

5. Electronic states of molecules

5.1 Chemical bond

A molecule is formed when 2 or more atoms bind together i.e. the total energy of the composite system is lower than the one of all its constituents.

The study of the electronic density between two atomic centers allows for a classification of the bond.

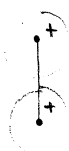
Def: BOND is the vector connecting the center of two atoms in a molecule whose distance strongly influence the total energy of the molecule.

Def: NODAL PLANE is the plane tangent to the portion of isosurface $|\psi_e(x)|^2 = 0$ intersecting the bond.

Depending on the number and position of the nodal planes in the electron density around the bond one distinguishes several types of bonds:

* σ bond: no nodal planes in the charge density containing the bond connecting the 2 atoms.

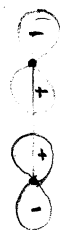
examples of σ bonds:



ss σ bond



sp σ bond



pp σ bond

A σ bond can be formed starting from different type of atomic orbitals. Similarly to the cases illustrated above also sd, sf, pd, pf, dd, df and ff σ bonds can be formed

* π bond: 1 nodal plane in the charge density containing the bond connecting the 2 bonded atoms.

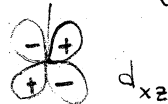
examples



pp π bond



dp π bond



pp df π bonds are also possible

* δ bond: 2 nodal planes in the charge density containing the bond. dd δ bond and df δ bonds are possible.

* φ bond: 3 nodal planes in the charge density containing the bond. Only ff φ bonds are possible.

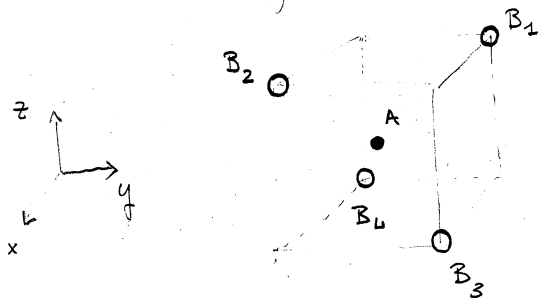
* finally one speaks of antibonding in presence of a nodal plane \perp to the bond between the 2 atoms.

5.2 Hybridization

In the examples associated to the bond classification we have used the atomic orbitals. Not always this description is the most closed to reality. One introduces the concept of hybridization:

DEF HYBRIDIZATION is the mixing of atomic orbitals of different angular momentum in order to obtain equivalent orbitals which respect the symmetry of the molecule.

EXAMPLE σ bonding of tetrahedral AB_4 molecule



$$\vec{R}_A = (0, 0, 0)$$

$$\vec{R}_{B_1} = (-a, a, a)$$

$$\vec{R}_{B_2} = (a, -a, a)$$

$$\vec{R}_{B_3} = (a, a, -a)$$

$$\vec{R}_{B_4} = (-a, -a, -a)$$

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

$h = 24$	T_d	E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$	
	A_1	1	1	1	1	1	$x^2+y^2+z^2$
	A_2	1	1	1	-1	-1	
	E	2	-1	2	0	0	$(x^2-y^2, 3z^2-r^2)$
	T_1	3	0	-1	-1	1	
	T_2	3	0	-1	1	-1	$(x, y, z) (xy, yz, zx)$

The 4 σ -bonds are equivalent \Rightarrow their representation is the same as the one of 4 s orbitals located at the position of the 4 B atoms. We call this representation Γ_σ . The characters of the Γ_σ are easily determined by counting how many s orbitals remain invariant under application of the symmetry operator \hat{R} ,

$$\chi^{\Gamma_\sigma}(E) = 4 \quad \chi^{\Gamma_\sigma}(C_3) = 1 \quad \chi^{\Gamma_\sigma}(C_2) = 0 \quad \chi^{\Gamma_\sigma}(\sigma_d) = 2 \quad \chi^{\Gamma_\sigma}(S_4) = 0$$

By application of the reduction formula we obtain:

$$\alpha_{A_1} = \frac{1}{24} (1 \cdot 1 \cdot 4 + 8 \cdot 1 \cdot 1 + 6 \cdot 1 \cdot 2) = 1$$

$$\alpha_{A_2} = \frac{1}{24} (1 \cdot 1 \cdot 4 + 8 \cdot 1 \cdot 1 + 6 \cdot (-1) \cdot 2) = 0$$

$$\alpha_E = \frac{1}{24} (1 \cdot 2 \cdot 4 + 8 \cdot (-1) \cdot 1 + 6 \cdot 0 \cdot 2) = 0$$

$$\alpha_{T_1} = \frac{1}{24} (1 \cdot 3 \cdot 4 + 8 \cdot 0 \cdot 1 + 6 \cdot (-1) \cdot 2) = 0$$

$$\alpha_{T_2} = \frac{1}{24} (1 \cdot 3 \cdot 4 + 8 \cdot 0 \cdot 1 + 6 \cdot 1 \cdot 2) = 1$$

$\Rightarrow \Gamma_\sigma = A_1 \oplus T_2$. The s orbital on A is a basis for the A_1 irrep and a good basis for T_2 is given by (x, y, z) or (xy, yz, zx) i.e. by p orbitals or the mentioned d orbitals. Possible hybridizations are thus sp^3 or sd^3 .

In general a molecular orbital ψ_{MO} would involve linear combination of s, p_x, p_y, p_z and d_{xy}, d_{yz}, d_{zx} atomic orbitals.

Some coefficients, though can be extremely small. Criterion:

- the energy gain by bond formation must exceed
- the energy loss by atomic excitation

- => 1 * minimize atomic excitation
- 2 * maximize overlap with bonding atoms

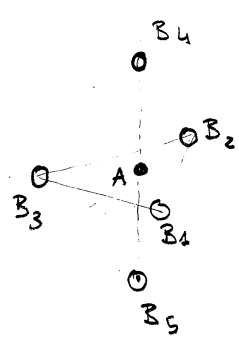
Example:

C: ground state: $[\text{He}]2s^2 2p^2$ $E_{3d} - E_{2p} \approx 10 \text{ eV} \Rightarrow sp^3$ dominates

Mn: $[\text{Ar}]3d^5 4s^2 \Rightarrow sd^3$ is the most favorable hybridization

Cr: $[\text{Ar}]3d^5 4s^1$

Let's consider another example, the molecule AB_5



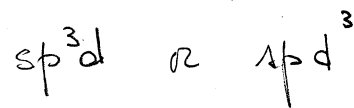
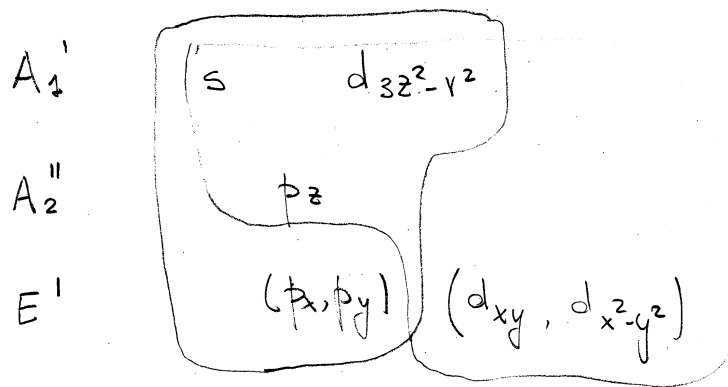
The point group of this molecule is D_{3h} with character table:

D_{3h}	E	$2C_3$	$3C_2'$	σ_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	
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	(yz, zx)

Using the same approach app' for the previous case we obtain

$$\Gamma_5: \{ 5 \ 2 \ 1 \ 3 \ 0 \ 3 \} \Rightarrow \Gamma_5 = 2A_1' \oplus A_2'' \oplus E'$$

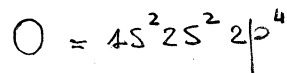
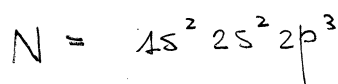
By checking in the character table we obtain the possible hybridizations which generate the same representation.



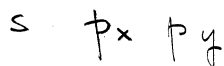
Summarizing: GT gives the possible hybridizations. The atomic and bonding energies involved decide for the specific one.

5.3 Equivalent bond orbitals

In the previous section we introduced the hybridization at a qualitative level. Now we consider a concrete example for which we calculate explicitly the sp^2 hybrid equivalent bond orbitals by means of group theory. We want to construct the σ bond structure of the ion NO_3^- . The molecule is planar and belongs to the D_{3h} group.



The σ bond involves all orbitals which do not show a nodal plane in the plane of the molecule, thus according to the character table and the ground state atomic configurations.



Let's first calculate the representation of the oxygen atoms

$$\Gamma^{a,s} \otimes (A_1' \oplus E')$$

$\Gamma^{a,s}$ is the atomic site representation which is the one generated by the s orbitals located at the position of the atoms

$$\Gamma^{a,s} = \{ 3 \ 0 \ 1 \ 3 \ 0 \ 1 \} = A_1' \oplus E'$$

$$(A_1' \oplus E') \otimes (A_2' \oplus E') = A_1' \oplus 2E' \oplus (E' \otimes E')$$

$$E' \otimes E' = \{ 4 \ 4 \ 0 \ 4 \ 1 \ 0 \} = A_1' \oplus A_2' \oplus E'$$

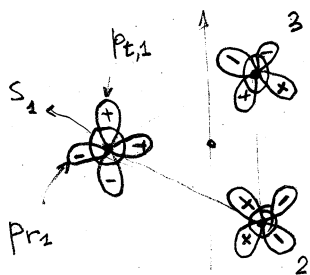
The 9 orbitals of the σ system associated to the 3 oxygen atoms are organized in the irrep:

$$\Gamma_\sigma = 2A_1' \oplus A_2' \oplus 3E'$$

By inspecting the basis functions we see that by no means neither the p nor the d orbitals are partners of the A_2' irrep which forms thus a non-bonding orbital only located on the oxygens.

Let's construct a basis for Γ_σ . For simplicity we start from the atomic basis

$$s_i \quad p_{xi} \quad p_{yi}$$



$$\hat{P}^{A_1'}(p_{x1}) = p_{x1} + (p_{x2} + p_{x3}) + (p_{x1} + p_{x2} + p_{x3}) + p_{x1} + (p_{x2} + p_{x3}) + (p_{x2} + p_{x2} + p_{x3}) \propto p_{x1} + p_{x2} + p_{x3}$$

$$\hat{P}^{A_1'}(s_1) = 4(s_1 + s_2 + s_3)$$

$$\hat{P}^{A_2'}(p_{t1}) = p_{t1} + (p_{t2} + p_{t3}) + (-p_{t1} - p_{t2} - p_{t3}) + p_{t1} + (p_{t2} + p_{t3}) + (-p_{t1} - p_{t2} - p_{t3}) = 0$$

$$\hat{P}^{A_2'}(p_{t1}) = 4(p_{t2} + p_{t2} + p_{t3}) \leftarrow \text{non-bonding orbital.}$$

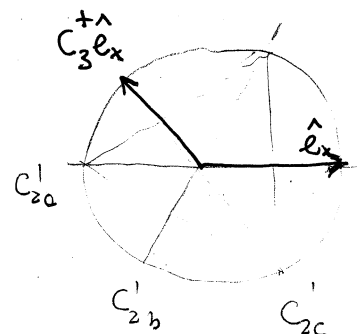
Now we are left with the construction of the partners of the $3E'$ imp. By checking the character table we see that (x, y) is a good basis set for E' . We start constructing the diagonal elements of the 12 matrix representatives:

$$E = \begin{pmatrix} 1 & \\ & 1 \end{pmatrix} \quad C_3 = \begin{pmatrix} -\frac{1}{2} & \\ & -\frac{1}{2} \end{pmatrix} \quad C_3^- = \begin{pmatrix} -\frac{1}{2} & \\ & -\frac{1}{2} \end{pmatrix}$$

$$C_{2a} = \begin{pmatrix} 1 & \\ & -1 \end{pmatrix} \quad C_{2b} = \begin{pmatrix} -\frac{1}{2} & \\ & \frac{1}{2} \end{pmatrix} \quad C_{2c} = \begin{pmatrix} -\frac{1}{2} & \\ & \frac{1}{2} \end{pmatrix}$$

$$\sigma_h = \begin{pmatrix} 1 & \\ & 1 \end{pmatrix} \quad S_3^+ = \begin{pmatrix} -\frac{1}{2} & \\ & -\frac{1}{2} \end{pmatrix} \quad S_3^- = \begin{pmatrix} -\frac{1}{2} & \\ & -\frac{1}{2} \end{pmatrix}$$

$$\sigma_{va} = \begin{pmatrix} 1 & \\ & -1 \end{pmatrix} \quad \sigma_{vb} = \begin{pmatrix} -\frac{1}{2} & \\ & \frac{1}{2} \end{pmatrix} \quad \sigma_{vc} = \begin{pmatrix} -\frac{1}{2} & \\ & \frac{1}{2} \end{pmatrix}$$



The results above stem from geometrical considerations as exemplified given above for the transformation of the \hat{e}_x into $C_3^+ \hat{e}_x = -\frac{1}{2} \hat{e}_x + \frac{\sqrt{3}}{2} \hat{e}_y$.

$$\hat{P}_{xx}^{E'}(s_1) = 2 \left[s_1 - \frac{1}{2}(s_2 + s_3) + s_1 - \frac{1}{2}(s_2 + s_3) \right] = 4 \left(s_1 - \frac{1}{2}(s_2 + s_3) \right)$$

$$\hat{P}_{yy}^{E'}(s_1) = 2 \left[s_1 - \frac{1}{2}(s_2 + s_3) - s_1 + \frac{1}{2}(s_2 + s_3) \right] = 0$$

$$\hat{P}_{yy}^{E'}(s_2) = 2 \left[s_2 - \frac{1}{2}(s_3 + s_1) - s_3 + \frac{1}{2}(s_1 + s_2) \right] = 3(s_2 - s_3)$$

With normalization: $e'_{x,s} = -\frac{1}{\sqrt{6}}(2s_1 - (s_2 + s_3))$

$$e'_{y,s} = -\frac{1}{\sqrt{2}}(s_2 - s_3)$$

In the same way one constructs the e' partners generated by the primitive orbitals:

$$e'_{x,pr} = \frac{1}{\sqrt{6}}(2p_{r1} - (p_{r2} + p_{r3}))$$

$$e'_{y,pr} = \frac{1}{\sqrt{2}}(p_{r2} - p_{r3})$$

We come now to the Laplacian components:

$$\hat{P}_{xx}^{E'}(\phi_{t1}) = 2 \left[\phi_{t1} - \frac{1}{2}(\phi_{t2} + \phi_{t3}) + (-\phi_{t1}) - \frac{1}{2}(-\phi_{t2} - \phi_{t3}) \right] = 0$$

$$\hat{P}_{xx}^{E'}(\phi_{t2}) = 2 \left[\phi_{t2} - \frac{1}{2}(\phi_{t3} + \phi_{t1}) - \phi_{t3} - \frac{1}{2}(-\phi_{t1} - \phi_{t2}) \right] = 3(\phi_{t2} - \phi_{t3})$$

$$\hat{P}_{yy}^{E'}(\phi_{t1}) = 2 \left[\phi_{t1} - \frac{1}{2}(\phi_{t2} + \phi_{t3}) - (-\phi_{t1}) + \frac{1}{2}(-\phi_{t2} - \phi_{t3}) \right] = 2(2\phi_{t1} - (\phi_{t2} + \phi_{t3}))$$

$$e'_{x,pt} = -\frac{1}{\sqrt{2}}(\phi_{t2} - \phi_{t3})$$

$$e'_{y,pt} = \frac{1}{\sqrt{6}}(2\phi_{t1} - \phi_{t2} - \phi_{t3})$$

Clearly the ϕ_t orbitals contribute to the π bond of the oxygens with the nitrogen. We thus concentrate from now on on the basis $(e'_{x,s}, e'_{y,s})$ and $(e'_{x,pr}, e'_{y,pr})$, together with $a'_{s,s}$ and $a'_{s,pr}$.

A molecular orbital for NO_3^- contributing to the σ bonds between N and O can generically be written as:

$$\psi_1 = s + b_s (a'_{s,s} + \alpha a'_{s,pr}) \frac{1}{\sqrt{1+\alpha^2}}$$

Analogously for the x and y components of the E' irrep:

$$\psi_2 = \phi_x + b_p (e'_{x,s} + \alpha e'_{x,pr}) \frac{1}{\sqrt{1+\alpha^2}}$$

$$\psi_3 = \phi_y + b_p (e'_{y,s} + \alpha e'_{y,pr}) \frac{1}{\sqrt{1+\alpha^2}}$$

To simplify the notation we can introduce $\sigma_i = (s_i + \alpha p_{r,i}) \frac{1}{\sqrt{1+\alpha^2}}$ and

$$\begin{pmatrix} a'_{s,s} \\ e'_{x,s} \\ e'_{y,s} \end{pmatrix} = M \begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \end{pmatrix}$$

where

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

We can thus write

$$\begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \end{pmatrix} = \begin{pmatrix} s \\ p_x \\ p_y \end{pmatrix} + BM \begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \end{pmatrix}$$

The equation above can be rewritten as:

$$\begin{pmatrix} \psi_1 \\ \psi_2 \\ \psi_3 \end{pmatrix} = \underbrace{MM^T}_{h_i} \begin{pmatrix} s \\ p_x \\ p_y \end{pmatrix} + BM \begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \end{pmatrix}$$

By construction the orbitals h_i will transform as σ_i since $M \begin{pmatrix} h_1 \\ h_2 \\ h_3 \end{pmatrix}$ is a basis for the same irrep's as $M \begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \end{pmatrix}$.

The sp^2 hybrid orbitals thus read:

$$h_1 = \frac{1}{\sqrt{3}} s - \frac{2}{\sqrt{6}} p_x$$

$$h_2 = \frac{1}{\sqrt{3}} s + \frac{1}{\sqrt{6}} p_x - \frac{1}{\sqrt{2}} p_y$$

$$h_3 = \frac{1}{\sqrt{3}} s + \frac{1}{\sqrt{6}} p_x + \frac{1}{\sqrt{2}} p_y$$

5.4 Conjugated π electrons

The molecular orbitals extend over many atoms. They are expressed as linear combination of atomic orbitals. Exemplarily let's consider a benzene molecule whose point group is $D_{6h} = D_6 \otimes C_i$. The classes of $D_6 = \{E, 2C_6, 2C_3, C_2, 3C_2', 3C_2''\}$. The classes of D_{6h} can be found simply multiplying the class representative of D_6 by the inversion symmetry i .

We consider sp^2 orbital per carbon atom we obtain the character set:

$$\chi^{\Gamma_{\pi}} = \left\{ \begin{array}{cccccccccccc} E & 2C_6 & 2C_3 & C_2 & 3C_2' & 3C_2'' & I & 2S_6 & 2S_6 & \sigma_h & 3\sigma_d & 3\sigma_v \\ 6 & 0 & 0 & 0 & -2 & 0 & 0 & 0 & 0 & -6 & 0 & 2 \end{array} \right\}$$

The application of the reduction formula produces:

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

Exemplarily we calculate the basis function associated to the irrep B_{2g}

$$B \leftrightarrow \chi(C_6) = -1 \quad "2" \leftrightarrow \chi(C_2) = -1 \quad g \leftrightarrow \chi(i) = 1$$

$$B_{2g} = \left\{ \begin{array}{cccccc|cccc} E & 2C_6 & 2C_3 & C_2 & 3C_2' & 3C_2'' & i & 2S_3 & 2S_6 & \sigma_h & 3\sigma_d & 3\sigma_v \end{array} \right\}$$

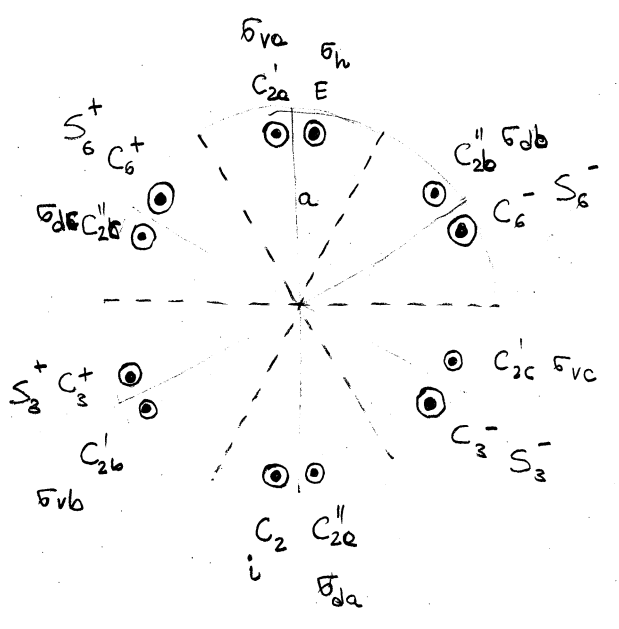
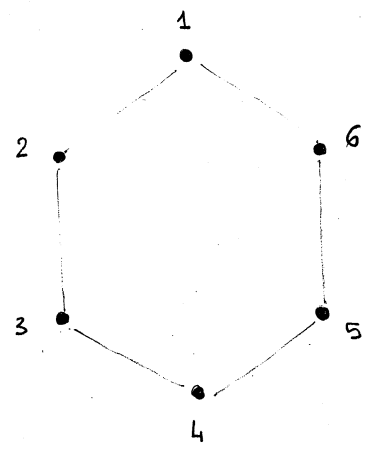
$$= \left\{ \begin{array}{cccccc|cccc} 1 & -1 & 1 & -1 & -1 & 1 & 1 & -1 & 1 & -1 & -1 & 1 \end{array} \right\}$$

$$\hat{P}^{B_{2g}}(\phi_1) = \left[\begin{array}{cccccccc} E & C_6^+ & C_6^- & C_3^+ & C_3^- & C_2 & C_{2a}' & C_{2b}' & C_{2c}' \\ \phi_1 & -1(\phi_2 + \phi_6) & +(\phi_3 + \phi_5) & -\phi_4 & -1(-\phi_1 - \phi_3 - \phi_5) \\ C_{2a}'' & C_{2b}'' & C_{2c}'' & i & S_3^+ & S_3^- & S_6^+ & S_6^- \\ +1(-\phi_4 - \phi_6 - \phi_2) & +1(-\phi_4) & -1(-\phi_3 - \phi_5) & +1(-\phi_2 - \phi_6) \\ \sigma_h & \sigma_a & \sigma_b & \sigma_c & \sigma_{va} & \sigma_{vb} & \sigma_{vc} \\ -1(-\phi_1) & -1(\phi_4 + \phi_6 + \phi_2) & +1(\phi_1 + \phi_3 + \phi_5) \end{array} \right] =$$

$$4(\phi_2 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_5)$$

For a given irrep $|\psi^j\rangle = \sum_{\alpha=1}^6 c_{\alpha}^j |\phi_{\alpha}\rangle$, The normalization is given by $1 = \langle \psi^j | \psi^j \rangle = |N_j|^2 \left[\sum_{\alpha} |c_{\alpha}^j|^2 + 2 \sum_{\alpha < \beta} \text{Re}(c_{\alpha}^{j*} c_{\beta}^j S_{\alpha\beta}) \right]$ where $S_{\alpha\beta} = \langle \phi_{\alpha} | \phi_{\beta} \rangle = S_{\beta\alpha}^*$ is the overlap matrix.

Benzene



5.5 Comment on matrix element of molecular Hamiltonians

Let's assume a molecule with a given point symmetry group G . We then fix a Hilbert space and construct the associated representation. The latter can be reduced to a direct sum of irreducible representations

$$\Gamma = \bigoplus_{j=1}^{N_{\text{irr}}} \alpha_j \Gamma^j$$

Given the presence of more than 1 irreducible representation of a certain kind (e.g. the one generated by the 2p orbitals of C and the 4s orbitals of H in a methane molecule) we need to label them with an extra index. It is now interesting to ask about the matrix element: $\langle a_j \mu | H | b_j \mu' \rangle$

We know that $[H, R] = 0$ in other words $RHR^\dagger = H \quad \forall R \in G$. Unitary
 $= R^\dagger H R$

$$\text{Moreover } R |a_j \mu\rangle = \sum_{\nu} \Gamma_{\nu \mu}^j(R) |a_j \nu\rangle \Rightarrow$$

$$\langle a_j \mu | R^\dagger = \sum_{\nu} \Gamma_{\nu \mu}^{j*}(R) \langle a_j \nu |$$

$$\langle a_j \mu | H | b_j \mu' \rangle = \langle a_j \mu | R^\dagger H R | b_j \mu' \rangle = \sum_{\nu \nu'} \langle a_j \nu | H | b_j \nu' \rangle \Gamma_{\nu \mu}^j(R) \Gamma_{\nu' \mu'}^{j*}(R)$$

But the relation above is valid $\forall R \in G$. It follows that

$$\langle a_j \mu | H | b_j \mu' \rangle = \sum_{\nu \nu'} \langle a_j \nu | H | b_j \nu' \rangle \frac{1}{h} \sum_R \Gamma_{\nu \mu}^{j*}(R) \Gamma_{\nu' \mu'}^j(R) \stackrel{\text{NOT}}{=} \delta_{\mu \mu'} \delta_{j j'} \frac{1}{g_j} \sum_{\nu} \langle a_j \nu | H | b_j \nu \rangle$$

From the last expression we can conclude that, if the irrep has dimension

$> 1 \Rightarrow$

- only diagonal elements in the repr. partners differ from 0
- all these elements are equal.

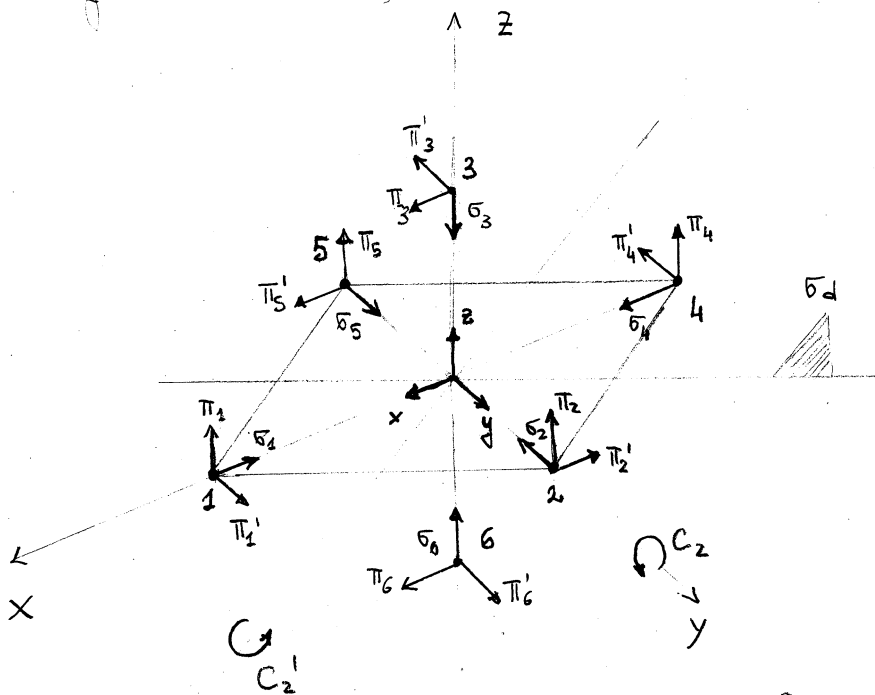
5.6 Transition metal complexes

Let's consider a metal-ligand complex in the form ML_6 where M stands for metal and L for ligand atom. The number of orbitals in the game:

$$\begin{aligned}
 M: & 5 \times nd + 1 \times (n+1)s + 3 \times (n+1)p = 9 \text{ AO} \\
 L: & 3 \times np \text{ for each ligand atom} = 18 \text{ AO} \\
 & \underline{\hspace{10em}} \\
 & 27 \text{ orbitals.}
 \end{aligned}$$

(C, N, O in the ligand use mainly p orbitals to form bonds with the metal.

Since L atoms are assumed identical \Rightarrow to minimize repulsive interaction among themselves they will sit at the vertices of an octahedron.



In the figure we have associated a set of R-oriented cartesian axes to each atom involved in the metal-ligand complex. They used x, y, z for the metal atom and σ_i, π_i, π'_i for each of the ligand atoms. Conventionally σ_i points towards the metal atom.

The point group of this system of 7 atoms is $O_h = O \otimes C_i$.

Let us list the classes:

$$O_h = \{ E, 3C_2, 8C_3, 6C_4, 6C_2' \mid I, 3\sigma_h, 8S_6, 6S_4, 6\sigma_d \}$$

$\{O\}$ $I\{O\}$

O is the group of proper rotations that brings a cube (or an octahedron) into itself. We shall divide the representation into metal and ligand.

Metal :

$s \rightarrow s$ under any operation $\sigma^p O_h \Rightarrow (n+1)s \Leftrightarrow A_{1g} = \Gamma_s$

$p \rightarrow p$
 $d \rightarrow d$ } it is enough to remember that p and d are associated to polynomials of different order.

It is useful to construct how the functions x, y and z are transformed by one representative per class of O_h , i.e. the Jones symbols

		C_2	C_3	C_4	C_2'	
$R =$	E	$R(\pi \hat{z})$	$R(\frac{2\pi}{3} \hat{n}_2)$	$R(\frac{\pi}{2} \hat{z})$	$R(\pi \hat{n}_2)$	$\vec{n}_2 = (111)$ $\vec{n}_2 = (110)$
$R^{-1}(xyz)$	xyz	$\bar{x}\bar{y}\bar{z}$	yzx	$y\bar{x}\bar{z}$	$y \times \bar{z}$	$\bar{x} = -x$ $\bar{y} = -y$ $\bar{z} = -z$

It is thus straightforward to calculate the character set of Γ_p .

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

From the Jones symbols we deduce that for the d basis functions it results

R	E	C_2	C_3	C_4	C_2'	
$R(d)$	xy	xy	yz	-xy	xy	completed with gerade character of 2 nd order polynomials
	yz	-yz	zx	-zx	-zx	
	zx	-zx	xy	yz	-yz	

$$\Gamma_{d_1} = \{ 3, -1, 0, -1, 1, 3, -1, 0, -1, 1 \}$$

For the other two basis elements of the d orbitals

R	E	C_2	C_3	C_4	C_2'
$R(d)$	x^2-y^2	x^2-y^2	y^2-z^2	y^2-x^2	y^2-x^2
	$3z^2-r^2$	$3z^2-r^2$	$3x^2-r^2$	$3z^2-r^2$	$3z^2-r^2$
χ	2	2	?	0	0

The character associated to the class $C(C_3)$ requires some care

We have to look for the matrix representative of C_3

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

$$\begin{cases} a = b \\ a + b = -1 \\ 2b = -1 \end{cases} \Rightarrow \begin{cases} a = -\frac{1}{2} \\ b = -\frac{1}{2} \end{cases}$$

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

$$\begin{cases} c - d = 2 \\ c + d = -1 \\ 2d = -1 \end{cases} \Rightarrow \begin{cases} c = \frac{3}{2} \\ d = -\frac{1}{2} \end{cases}$$

$$\Gamma(C_3) = \begin{pmatrix} -\frac{1}{2} & \frac{3}{2} \\ -\frac{1}{2} & -\frac{1}{2} \end{pmatrix} \Rightarrow \chi(C_3) = -1$$

Summarizing $\Gamma_{d_2} = \{2, 2, -1, 0, 0 \mid 2, 2, -1, 0, 0\}$

Ligand It is clear by construction that σ and π orbitals are not mixed by the symmetry operations of O_h . By counting how many orbitals are invariant or change sign.

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

$$\Gamma_{\pi} = \{12, -4, 0, 0, 0, 0, 0, 0, 0, 0\}$$

Not gerade nor ungerade. They are necessarily reducible.

By means of the reduction formula we obtain

METAL

LIGAND

$$\Gamma_s = A_{1g}$$

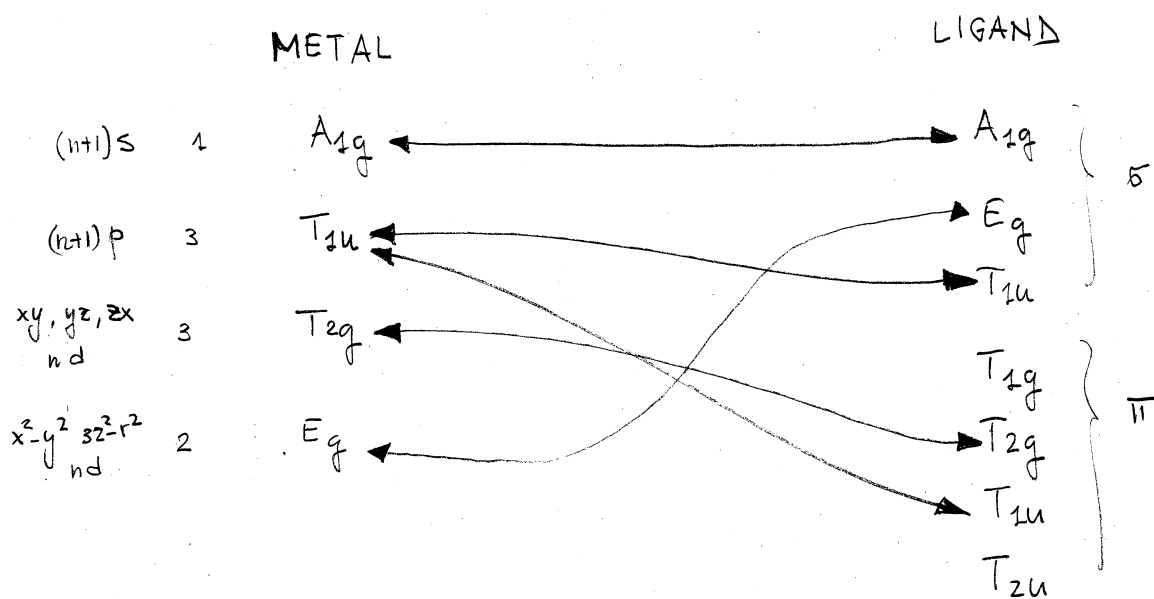
$$\Gamma_{\sigma} = A_{1g} \oplus E_g \oplus T_{1u}$$

$$\Gamma_p = T_{1u}$$

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

$$\Gamma_d = \Gamma_{d_2} \oplus \Gamma_{d_2} = T_{2g} \oplus E_g$$

We have now to determine the molecular orbitals involving metal and ligand



We can classify: A_{1g} and E_g forming 3 σ -bonds. T_{1u} is a clear example of σ - π mixing induced by the geometry. T_{2g} is forming 3 π bonds. Finally 6 orbitals are only located on the ligand and have T_{1g} and T_{2u} symmetry.

The σ -bonding

First we construct the ligand states: using the projection operator

$$\hat{P}A_{1g}(\sigma_i) = \sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6$$

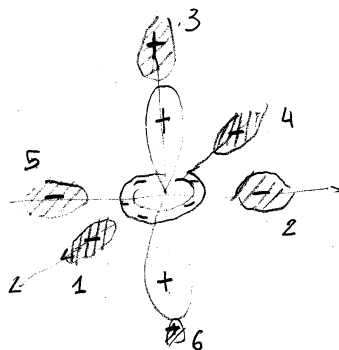
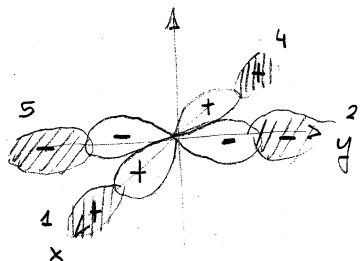
$$E_g = \{22-100 \quad 22-100\}$$

$$\hat{P}E_g(\sigma_1) = 2\sigma_1 - \sigma_2 - \sigma_3 + 2\sigma_4 - \sigma_5 - \sigma_6$$

$$\hat{P}E_g(\sigma_2) = 2\sigma_2 - \sigma_3 - \sigma_4 + 2\sigma_5 - \sigma_6 - \sigma_1$$

$$\hat{P}E_g(\sigma_3) = 2\sigma_3 - \sigma_4 - \sigma_5 + 2\sigma_6 - \sigma_1 - \sigma_2$$

Remembering the form of the E_g orbitals on the metal



$$\psi_1(E_g) = \hat{P}^{E_g}(\sigma_1) - \hat{P}^{E_g}(\sigma_2) = \sigma_1 - \sigma_2 + \sigma_4 - \sigma_5$$

$$\psi_2(E_g) = \hat{P}^{E_g}(\sigma_3) = 2\sigma_3 - \sigma_4 - \sigma_5 + 2\sigma_6 - \sigma_1 - \sigma_2$$

The σ -bond molecular orbitals are linear combinations of the ones on the A_{1g} and E_g ineq on the metal and on the ligand.

The π -bonding We need the characters of the T_{2g} representation

$$T_{2g} = \begin{Bmatrix} E & C_2 & C_3 & C_4 & C_2' \\ 3 & -1 & 0 & -1 & 1 \\ 3 & -1 & 0 & -1 & 1 \end{Bmatrix}$$

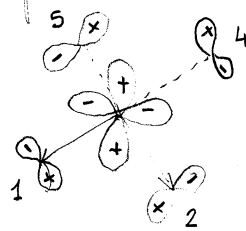
Projection operation technique would give, after a tedious calculation, the right answer. We can also try to match the orbital sign distribution of the xy , yz and zx orbitals, obtaining

$$\psi_1(T_{2g}) = \pi_1 - \pi_4 + \pi_3 - \pi_6 \leftrightarrow d_{zx}$$

$$\psi_2(T_{2g}) = \pi_1' - \pi_2' + \pi_4' - \pi_5' \leftrightarrow d_{xy}$$

$$\psi_3(T_{2g}) = \pi_2 - \pi_3' - \pi_5 - \pi_6' \leftrightarrow d_{yz}$$

Example



The σ - π mixed states

The 3 dimensional ineq T_{2u} is associated to the p_x, p_y, p_z orbitals on the metal. For what concerns the σ system we obtain, naturally,

$$\psi_1^\sigma(T_{2u}) = \sigma_1 - \sigma_4 \leftrightarrow p_x$$

$$\psi_2^\sigma(T_{2u}) = \sigma_2 - \sigma_5 \leftrightarrow p_y$$

$$\psi_3^\sigma(T_{2u}) = \sigma_3 - \sigma_6 \leftrightarrow p_z$$

Similarly for the π system

$$\psi_1^\pi(T_{2u}) = \pi_3 + \pi_5' + \pi_6 - \pi_2' \leftrightarrow p_x$$

$$\psi_2^\pi(T_{2u}) = \pi_1' - \pi_3' - \pi_4' + \pi_6' \leftrightarrow p_y$$

$$\psi_3^\pi(T_{2u}) = \pi_1 + \pi_2 + \pi_4 + \pi_5 \leftrightarrow p_z$$

The molecular orbitals are obtained by diagonalizing the same 3×3 matrix

$$\begin{pmatrix} \Sigma_p & t_{p\sigma} & t_{p\pi} \\ t_{p\sigma}^* & \Sigma_c & \\ t_{p\pi} & & \Sigma_\pi \end{pmatrix}$$

for each of the triplets of orbitals $p_i, \psi_i^\sigma, \psi_i^\pi$ $i=1,2,3$.

Finally we analyze the 2 triplets of non-bonding orbitals with symmetry

T_{1g} and T_{2u}

$E \quad 3C_2 \quad 8C_3 \quad 6C_4 \quad 6C_2'$

$$T_{1g} = \{ 3, -1, 0, 1, -1 \mid 3, -1, 0, 1, -1 \}$$

$$T_{2u} = \{ 3, -1, 0, -1, 1 \mid -3, 1, 0, 1, -1 \}$$

$$\hat{P}^{T_{1g}}(\pi_1) \propto \pi_1 - \pi_3 - \pi_4 + \pi_5$$

$$\hat{P}^{T_{1g}}(\pi_2) \propto \pi_2 + \pi_3' - \pi_5 + \pi_6'$$

$$\hat{P}^{T_{1g}}(\pi_1') \propto \pi_1' + \pi_2' + \pi_4' + \pi_5'$$

$$\hat{P}^{T_{2u}}(\pi_1) \propto \pi_1 - \pi_2 + \pi_4 - \pi_5$$

$$\hat{P}^{T_{2u}}(\pi_1') \propto \pi_1' - \pi_6' - \pi_4' + \pi_3'$$

$$\hat{P}^{T_{2u}}(\pi_2') \propto \pi_2' + \pi_3 - \pi_5' + \pi_5$$