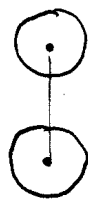# 5. ELECTRONIC STATES OF MOLECULES

## 5.1 Hybridization

A molecule is formed when 2 or more atoms bind together.
The number and position of the nodal planes in the electron density between the atoms determine the nature of the bond.
One distinguishes:

- $\sigma$ bond : <u>no</u> nodal planes in the charge density along the bond connecting the 2 atoms.

  examples of $\sigma$ bonds

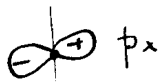  ss $\sigma$ bond

  sp $\sigma$ bond

  pp $\sigma$ bond

  conventionally the bond is oriented in the z direction.

- $\pi$ bond : <u>1</u> nodal plane in the charge density along the bond connecting the 2 atoms

  example

  $p_x$
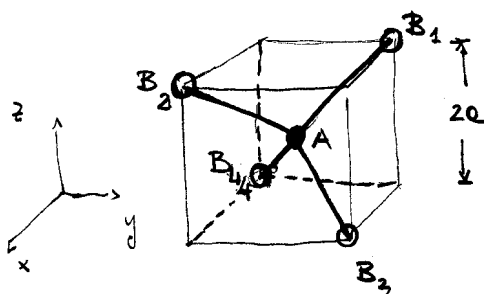
  pp $\pi$ bond

  $p_x$

  dp $\pi$ bond

- finally one speaks of ANTIBONDING in presence of a nodal plane $\perp$ to the bond between the 2 atoms.

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An important remark concerns the concept of __Hybridization__: mixing of atomic orbitals of different angular momentum in order to obtain equivalent bond orbitals which respect the symmetry of the molecule:

__EXAMPLE__    σ bonding of tetrahedral $AB_4$ molecule



$$R_A = (0,0,0)$$
$$R_{B_1} = (-a, a, a)$$
$$R_{B_2} = (a, -a, +a)$$
$$R_{B_3} = (+a, +a, -a)$$
$$R_{B_4} = (-a, -a, -a)$$

The point group of this molecule is the $T_d$ tetrahedral group, whose character table reads

| $T_d$ | $E$ | $8C_3$ | $3C_2$ | $6\sigma_d$ | $6S_4$ | | $h = 24$ |
|---|---|---|---|---|---|---|---|
| | | | | | | | |

| | $T_d$ | $E$ | $8C_3$ | $3C_2$ | $6\sigma_d$ | $6S_4$ |
|---|---|---|---|---|---|---|
| $x^2+y^2+z^2$ | $A_1$ | 1 | 1 | 1 | 1 | 1 |
| | $A_2$ | 1 | 1 | 1 | -1 | -1 |
| $x^2-y^2, 3z^2-r^2$ | $E$ | 2 | -1 | 2 | 0 | 0 |
| $R_x, R_y, R_z$ | $T_1$ | 3 | 0 | -1 | -1 | 1 |
| $(x,y,z)$ $(xy, yz, zx)$ | $T_2$ | 3 | 0 | -1 | 1 | -1 |

We take as basis for the representation of the σ bonds through the molecule the set of unitary vectors from A to the atoms $B_r$. We call this representation $\Gamma_\sigma$. The character of the $\Gamma_\sigma$ representation is easily determined by counting how many vectors remain invariant under application of the group element transformation.

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$\chi^{\Gamma_6}(E) = 4$      the identity leaves all bonds where they are

$\chi^{\Gamma_6}(C_3) = 1$      the axis of $C_3$ coincides with one of the bonds

$\chi^{\Gamma_6}(C_2) = 0$      all bonds move. the rotation axis bisects the angle between 2 bonds

$\chi^{\Gamma_6}(\sigma_d) = 2$      the symmetry element is defined by 2 bonds

$\chi^{\Gamma_6}(S_4) = 0$      the same as $C_2$ with extra mirroring through a $\perp$ plane.

Now we can apply the reduction formula and obtain

$$c(A_1) = \frac{1}{24}\left[1(1)(4) + 8(1)(1) + 6(1)(2)\right] = 1$$

$$c(A_2) = \frac{1}{24}\left[1(1)(4) + 8(0)(1) + 6(-1)(2)\right] = 0$$

$$c(E) = \frac{1}{24}\left[1(2)(4) + 8(-1)(1) + 6(0)(2)\right] = 0$$

$$c(T_1) = \frac{1}{24}\left[1(3)(4) + 8(0)(1) + 6(-1)(2)\right] = 0$$

$$c(T_2) = \frac{1}{24}\left[1(3)(4) + 8(0)(1) + 6(1)(2)\right] = 1$$

$$\Rightarrow \quad \Gamma_6 = A_1 \oplus T_2$$

The $s$ orbital on A forms a basis for $A_1$ and, from the character table we know that a good basis for $T_2$ is $(x,y,z)$ or $(xy, yz, zx)$

$\Rightarrow$ $\sigma$ bonds are formed out of $sp^3$ and/or $sd^3$ hybridization.
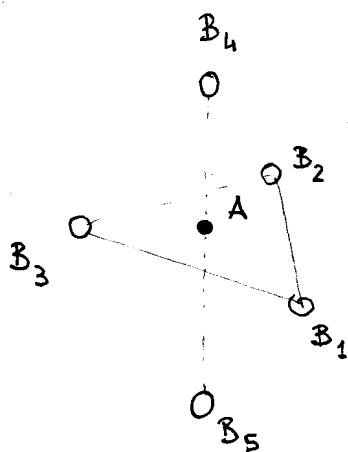
In general a molecular orbital $\psi_{MO}$ would involve linear combination of $s$, $p_x, p_y, p_z$ and $d_{xy}$, $d_{yz}$, $d_{zx}$ atomic orbitals (AOs) Some coefficients though can be extremely small. Criteria.

* contributing AOs must have comparable energy

* in bonding MO the bond should provide maximum overlap of charge density in the region between the atoms.

In Carbon $E_{3d} - E_{2p} \approx 10\,eV \Rightarrow sp^3$ dominates.

Manganese, Chromium $|E_{4s} - E_{3d}| < |E_{4s} - E_{4p}| \Rightarrow sd^3$ dominates.
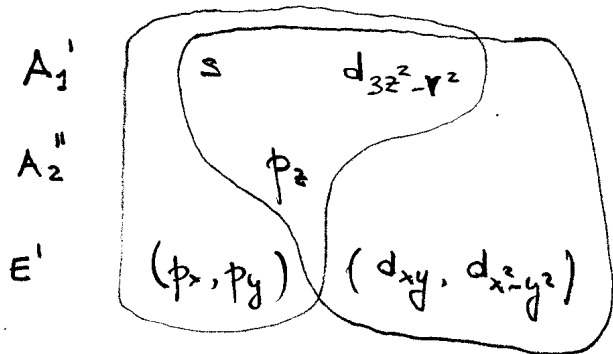
Another example is the $AB_5$ molecule



The point group of this molecule is $D_{3h}$ with character table

| | E | $2C_3$ | $3C_2'$ | $\sigma_h$ | $2S_3$ | $3\sigma_v$ | Bases |
|---|---|---|---|---|---|---|---|
| $A_1'$ | 1 | 1 | 1 | 1 | 1 | 1 | $x^2+y^2, z^2$ |
| $A_2'$ | 1 | 1 | -1 | 1 | 1 | -1 | $R_z$ |
| $E'$ | 2 | -1 | 0 | 2 | -1 | 0 | $(x,y), (xy, x^2-y^2)$ |
| $A_1''$ | 1 | 1 | 1 | -1 | -1 | -1 | |
| $A_2''$ | 1 | 1 | -1 | -1 | -1 | 1 | $z$ |
| $E''$ | 2 | -1 | 0 | -2 | 1 | 0 | $(R_x, R_y), (yz, zx)$ |

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With the same procedure implied before

$$\begin{array}{ccccccc} & E & 2C_3 & 3C_2' & \sigma_h & 2S_3 & 3\sigma_v \\ \Gamma_\sigma = \{ & 5 & 2 & 1 & 3 & 0 & 3 \} \end{array} \longleftarrow \text{ character system}$$

$$\Rightarrow \qquad \Gamma_\sigma = 2A_1' \oplus A_2'' \oplus E'$$

$A_1'$

$A_2''$

$E'$



$\Rightarrow$ hybridization scheme

$dsp^3$ or

$d^3sp$ or

$dsp^3 + d^3sp$

Summarizing, GT gives the possible hybridization solutions, the energies involved decide for the specific ones.

## 5.2 π Election system

MO extend over many atoms. They can be expressed as linear combination of atomic orbitals.

$$|\psi_j\rangle = \sum_r |\phi_r\rangle c_{rj}$$

For example in benzene. The group of the molecule is $D_{6h}$

$$D_{6h} = D_6 \otimes C_i = \{D_6\} \oplus I\{D_6\}$$

The classes of $D_6 = \{E \ 2C_6 \ 2C_3 \ C_2 \ 3C_2' \ 3C_2''\}$ and the one of $D_{6h}$ can be found simply multiplying the class representative by $I$. If now I take one $p_z$ orbital per Carbon atom I obtain the character system

$$\begin{array}{cccccccccccc} & E & 2C_6 & 2C_3 & C_2 & 3C_2' & 3C_2'' & I & 2S_3 & 2S_6 & \sigma_h & 3\sigma_d & 3\sigma_v \\ \chi(\Gamma_\phi) = \{ & 6 & 0 & 0 & 0 & -2 & 0 & 0 & 0 & 0 & -6 & 0 & 2 \} \end{array}$$

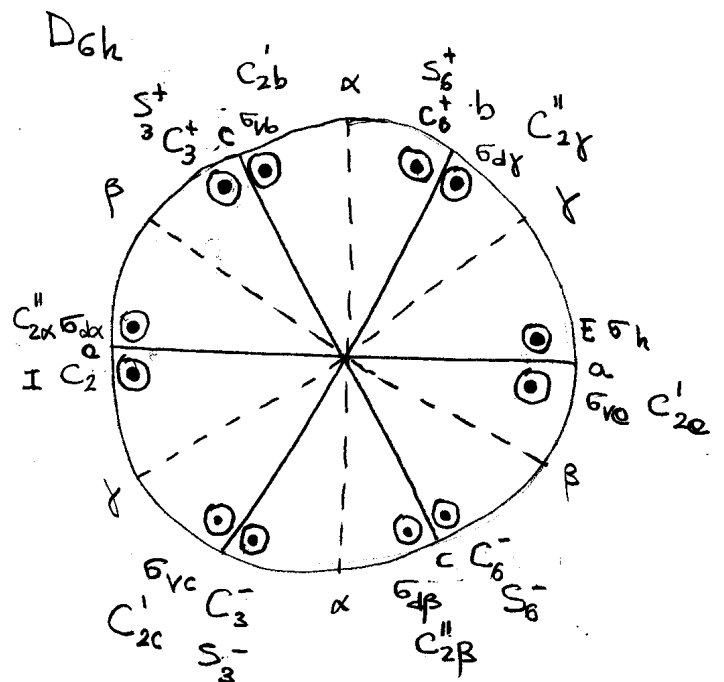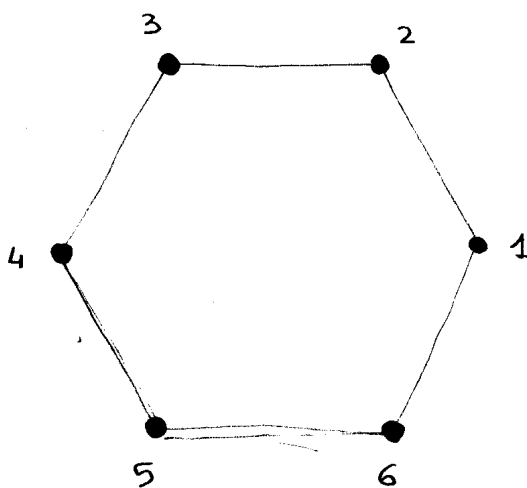The application of the reduction formula produces

$$\Gamma_\phi = A_{2u} \oplus B_{2g} \oplus E_{1g} \oplus E_{2u}$$

The character system of the one dimensional irreducible representation $B_{2g}$ reads:

$$B_{2g} = \{1 \ -1 \ 1 \ -1 \ -1 \ +1 \ 1 \ -1 \ 1 \ -1 \ -1 \ +1\}$$

$$P^{B_{2g}}(\phi_1) = N(B_{2g})\Big[ \overset{E}{\phi_1} \overset{C_6^+ \quad C_6^-}{- 1(\phi_2 + \phi_6)} + \overset{C_3^+ \quad C_3^-}{(\phi_3 + \phi_5)} \overset{C_2}{- \phi_4} \overset{C_{2a}' \quad C_{2b}' \quad C_{2c}'}{- 1(-\phi_1 - \phi_3 - \phi_5)}$$

$$\overset{C_{2\alpha}'' \quad C_{2\beta}'' \quad C_{2\gamma}''}{+ 1(-\phi_4 - \phi_6 - \phi_2)} + \overset{I}{1(-\phi_4)} \overset{S_3^+ \quad S_3^-}{- 1(-\phi_3 - \phi_5)} \overset{S_6^+ \quad S_6^-}{+ 1(-\phi_2 - \phi_6)}$$

$$\overset{\sigma_h}{- 1(-\phi_1)} \overset{\sigma_{d\alpha} \quad \sigma_{d\beta} \quad \sigma_{d\gamma}}{- 1(\phi_4 + \phi_6 + \phi_2)} + \overset{\sigma_{va} \quad \sigma_{vb} \quad \sigma_{vc}}{1(\psi_1 + \phi_3 + \phi_5)} \Big] =$$

$$= N(B_{2g})\Big[4\phi_1 - 4\phi_2 + 4\phi_3 - 4\phi_4 + 4\phi_5 - 4\phi_6\Big] = \psi_{B_{2g}}$$

Benzene



$D_{6h}$

The normalization comes from the quantum mechanical requirement

$$1 = \langle \psi^j | \psi^j \rangle = |N_j|^2 \Big[ \sum_r |c_{rj}|^2 + \sum_{s \neq r} c_{rj}^* c_{sj} S_{rs} \Big]$$
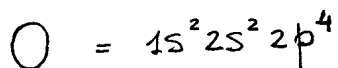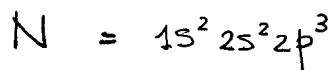
In the zero Overlap Approximation $S_{rs} = \delta_{rs} \Rightarrow$

$$\psi_{B_{2g}} = \frac{1}{\sqrt{6}} \left[ \phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6 \right]$$
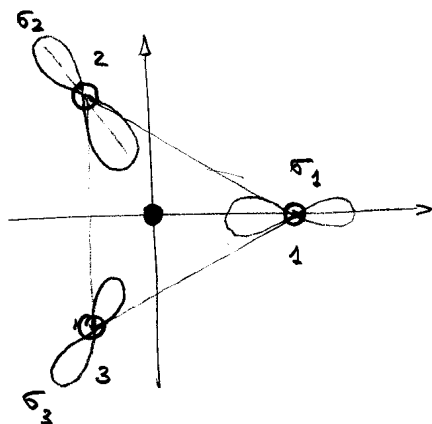
Notice that if we relax the ZOA the relative phase between the atomic orbitals does not change, only the normalization would be effected.

## 5.3 Equivalent bond orbitals

In section 5.1 we introduced hybridization at a qualitative level. Now we consider a concrete example for which we calculate explicitly the $sp^2$ hybrid orbitals by means of group theory.

$$N = 1s^2 2s^2 2p^3$$
$$O = 1s^2 2s^2 2p^4$$

We consider the $\sigma$ bond structure of the ion $NO_3^-$. The molecule is planar and belongs to the $D_{3h}$ group. Let us introduce the $\sigma$ basis formed by 3 $p$ orbitals, one for each Oxygen atom and pointing towards the Nitrogen



It is (now) straightforward to obtain $\Gamma_\sigma = A_1' \oplus E'$

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Starting from the observation

$$\Pi_\sigma = \begin{Bmatrix} E & 2C_3 & 3C_2' & \sigma_h & 2S_3 & 3\sigma_v \\ 3 & 0 & 1 & 3 & 0 & 1 \end{Bmatrix}$$

and the character table

| $D_{3h}$ | $E$ | $2C_3$ | $3C_2'$ | $\sigma_h$ | $2S_3$ | $3\sigma_v$ | |
|---|---|---|---|---|---|---|---|
| $A_1'$ | 1 | 1 | 1 | 1 | 1 | 1 | $x^2+y^2, z^2$ |
| $A_2'$ | 1 | 1 | -1 | 1 | 1 | -1 | $R_z$ |
| $E'$ | 2 | -1 | 0 | 2 | -1 | 0 | $(x,y), (xy, x^2-y^2)$ |
| $A_1''$ | 1 | 1 | 1 | -1 | -1 | -1 | |
| $A_2''$ | 1 | 1 | -1 | -1 | -1 | 1 | $z$ |
| $E''$ | 2 | -1 | 0 | -2 | 1 | 0 | $(R_x, R_y) (yz, zx)$ |

Using the projector operator technique we also obtain, for the ligand
orbitals (=linear combination of the $\sigma$ orbitals)

$$\psi(A_1'| = N(A_1')\left[\sigma_1 + (\sigma_2+\sigma_3) + (\sigma_1 + \sigma_3 + \sigma_2) + (\sigma_1| + (\sigma_2+\sigma_3) + (\sigma_1+\sigma_3+\sigma_2)\right]$$

$$a_1' = \frac{1}{\sqrt{3}}\left[\sigma_1 + \sigma_2 + \sigma_3\right]$$

An MO for $NO_3^-$ is now found as a linear superposition of a $A_1'$ state
of the central atom (s) and the $a_1'$ of the oxigens

$$\psi_1 = s + b_1\, a_1'$$

$b_1 > 0$ is a bonding state $b_1 < 0$ antibonding state. The value of
$b_1$ depend on the on-site and hopping parameters. Notice though that
it results from solving a 2x2 secular problem.

$$\psi_1(E'| = N_1(E')\left[2(\sigma_1| -1(\sigma_2+\sigma_3) + 2(\sigma_1| - 1(\sigma_2+\sigma_3)\right]$$

$$= \frac{1}{\sqrt{6}}\left[2\sigma_1 - (\sigma_2+\sigma_3)\right]$$

Starting with $\sigma_2$ or $\sigma_3$ seeds I obtain 2 other basis vectors for $E'$

$$\psi_2(E') = \frac{1}{\sqrt{6}}\left[2\sigma_2 - (\sigma_3 + \sigma_1)\right]$$

$$\psi_3(E') = \frac{1}{\sqrt{6}}\left[2\sigma_3 - (\sigma_1 + \sigma_2)\right]$$

$\psi_1$, $\psi_2$, $\psi_3$ are NOT linearly independent $\psi_3 = -\psi_1 - \psi_2$. A useful basis is one that has finite overlap with $p_x$ and $p_y$ on the Nitrogen. The character table is infact stating that $(x,y)$ is a good basis for $E'$.

$$e_1' = \frac{1}{\sqrt{6}}\left[2\sigma_1 - (\sigma_2 + \sigma_3)\right] \qquad \left\{\begin{array}{l}\text{overlaps with } p_x \\ \perp \text{ to } p_y\end{array}\right.$$

$$e_2' = \frac{1}{\sqrt{2}}\left[\sigma_2 - \sigma_3\right] = N(\psi_2 - \psi_3) \qquad \left\{\begin{array}{l}\text{overlaps with } p_y \\ \perp \text{ to } p_x\end{array}\right.$$

$$\psi_2 = p_x + b_2\, e_1'$$
$$\psi_3 = p_y + b_3\, e_2'$$

complete the basis set for $A_1'$ and $E'$.

Somehow the answer is unsatisfactory since the 3 bonds are treated asymmetrically. In order to find equivalent bond orbitals on the metal, let us first summarize the previous results in a matrix form:

$$\langle \psi_1\, \psi_2\, \psi_3 | = \langle s\, p_x\, p_y | + \langle a_1'\, e_1'\, e_2' |\, B$$

$$B = \begin{bmatrix} b_1 & 0 & 0 \\ 0 & b_2 & 0 \\ 0 & 0 & b_3 \end{bmatrix}$$

The ligand linear combination of atomic orbitals (LCAO) reads:

$$\langle a_1'\, e_1'\, e_2' | = \langle \sigma_1\, \sigma_2\, \sigma_3 |\, M$$

where

$$M = \begin{bmatrix} 1/\sqrt{3} & 2/\sqrt{6} & 0 \\ 1/\sqrt{3} & -1/\sqrt{6} & 1/\sqrt{2} \\ 1/\sqrt{3} & -1/\sqrt{6} & -1/\sqrt{2} \end{bmatrix}$$

We can thus write ( remembering $[B,M] = 0$ )

$$\langle \psi_1 \, \psi_2 \, \psi_3 | = \langle s \, p_x \, p_y | + \langle \sigma_1 \, \sigma_2 \, \sigma_3 | B M$$

Now we multiply from the right with $M^{-1} = M^T$

$$\langle \psi_1' \, \psi_2' \, \psi_3' | = \langle \psi_1 \, \psi_2 \, \psi_3 | M^{-1} = \langle s \, p_x \, p_y | M^{-1} + \langle \sigma_1 \, \sigma_2 \, \sigma_3 | B$$

The $sp^2$ hybrid nitrogen AOs are

$$\langle h_1 \, h_2 \, h_3 | = \langle s \, p_x \, p_y | M^T = \langle s \, p_x \, p_y | \begin{bmatrix} 1/\sqrt{3} & 1/\sqrt{3} & 1/\sqrt{3} \\ 2/\sqrt{6} & -1/\sqrt{6} & -1/\sqrt{6} \\ 0 & 1/\sqrt{3} & -1/\sqrt{2} \end{bmatrix}$$

Notice that $h_1 \, h_2 \, h_3$ is a good orthogonal basis for the central atom N since it is obtained as a unitary transformation of an orthogonal set of vectors.
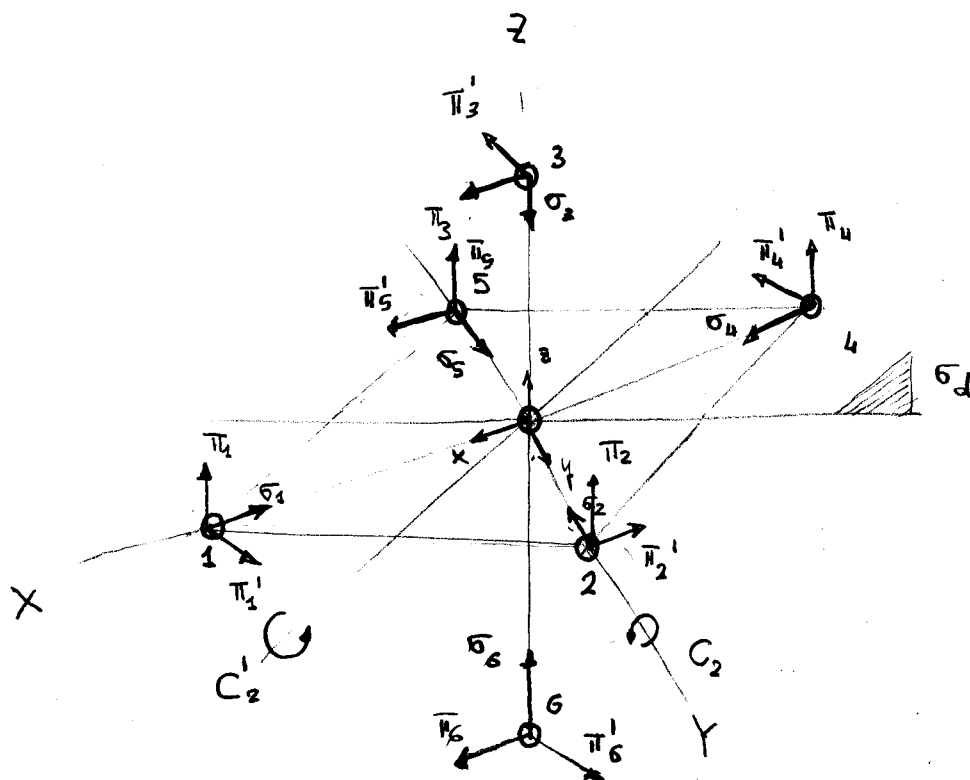
# 5.4 Transition metal complexes

Let us consider a metal-ligand complex in the form $ML_6$ where M stands for metal and L for ligand. Let us count first the atomic orbitals in the game:

$$M: \quad 5 \times nd + 1 \times (n+1)s + 3 \times (n+1)p \quad = \quad 9 \; AO \quad +$$

$$L: \quad 3 \times p \text{ for each ligand atom} \quad = \quad 18 \; AO$$

(C, N, O in the ligand use mainly $p$ states to form bonding)

$$\underline{\phantom{xxxxxxxx}} \\ 27 \text{ orbitals.}$$

The number is already large enough to require a systematic analysis



In the figure we have associated a set of R-oriented cartesian axes to each atom involved in the metal-ligand complex. $xyz$ for the Metal $\sigma_i \pi_i \pi_i'$ for the ligand atoms. Conventionally $\sigma_i$ points towards the metal atom.
The point group of this system of 7 atoms is $O_h = O \otimes C_i$

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Let us list the classes:

$$O_h = \{ \underbrace{E, \; 3C_2, \; 8C_3 \; 6C_4 \; 6C_2'}_{\{O\}} \; | \; \underbrace{I \; 3\sigma_h \; 8S_6 \; 6S_4 \; 6\sigma_d}_{I\{O\}} \}$$

$O$ is the group of transformations that bring a cube (or an octahedron) into itself.

Definitely, metal orbitals go to metal orbitals under transformations belonging to $O_h$. Moreover $s \to s$, $d \to d$ and $p \to p$. The character system.

$(n+1)s$ forms a $A_{1g}$ representation of $O_h$

In order to find the irreducible representations associated to the $\Gamma_d$ and $\Gamma_p$ of the metal.

i) Consider the 5 classes of $\{O\}$. Take one representative per class:

| $T =$ | $E$ | $R(\pi z)$ | $R(\phi \vec{n})$ | $R(\beta z)$ | $R(\pi a)$ | $\phi = \frac{2\pi}{3}$ |
|---|---|---|---|---|---|---|
| $T^{-1}(xyz) =$ | $xyz$ | $\bar{x}\bar{y}z$ | $yzx$ | $y\bar{x}z$ | $yx\bar{z}$ | $n = \frac{1}{\sqrt{3}}(1\,1\,1)$ |

$$\beta = \overline{\pi}/2$$
$$a = \frac{1}{\sqrt{2}}(1\,1\,0)$$

$$\Gamma_p = \{3, -1, 0, 1, -1, -3, 1, 0, -1, 1\}$$

The set of transformations for $xyz$ listed above are also called Jones symbols for the group. We deduce that for the basis functions

| | | | | | |
|---|---|---|---|---|---|
| $xy$ | $xy$ | $yz$ | $-xy$ | $xy$ | ... repeat; gerade |
| $yz$ | $-yz$ | $zx$ | $-zx$ | $-zx$ | ... repeat; gerade |
| $zx$ | $-zx$ | $xy$ | $yz$ | $-yz$ | ... repeat; gerade |

$$\Gamma_{d\varepsilon} = \{3, -1, 0, -1, 1, 3, -1, 0, -1, 1\}$$

Analogously for the remaining d orbitals of the metal

|  | E | $R(\pi z)$ | $R(\phi\vec{n})$ | $R(\beta z)$ | $R(\pi a)$ | |
|---|---|---|---|---|---|---|
| $x^2-y^2$ | $x^2-y^2$ | $x^2-y^2$ | $y^2-z^2$ | $-(x^2-y^2)$ | $-(x^2-y^2)$ | repeat: gerade! |
| $3z^2-r^2$ | $3z^2-r^2$ | $3z^2-r^2$ | $3x^2-r^2$ | $3z^2-r^2$ | $3z^2-r^2$ | |

$$\Gamma_{d\gamma} = \{2, 2, \underline{-1}, 0, 0, 2, 2, \underline{-1}, 0, 0\}$$

A special comment for these $-1$. At first glance $y^2-z^2 \neq x^2-y^2$ and $3x^2-r^2$
$\neq 3z^2-r^2$ but :

$$y^2-z^2 = a(x^2-y^2) + b(3z^2-r^2) = (a-b)x^2 - (a+b)y^2 + 2bz^2$$

$2x^2-y^2-z^2 \quad = 3x^2-r^2 = c(x^2-y^2) + d(3z^2-r^2) = (c-d)x^2 - (c+d)y^2 + 2dz^2$

$$a=b \qquad 2b=-1 \qquad a+b=-1 \qquad \Rightarrow \quad a=b=-\tfrac{1}{2}$$

$$c-d=2 \qquad c+d=1 \qquad 2d=-1 \qquad \Rightarrow \quad d=-\tfrac{1}{2} \quad c=\tfrac{3}{2}$$

$$\begin{pmatrix} y^2-z^2 \\ 3x^2-r^2 \end{pmatrix} = \begin{pmatrix} -\tfrac{1}{2} & -\tfrac{1}{2} \\ \tfrac{3}{2} & -\tfrac{1}{2} \end{pmatrix} \begin{pmatrix} x^2-y^2 \\ 3z^2-r^2 \end{pmatrix} \Rightarrow \overset{\Gamma_{d\gamma}}{\chi(R\phi\vec{n})} = -1$$

The ligand atomic orbitals can also be classified. It is clear that $\sigma$ and $\pi$ states cannot be mixed. By counting how many orbitals are **NOT** modified by the transformation

$$\Gamma_\sigma = \{6, 2, 0, 2, 0, 0, 4, 0, 0, 2\}$$

$$\Gamma_\pi = \{\overset{E}{12}, \overset{C_2}{-4}\}$$

Notice that both $\Gamma_\sigma$ and $\Gamma_\pi$ are neither gerade nor ungerade: they are reducible !

By comparison with the character table for $O_h$:

$$\Gamma_s = A_{1g} \quad , \quad \Gamma_p = T_{1u} \qquad \Gamma_d = \Gamma_{d\varepsilon} \oplus \Gamma_{d\gamma} = T_{2g} \oplus E_g$$

The $\Gamma_\sigma$ and $\Gamma_\pi$ can be reduced by means of the reduction formula, one obtains:

$$\Gamma_\sigma = A_{1g} \oplus E_g \oplus T_{1u}$$

$$\Gamma_\pi = T_{1g} \oplus T_{2g} \oplus T_{1u} + T_{2u}$$

Now we have to determine the bonding ( molecular orbitals ) involving metal and ligand.



| | | M | | L | |
|---|---|---|---|---|---|
| $(n+1)s$ | 1 | $A_{1g}$ | | $A_{1g}$ } $\sigma$ | 6 |
| $(n+1)p$ | 3 | $T_{1u}$ | | $E_g$ / $T_{1u}$ | |
| $(xy, yz, xz)$ $nd$ | 3 | $T_{2g}$ | | $\boxed{T_{1g}}$ → non-bonding | |
| $(x^2-y^2, 3z^2-r^2)$ $nd$ | 2 | $E_g$ | | $T_{2g}$ } $\pi$ / $T_{1u}$ | 12 |
| | | | | $\boxed{T_{2u}}$ → non-bonding | |

## $\sigma$ bonding

First the ligand states:

$$\psi(A_{1g}) = \sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6$$
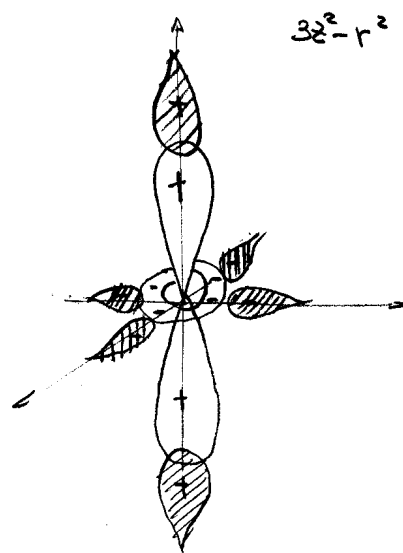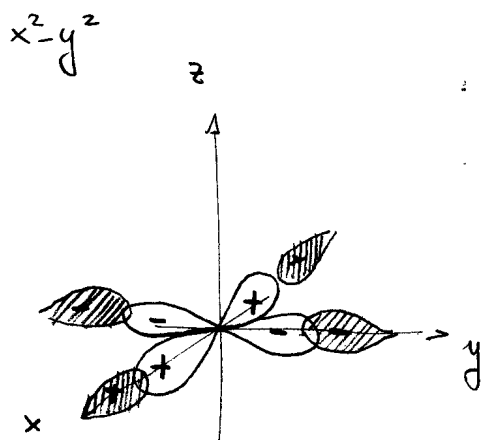
$$\psi_1(E_g) = 2\sigma_1 - \sigma_2 - \sigma_3 + 2\sigma_4 - \sigma_5 - \sigma_6 \quad = \quad \hat{P}^{E_g}(\sigma_1)$$

$$\psi_2(E_g) = 2\sigma_2 - \sigma_3 - \sigma_4 + 2\sigma_5 - \sigma_6 - \sigma_1 \quad = \quad \hat{P}^{E_g}(\sigma_2) \qquad \text{cyclic permutation!}$$

$$\psi_3(E_g) = 2\sigma_3 - \sigma_4 - \sigma_5 + 2\sigma_4 - \sigma_1 - \sigma_2 \quad = \quad \hat{P}^{E_g}(\sigma_3)$$

Let us remember the form of the $E_g$ orbitals on the metal:

$x^2-y^2$

$3z^2-r^2$



$x=y$ is a nodal plane
$x=-y$

$$\psi_1(E_g) - \psi_2(E_g) = \sigma_1 - \sigma_2 + \sigma_4 - \sigma_5$$

$$\psi_3(E_g) = 2\sigma_3 - \sigma_4 - \sigma_2 + 2\sigma_6 - \sigma_1 - \sigma_2$$

Now we turn to the 3 dimensional irreducible representation $T_{1u}$

$$\hat{P}^{T_{1u}}(\sigma_1) = \sigma_1 - \sigma_4 = \sum_{i=1}^{6} (\vec{R_i})_x \sigma_i$$

The other 2 orbitals are readily obtained as $\sum_{i=1}^{6}(\vec{R_i})_y \sigma_i$ and $\sum_{i=1}^{6}(\vec{R_i})_z \sigma_i$ when $\vec{R_i}$ indicates the atomic position.

$$\psi_1(T_{1u}) = \sigma_1 - \sigma_4$$

$$\psi_2(T_{1u}) = \sigma_2 - \sigma_5$$

$$\psi_2(T_{1u}) = \sigma_3 - \sigma_6$$

The $\sigma$ bonded MOs:

$$a_{1g} = a_1[(n+1)s] + b_1[\sigma_1+\sigma_2+\sigma_3+\sigma_4+\sigma_5+\sigma_6]$$

$$e_g = a_2[n d_{x^2-y^2}] + b_2[\sigma_1-\sigma_2+\sigma_4-\sigma_5]$$

$$e_g' = a_3[n d_{3z^2-r^2}] + b_3[2\sigma_3 + 2\sigma_6 - \sigma_1 - \sigma_2 - \sigma_4 - \sigma_5]$$

$$t_{1u} = a_4[(n+1)p_x] + b_4[\sigma_1-\sigma_4]$$

$$''t_{1u} = a_6[(n+1)p_z] + b_6[\sigma_3-\sigma_6]$$

$$'t_{1u} = a_5[(n+1)p_y] + b_5[\sigma_2-\sigma_5]$$

# $\pi$ bonding

Let us start with the $\boxed{T_{1u}}$ irreducible representation

$$\psi_1 (T_{1u}) = \bar{\pi}_1 + \bar{\pi}_2 + \bar{\pi}_4 + \bar{\pi}_z = \bar{\pi}_z$$

The 4 orbitals are symmetrically disposed around the $z$ axis, but $x, y$ and $z$ axes are equivalent

$$\psi_2 (T_{1u}) = -\bar{\pi}_2' + \bar{\pi}_3 + \bar{\pi}_5' + \bar{\pi}_6 = \pi_x$$

$$\psi_3 (T_{1u}) = \bar{\pi}_1' + \bar{\pi}_6' - \bar{\pi}_4' - \bar{\pi}_3' = \pi_y$$

$\Rightarrow$ the associated molecular orbitals:

$$t_{1u,x} = a_7 [(n+1)p_x] + b_7 \pi_x$$

$$t_{1u,y} = a_8 [(n+1)p_y] + b_8 \pi_y$$

$$t_{1u,z} = a_9 [(n+1)p_z] + b_9 \pi_z$$

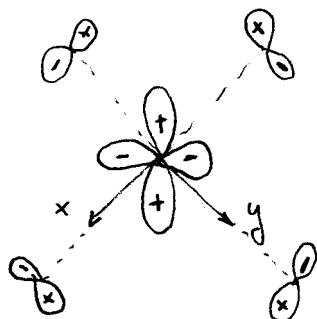Similarly, for the $\boxed{T_{2g}}$ using the projection operator technique

$$\psi_1 (T_{2g}) - \bar{\pi}_1 - \pi_4 + \pi_3 - \bar{\pi}_6 = \bar{\pi}_{zx} \quad (xz \text{ plane})$$

By inspection we can construct an orbital transforming as $xy$ $yz$

$$\psi_2 (T_{2g}) = \bar{\pi}_1' - \bar{\pi}_2' + \bar{\pi}_4' - \pi_5' = \bar{\pi}_{xy} \quad (xy \text{ plane})$$

$$\psi_3 (T_{2g}) = \pi_2 - \bar{\pi}_3' - \pi_5 - \bar{\pi}_6' = \bar{\pi}_{yz} \quad (yz \text{ plane})$$

Example



orbital $\pi_{xy}$ and $d_{xy}$.

The associated molecular orbitals:

$$t_{2g,xy} = a_{10}[nd_{xy}] + b_{10}\pi_{xy}$$

$$t_{2g,yz} = a_{11}[nd_{yz}] + b_{11}\pi_{yz}$$

$$t_{2g,xz} = a_{12}[nd_{xz}] + b_{12}\pi_{xz}$$

There are not atomic orbitals transforming as $\boxed{T_{1g}}$ => the associated orbitals are NON-BONDING

$$t_{1gx} = \frac{1}{2}\left[\pi_2 + \pi_3' - \pi_5 + \pi_6'\right]$$

$$t_{1g,y} = \frac{1}{2}\left[\pi_1 - \pi_3 - \pi_4 + \pi_6\right] \quad \leftarrow \text{ directly from } T_{1g} = \{3,-1,0,1,-1\}$$

$$t_{1g,z} = \frac{1}{2}\left[\pi_1' + \pi_2' + \pi_4' + \pi_5'\right] \quad \text{as} \quad \hat{P}^{T_{1g}}(\pi_1).$$

Analogously for the $\boxed{T_{2u}}$ which are also NON-bonding.

$$t_{2u,x} = \frac{1}{2}\left[\pi_2' + \pi_3 - \pi_5' + \pi_6\right]$$

$$t_{2u,y} = \frac{1}{2}\left[\pi_4' - \pi_6' - \pi_4' - \pi_3'\right]$$

$$t_{2u,z} = \frac{1}{2}\left[\pi_1 - \pi_2 + \pi_4 - \pi_5\right] \quad \leftarrow \text{ directly from } \hat{P}^{T_{2u}}(\pi_1)$$

Using group theory we could break down the original $27 \times 27$ hamiltonian defining the secular equation into set of $2\times2$ matrices or $1\times1$ in the case of the non bonding and $3\times3$ for the $T_{1u}$ symmetry which involves both $\sigma$ and $\pi$ bonding.