{H}_2\text{O})_6^{2+}$. Often the details of the ligand are not considered as important as the overall symmetry of the lone pairs that interact with the metal. Thus, we can speak of the octahedral ligand field. The same logic applies as above to the tetrahedral or trigonal pyramidal ligand field. Namely, the s -donation by ligands to the electron poor metal will repel the d -electrons so that they will tend occupy d -orbitals that do not have the symmetry of the ligand.

Idealized Octahedral Geometry

To determine the ligand field in the O_h point group, our first task is to consider the reducible representation that arises from a collection of six charged spheres (effectively six s orbitals). These represent the electron density of σ -donation by the ligand.



The octahedral ligand field shown in idealized form.

Reducible representation in O_h

Using the O_h character table we first determine the reducible representation of these six charges. This is a sigma orbital representation. As we show in the following it is also valid for ligands such as H_2O or NH_3 where we can treat the lone pair as a sigma donor (an approximation that ignores the H atoms).

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$ $=(C_4)^2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
Γ_σ	6	0	0	2	2	0	0	0	4	2

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$ $=(C_4)^2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	#Irr
A_{1g}	1	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1	0
E_g	2	-1	0	0	2	2	0	-1	2	0	1
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	0
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	0
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	0
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1	0
E_u	2	-1	0	0	2	-2	0	1	-2	0	0
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	1
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1	0

Therefore, the reducible representation is:

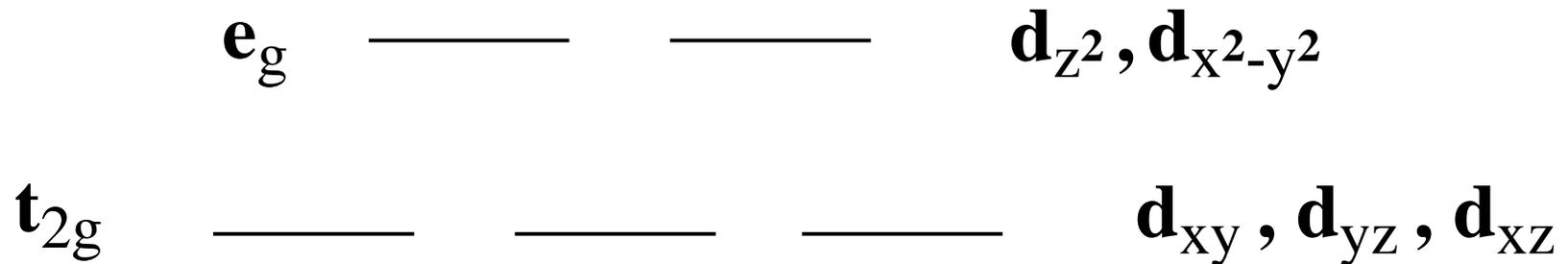
$$\Gamma_{\sigma} = a_{1g} + t_{1u} + e_g$$

Energy level diagram in O_h

Next we determine which irreps correspond to d-orbitals in the O_h point group. From inspection of the quadratic column in the O_h character table we find,

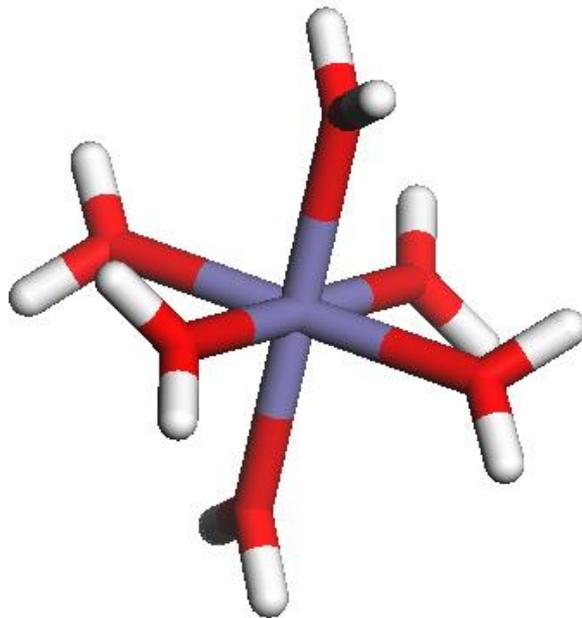
$$\Gamma_{d\text{-orbitals}} = t_{2g} + e_g$$

Thus, the occupation of the d_{z^2} and $d_{x^2-y^2}$ orbitals of e_g symmetry is energetic unfavorable due to the electronic repulsion of the ligand. The energy level diagram is show.



Energy levels of the d-orbitals in an octahedral ligand field

The compound $\text{Fe}(\text{OH}_2)_6^{2+}$ is a pseudo- O_h molecule. Specifically, it has an O_h ligand field if only the Fe and O atoms are included. The central Fe atom in this molecule is d^6 . The calculation was carried out for a charge of 2+ and for 4 unpaired electrons. The geometry-optimized structure is shown

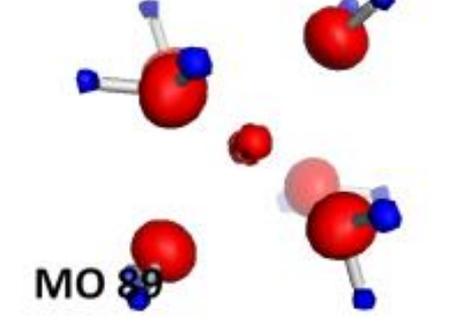
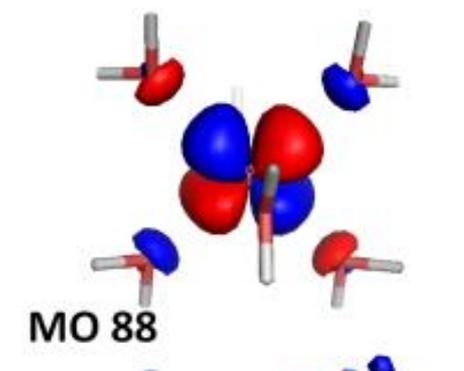
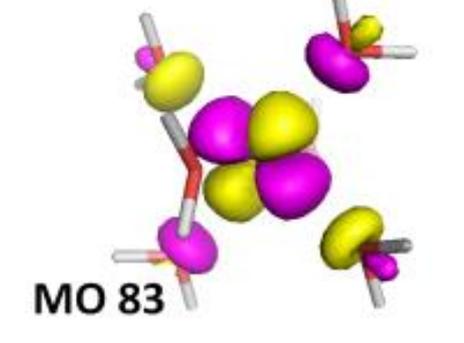
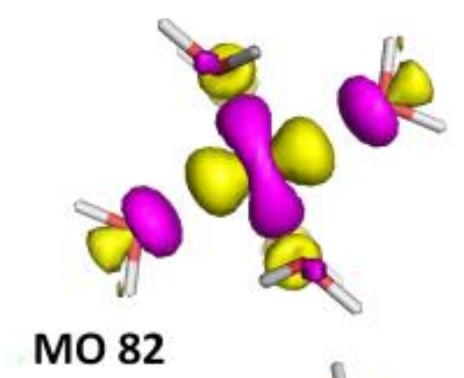
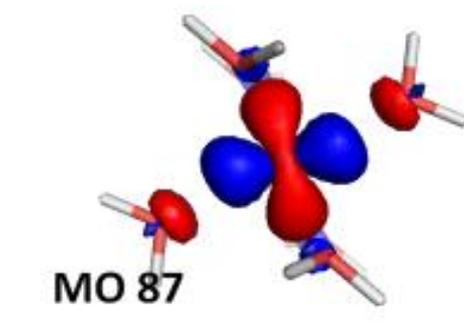
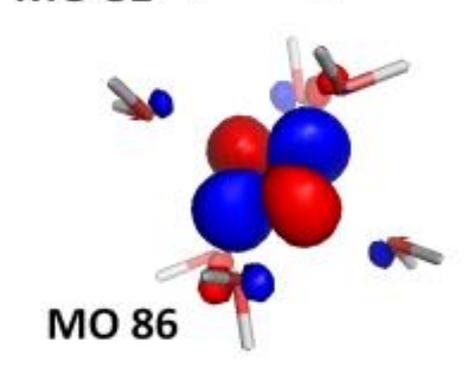
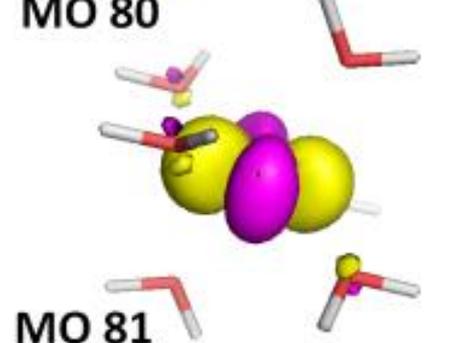
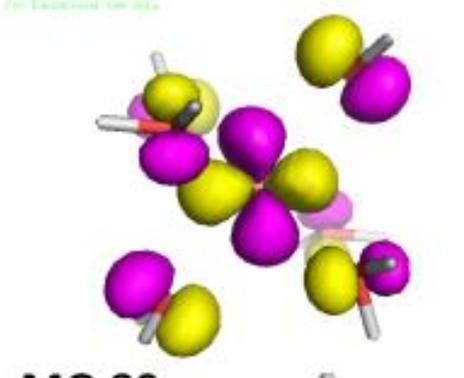
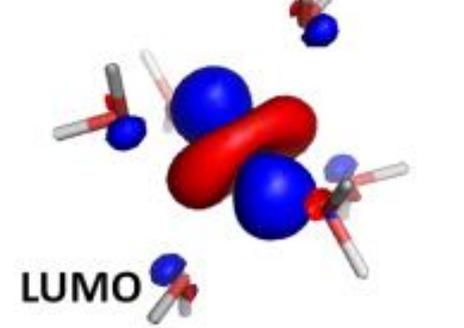
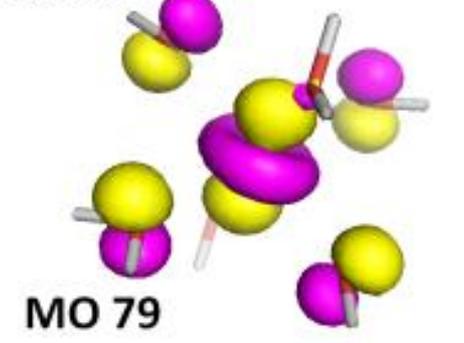
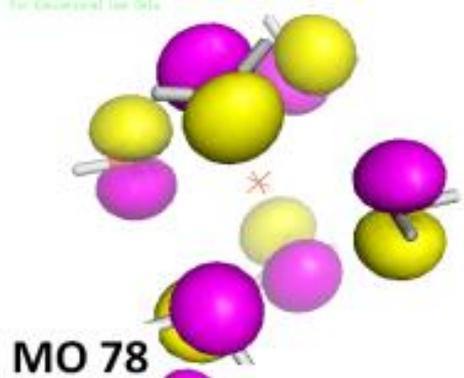


Geometry optimized structure for $\text{Fe}(\text{OH}_2)_6^{2+}$. Although the molecule has nominal O_h symmetry, it belongs to the C_{2h} point group when the H atoms are included.

$\text{Fe}(\text{H}_2\text{O})_6$ pseudo- O_h example

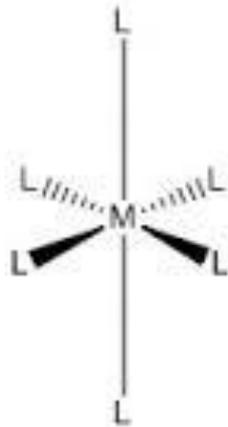
In this case one finds that the spin density on the metal d orbitals is 3.73 calculated by the Mulliken method. The spin density on the Fe 4p orbitals is 0.06. The remaining spin density of approximately 0.2 is spread over the 6 coordinating oxygen atoms. The occupied and unoccupied MOs are shown in the Figure on the next slide.

It is evident that six of the ten d-orbitals are occupied and four are unoccupied. The character of the HOMO and LUMO is almost perfectly d orbital. The water molecules contribute more the MOs as one moves higher and lower in energy than the HOMO/LUMO.

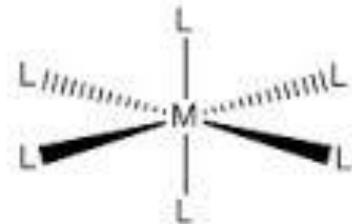


Jahn-Teller Effect

The Jahn-Teller theorem states that a molecule will distort to lower its symmetry in cases where there is a degenerate ground state. A degenerate ground state arises if there is an unpaired electron in a doubly or triply degenerate orbital. In that case an energy splitting can cause the electron to achieve a lower energy. However, the energy lowering must be the result of a distortion of the molecule structure away from the original symmetry.



Elongated

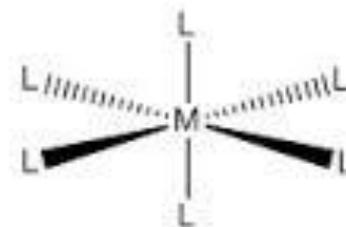
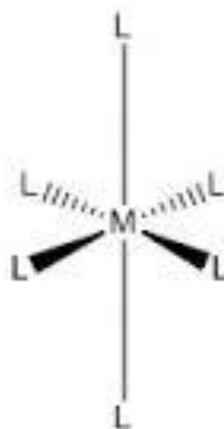
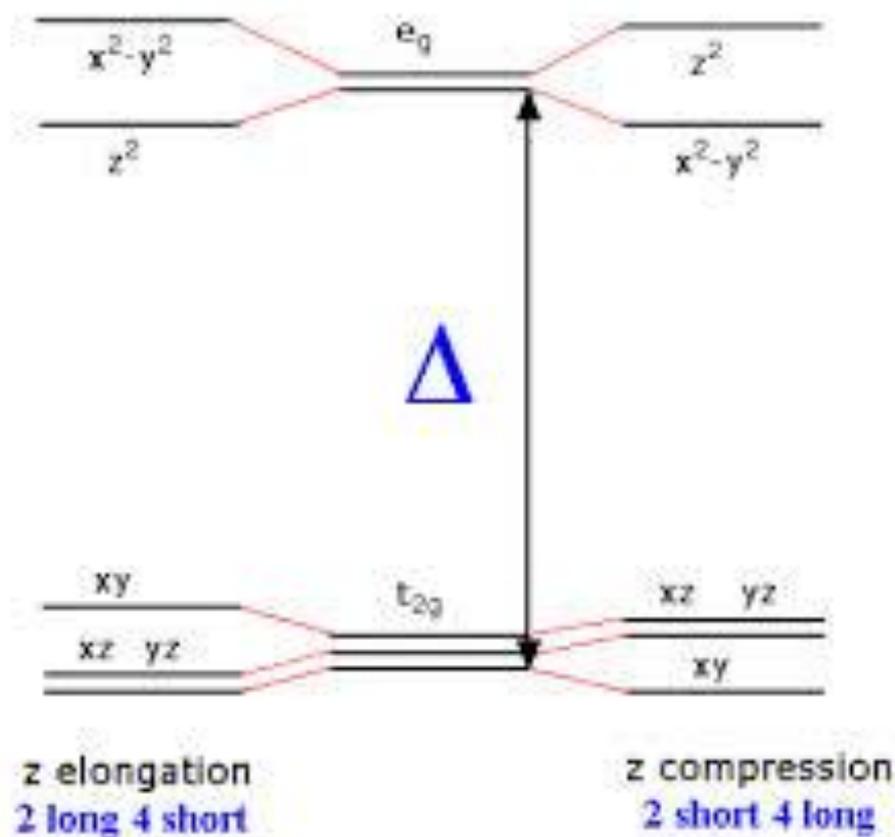
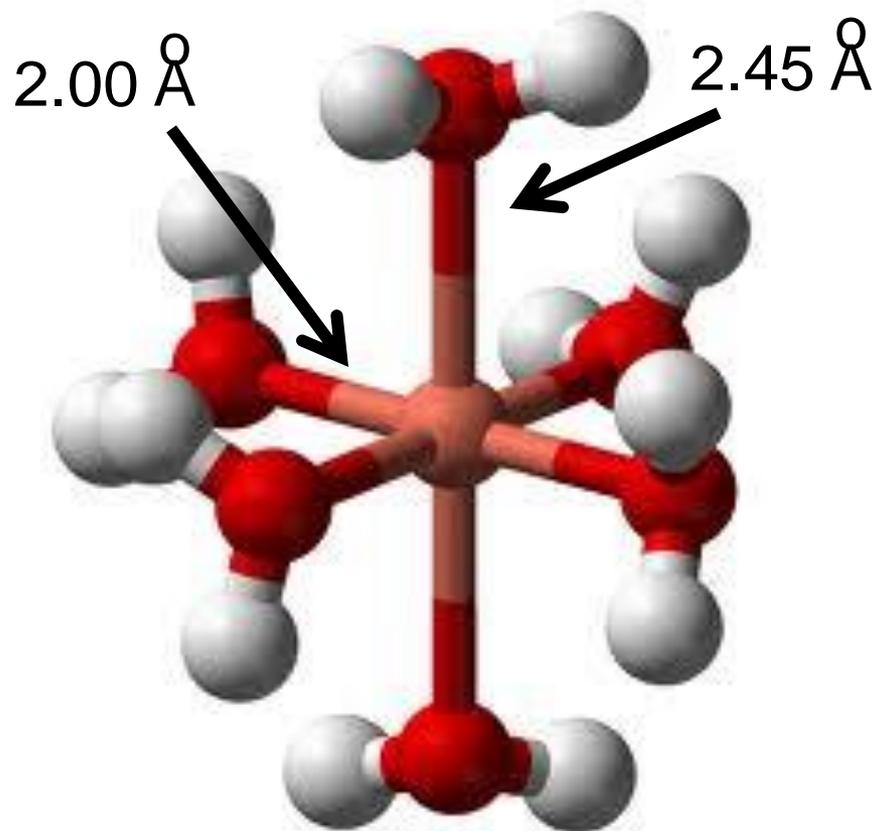


Compressed

Jahn-Teller Effect in O_h

The Jahn–Teller effect is most commonly observed in octahedral complexes of the transition metals. When an odd number of electrons occupy the e_g orbitals there is a degenerate ground electronic state. This situation arises in complexes with the configurations d^9 , low-spin d^7 and high-spin d^4 . In such compounds the e_g orbitals involved in the degeneracy point directly at the ligands, so distortion can result in a large energetic stabilization. For example, six-coordinate Cu(II) complexes have a d^9 electronic configuration, which results in three electrons occupying the two degenerate e_g orbitals.

$\text{Cu}(\text{H}_2\text{O})_6^{2+}$ shows an elongation Jahn-Teller distortion. The compression is also shown in the energy diagram for completeness.



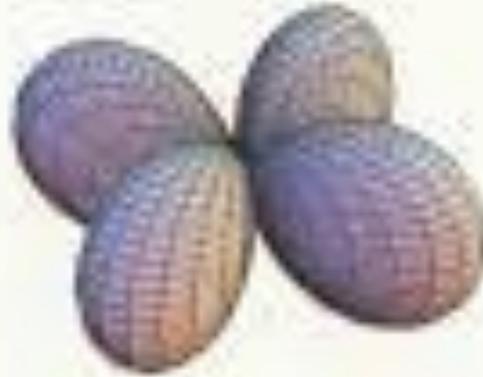
Manifestations of J-T Effect

This is a doubly degenerate electronic ground state. Such complexes distort along one of the molecular fourfold axes. This distortion removes the orbital degeneracy and lowers the overall energy. The distortion normally takes the form of elongating the bonds to the ligands lying along the z axis, but occasionally occurs as a shortening of these bonds instead.

The Jahn–Teller theorem does not predict the direction of the distortion, only the presence of an unstable geometry.

Although the Jahn-Teller effect is observed in tetrahedral complexes, the distortion is relatively small because the ligands are not pointing directly at the orbitals. There is less stabilization possible from the symmetry lowering distortion.

e_g orbitals



Shapes of d-orbitals. The e_g set points at ligands lying along x,y,z. The t_{2g} do not point at the ligands.

t_{2g} orbitals

