Chapter 4

Applications to Chemical Bonding

Group theoretical discussions presented in earlier chapters will now be applied to chemical bonding theories. In doing so, the following systematic procedure may be followed:

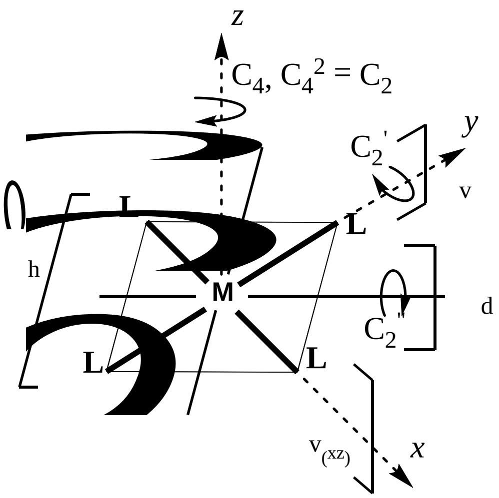
1) Determine the symmetry point group of the given species.
2) Choose an appropriate basis on which the group operations will be performed in order to generate a reducible representation.
3) Reduce the resulting representation into its corresponding irreducible ones, using the reduction formula discussed earlier.
4) Maneuver to reach out conclusions according to objectives.

Three common applications will now be discussed, namely:

a) Finding out a set of central atom hybrid orbitals that can be used in bonding. This is a procedure that is needed in understanding ***Valence Bond Theory***
b) Construction of a molecular orbital energy level correlation diagram of a given molecule (ion) with a given symmetry. This is a procedure that is needed in understanding ***Molecular Orbital Theory***.
c) Finding out Ligand Group Orbitals (LGOs) using the Projection Operator Method.

a) Finding Hybrid Orbitals

Consider a square planer transition metal atom complex ion with D_{4h} symmetry, structure I. Group theory can be used to find out the set of hybrid orbitals, of the central metal atom, that are used in σ-bonding system. The step-wise procedure is:



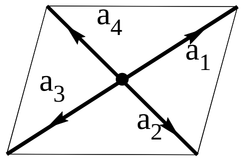
I

1) The square planar ion has a ***D*$_{4h}$** symmetry point group, with symmetry operations

$$E \quad 2C_4 \quad C_2 \quad 2C_2^{'} \quad 2C_2^{''} \quad i \quad 2S_4 \quad \sigma_h \quad 2\sigma_v \quad 2\sigma_d$$

as shown in structure I above.

2) Since the central metal atom hybrid orbitals are used in directional metal-ligand σ-bonds, each of these metal-ligand bonds may be understood as an arrow, as shown below. The result is a set of four arrows. This set of four arrows can now be used as a basis.



To generate a reducible representation, the 4-arrow basis may be used. All ***D*$_{4h}$** symmetry operations will then be performed on the basis using either of the following two techniques:

i) The discussion presented in Chapter 3 may be followed. In this technique, the effect of each operation (on the four-arrow basis) can be represented by a matrix.

The matrix $\begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{bmatrix}$ represents the basis with the four arrows before performing the $C_{4(z)}$ operation. When a $C_{4(z)}$ operation is performed, the following transformations, shown in equation (1) occur

$$\begin{array}{llllll} new & arrow & a_1 & \rightarrow & old & arrow \quad a_4 \\ new & arrow & a_2 & \rightarrow & old & arrow \quad a_1 \\ new & arrow & a_3 & \rightarrow & old & arrow \quad a_2 \\ new & arrow & a_4 & \rightarrow & old & arrow \quad a_3 \end{array} \tag{1}$$

and the new matrix is $\begin{bmatrix} a_4 \\ a_1 \\ a_2 \\ a_3 \end{bmatrix}$.

The question now is: based on equation (2), what is the matrix that changes the original matrix into the new one?

$$\begin{bmatrix} \quad & \quad & \quad & \quad \\ & & & \\ & & & \\ & & & \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \\ a_3 \\ a_4 \end{bmatrix} = \begin{bmatrix} a_4 \\ a_1 \\ a_2 \\ a_3 \end{bmatrix} \tag{2}$$

From matrix algebra, the representing matrix is:

$$\begin{bmatrix} 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix} \qquad \text{(with } \chi = 0\text{)}$$

This matrix represents the effect of $C_{4(z)}$ operation on the basis. Other matrices that represent other operations can similarly be found, and their characters can be calculated. The reducible representation is:

$\boldsymbol{D_{4h}}$	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ_σ	4	0	0	2	0	0	0	4	2	0

ii) Having understood the technique discussed above, another yet easier technique may now be used. *The character, of the matrix representing the effect of each operation on the basis, is equal to the number of unshifted arrows by that operation*. To clarify this, we can find the character of each operation of $\boldsymbol{D_{4h}}$ group when performed on the 4-arrow basis:

operation	Number of unshifted arrows	Character χ
E	4	4
C_4	0	0
C_2	0	0
C_2'	2	2
C_2''	0	0

i	0	0
S_4	0	0
σ_h	4	4
σ_v	2	2
σ_d	0	0

Therefore, the reducible representation that results is necessarily the same as that shown earlier with no need for repetition. Having understood both techniques, it is recommended to use method (ii) since it is more convenient and saves time.

3) Reducing the resulting representation. The Γ_σ shown above can now be reduced using the reduction formula, discussed earlier in Chapter 3. The reduction result is: $\Gamma_\sigma = A_{1g} + B_{1g} + E_u$
4) Referring back to the constructed reducible representation, to interpret these results, it is necessary to recall the ***D*$_{4h}$** group Character Table. From the right hand columns of the ***D*$_{4h}$** Character Table, it appears that the orbitals which belong to A_{1g}, B_{1g} and E_u are as:

$S \longrightarrow A_{1g}$

$d_{x^2-y^2} \longrightarrow B_{1g}$

$p_x \,\&\, p_y \longrightarrow E_u$

These are the only orbitals that have symmetries belonging to the A_{1g}, B_{1g} and E_u. Therefore, one may conclude that the hybrid orbitals involved in bonding are (dsp^2), where $d_{x^2-y^2}$, p_x and p_y orbitals are specifically involved.

Exercise: use group theory to find out central atom hybrid orbitals in BF_3 (with ***D*$_{3h}$** symmetry) and in CH_4 (with T_d). Discuss which specific atomic orbitals are involved in hybridization.

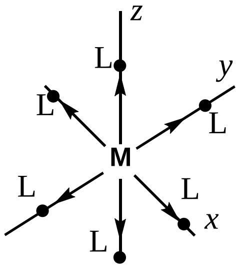
b) Molecular Orbital Energy Level Diagrams

To know how group theory applies to molecular orbital energy level diagrams consider the example of $[Co(NH_3)_6]^{3+}$ with ***O*$_h$** symmetry. Note that the discussion involves metal-ligand σ-bonding system only since the amine ligand is not a π-bonder. The symmetry for a set of ligand group orbitals (LGOs) used in σ-bonding system can be found for ***O*$_h$** system as follows.

From ***O**$_h$* Character Table, the symmetry species of each of the nine central-atom-orbitals are:

2s	a_{1g}
$4p_x$, $4p_y$, $4p_z$	t_{1u}
$3d_{z^2}$, $3d_{x^2-y^2}$	e_g
$3d_{xy}$, $3d_{xz}$, $3d_{yz}$	t_{2g}

Then it is necessary to find out symmetries of Ligand Group Orbitals (LGOs) that will interact with the central metal orbitals. This can be achieved as follows: The six metal-ligand σ-bonds can be thought of as a set of six arrows as shown in structure II below:



II

The set of arrows is considered as a basis on which all ***O**$_h$* operations may be performed to generate the reducible representation:

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

which reduces to:

$$\Gamma_\sigma = A_{1g} + E_g + T_{1u} \qquad (3)$$

These are the symmetries of the so called LGO's. The two conditions for orbital-orbital interaction are:

i) The two orbitals must have comparable energy levels.
ii) The two orbitals must have same symmetry species.

Therefore, the interactions (between the central metal atomic orbitals and the corresponding ligand group orbitals) must obey the symmetry requirements. The interactions must therefore be:

Metal atomic orbitals	Interaction	L.G.O.	Resulting Molecular Orbitals

a_{1g}	4s	with	A_{1g}	One σ and one σ*
e_g	(d_{z^2}, $d_{x^2-y^2}$)	with	E_g	Two σ and two σ*
t_{1u}	(p_x, p_y, p_z)	with	T_{1u}	Three σ and three σ*
t_{2g}	$3d_{xy}$, $3d_{xz}$, $3d_{yz}$	none	--	Non-bonding

where the other remaining atomic orbitals with t_{2g} symmetry have no matching LGO's, and remain as nonbonding orbitals in the σ-bonding system.

The bonding and antibonding molecular orbitals (MO's) resulting from the metal orbital-ligand group orbital interactions are shown in Figure (4.1) below.

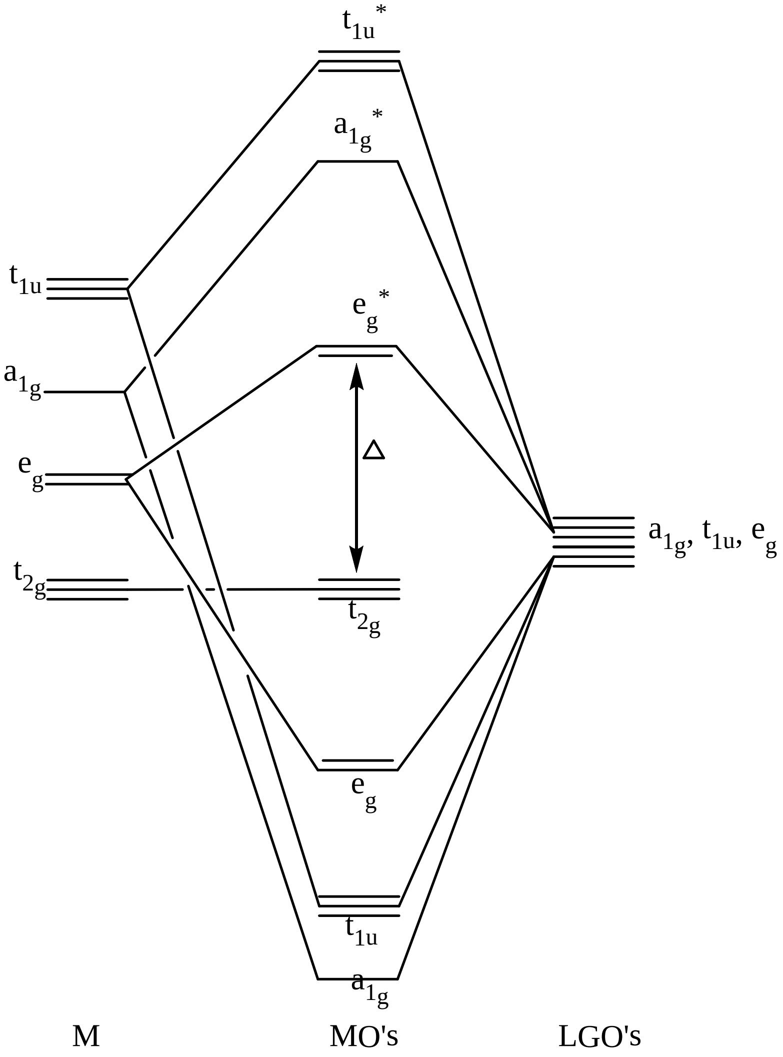


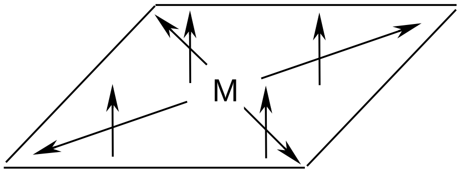
Figure (4.1): A qualitative M.O. energy level diagram for the σ-bonding system in $\boldsymbol{O_h}$ complexes.

Example:

In a square planar metal complex, with $\boldsymbol{D_{4h}}$ symmetry, use group theory to find out each of the following:

1) Symmetries of LGOs used for σ-bonding system
2) Symmetries of LGOs used for out-of plane π-bonding system
3) Construct a qualitative molecular orbital energy level diagram showing both σ- and π-bonding systems.

Solution: Based on the drawing below, showing the σ-bonding basis as four arrows in the molecular plane, and π-bonding basis as four perpendicular arrows, then:



The σ-bonding system: performing the $\boldsymbol{D_{4h}}$ operations on the σ 4-arrow basis gives the reducible representation:

$\boldsymbol{D_{4h}}$	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ_σ	4	0	0	2	0	0	0	4	2	0

which reduces as $\Gamma_\sigma = A_{1g} + B_{1g} + E_u$ showing symmetries of all LGOs involved in the σ-bonding system.

The π-bonding system: performing the operations on the π 4-arrow basis yields the reducible representation:

$\boldsymbol{D_{4h}}$	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ_π	4	0	0	-2	0	0	0	-4	2	0

Which reduces to: $\Gamma_\pi = E_g + A_{2u} + B_{2u}$

From the $\boldsymbol{D_{4h}}$ character table, we know that the symmetries for the metal atomic orbitals being:

4s A_{1g}; 4p_x & 4p_y E_u; 4 p_z A_{2u}; 3d_{z^2} A_{1g}; $d_{x^2-y^2}$ B_{1g}; d_{xy} B_{2g}; d_{xz} & d_{yz} E_g.

Thus based on symmetry and geometrical considerations, the following interactions will occur:

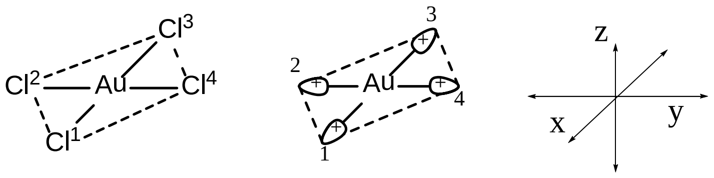
Symmetry	Metal orbital(s)	Interacting LGO	Resulting MO(s)
A_{1g}	4s	A_{1g}	One σ and one σ* MOs
E_u	$4p_x$ & $4p_y$	E_u	Two σ and two σ* MOs
B_{1g}	$d_{x^2-y^2}$	B_{1g}	One σ and one σ* MOs
A_{2u}	4 p_z	A_{2u}	One π and one π* MOs
E_g	d_{xz} & d_{yz}	E_g	Two π and two π* MOs
A_{1g}	$3d_{z^2}$	No geometry matching	Non bonding
B_{2g}	d_{xy}	No symmetry matching	Non-bonding

The resulting molecular orbital energy level diagram can now be easily constructed based on these interactions.

c) The Projection Operator Method

The above discussion explained how group theory can be used to find out symmetries for LGOs used in bonding. It showed also how molecular orbital energy level diagrams can be constructed based on group theory. However, the LGO wave functions themselves have not been found, nor were the balloon shapes of the LGOs. In order to do so, a technique so-called ***Projection Operator Method*** is needed.

To explain these ideas, let us find the σ-LGO's for the square planar $AuCl_4^-$ ion with $\boldsymbol{D_{4h}}$ point group. Figure (4.2) shows the structure of the ion.



a

b

Figure (4.2): Schematics showing (a) $AuCl_4^-$ ion and (b) σ-basis functions of $\boldsymbol{D_{4h}}$ point.

The step-wise process is as follows:

Step 1: Using the set of 4 atomic orbitals shown above (Figure 4.2) as a basis, the group operations for $\boldsymbol{D_{4h}}$ are performed.

Step 2: Using reduction formula discussed earlier (Chapter 3) the correct reducible representation can then be constructed as:

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

Step 3: Choosing one σ orbital (e.g. σ_1 in this case) and performing all symmetry operations separately on it. The E operation, for instance, leaves σ_1 unchanged while C_4 shifts it to the place of σ_2. By performing all $\boldsymbol{D_{4h}}$ operations separately on σ_1, then:

E	C_4	C_4^3	C_2	$C_2^{'1}$	$C_2^{'2}$	$C_2^{''1}$	$C_2^{''2}$	i	S_4	S_4^3	σ_h	σ_v^1	σ_v^2	σ_d^1	σ_d^2
σ_1	Σ_2	σ_4	σ_3	σ_1	σ_3	σ_2	σ_4	σ_3	Σ_2	σ_4	σ_1	σ_1	σ_3	σ_2	σ_4

The table shows Effects of all symmetry operations as separately performed onto σ_1 in $\boldsymbol{D_{4h}}$ symmetry. Note that each symmetry operation is written separately without a class, and then performed separately.

Step 4: To find the linear combinations of σ orbitals with A_{1g} representation, each generated orbital is multiplied by the character of each operation corresponding to A_{1g} (+1 in this case) as shown in $\boldsymbol{D_{4h}}$ Character Table.
This gives:

A_{1g}: σ_1 σ_2 σ_4 σ_3 σ_1 σ_3 σ_2 σ_4 σ_3 σ_2 σ_4 σ_1 σ_1 σ_3 σ_2 σ_4

By simple addition of same items, then:

$\Psi_\sigma (A_{1g})$: $4\sigma_1$ $4\sigma_2$ $4\sigma_3$ $4\sigma_4$

The values are then written in simplest possible ratio as:

$\Psi_\sigma (A_{1g})$: σ_1 σ_2 σ_3 σ_4

The wave function for resulting LGO is thus normalized as:

$$\Psi (A_{1g}) = \frac{1}{\sqrt{4}} (\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4) \qquad (3)$$

Step 5: Construct the LGO corresponding to other symmetry species B_{1g} in a similar manner to that done for A_{1g}. In this case the values shown in Table (4.1) are multiplied by characters corresponding to B_{1g} of the ***D_{4h}*** Character Table. The LGO belonging to B_{1g} is thus:

$$\Psi (B_{1g}) = \frac{1}{\sqrt{4}} (\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4) \qquad (4)$$

Step 6: Construct the two doubly degenerate LGOs (E_u), one by one, as follows:

The First* E_u *LGO: can be obtained using a similar procedure as described in Step 4 above, but using character values of E_u in this case. The result is shown in equation 5 below.

$$\Psi_1(E_u) = \frac{1}{\sqrt{2}} (\sigma_1 - \sigma_3) \qquad (5)$$

The Second* E_u *LGO:

The second LGO of the doubly degenerate E_u pair, can be constructed by applying any ***D_{4h}*** operation that shifts all σ's to new places. Starting with the first degenerate LGO, $\sigma_1 - \sigma_3$, performing C_4 on it gives $\sigma_2 - \sigma_4$. Thus the second LGO of the doubly degenerate E_u is expected to be:

$$\Psi_2(E_u) = \frac{1}{\sqrt{2}} (\sigma_2 - \sigma_4) \qquad (6)$$

In order to be accepted as an LGO, the second one must be orthogonal with the first LGO. That is to say

$$\int \Psi_1 \Psi_2 \, d\tau = 0 \qquad (7)$$

By substituting equations (5) and (6) in (7) then:

$$\int \Psi_1 \Psi_2 \, d\tau = (1/2)\int (\sigma_1 - \sigma_3)(\sigma_2 - \sigma_4) \, d\tau =$$

$$(½)\int (\sigma_1 \sigma_2 - \sigma_1 \sigma_4 - \sigma_2 \sigma_3 + \sigma_3 \sigma_4) d\tau =$$

$$(½)[\int\sigma_1\sigma_2 d\tau - \int\sigma_1\sigma_4 d\tau - \int\sigma_2\sigma_3 d\tau + \int\sigma_3\sigma_4 d\tau \qquad (8)$$

Atomic orbitals are orthogonal, thus each of the integrals $\int\sigma_1\sigma_2 d\tau$, $\int\sigma_1\sigma_4 d\tau$, $\int\sigma_2\sigma_3 d\tau$ and $\int\sigma_3\sigma_4 d\tau$ is equal to zero.

Therefore

$$(½)[\int\sigma_1\sigma_2 d\tau - \int\sigma_1\sigma_4 d\tau - \int\sigma_2\sigma_3 d\tau + \int\sigma_3\sigma_4 d\tau = 0 \qquad (9)$$

From equation (9), the condition shown in equation (7) is satisfied. This means that the first and the second E_u LGO’s are orthogonal, and that the second one constructed above is acceptable.

Figure (4.3) shows the balloon representations for all σ LGOs in a ***D*$_{4h}$** symmetry, as defined by the equations (3 – 6).

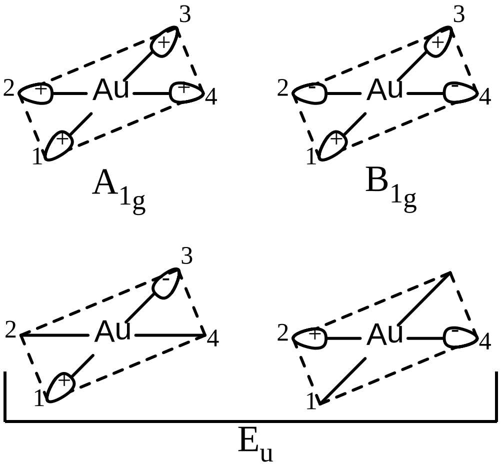


Figure (4.3): Schematics showing balloon representations for all σ LGOs of ***D*$_{4h}$** point group.

Step 7: Recheck the solutions: After wave functions for all LGOs are calculated, they should be rechecked for errors. The sum of squared values of coefficients, of each original atomic orbital, in the resulting LGOs should be equal to 1. Therefore, based on equations (3-6), the squared values of coefficients of each original atomic orbital are shown below:

Atomic Orbital	$(\text{Coefficient})^2$ in LGO				Total
	A_{1g}	B_{1g}	First E_u LGO	Second E_u	
σ_1	1/4	¼	1/2	--	1
σ_2	1/4	¼	--	1/2	1
σ_3	1/4	¼	1/2	--	1
σ_4	1/4	¼	--	1/2	1

From these calculations, it is obvious that the total number of resulting LGOs equals the total number original atomic orbitals. Thus, the whole process obeys the principle of conservation of atomic orbitals.

Example:

Consider the $Cr(C_6Me_6)(C_6H_6)$ molecule with a C_{6v} symmetry. Use group theory to find out LGOs for the H-atoms involved in σ-bonding system in this molecule.

Solution:

Figure (4.4a) shows the structure for the molecule, whereas Figure (4.4b) shows the six H-atomic orbitals to be used in σ-bonding system with the six carbon atoms.

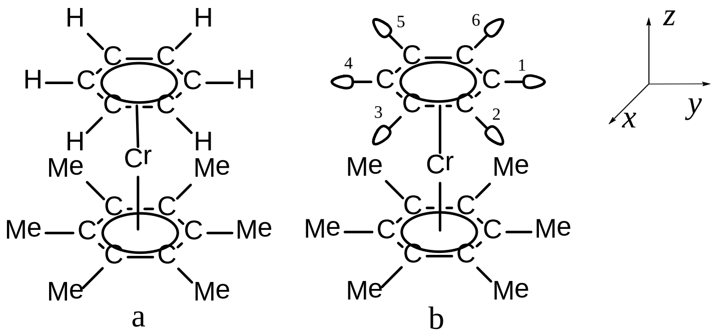


Figure (4.4): A schematic showing (a) Cr(C_6Me_6)(C_6H_6) molecule with $\boldsymbol{C_{6v}}$ symmetry, and (b) different H atom σ-orbitals.

Using the six H-atomic orbitals a basis, the resulting reducible representation is:

$$\Gamma_\sigma = A_1 + B_1 + E_1 + E_2 \tag{10}$$

Using σ_3 as a reference basis function, then group operations will shift σ_3 as:

E	C_6	C_6^5	C_3	C_3^2	C_2	$\sigma_v^{(1)}$	$\sigma_v^{(2)}$	$\sigma_v^{(3)}$	$\sigma_d^{(1)}$	$\sigma_d^{(2)}$	$\sigma_d^{(3)}$
σ_3	σ_4	σ_2	σ_5	σ_1	σ_6	σ_5	σ_1	σ_3	σ_6	σ_2	σ_4

After multiplications with proper characters of the A_1 and B_1, the LGOs for A_1 and B_1 are:

$$\Psi(A_1) = \frac{1}{\sqrt{6}}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6) \tag{11}$$

$$\Psi(B_1) = \frac{1}{\sqrt{6}}(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4 + \sigma_5 - \sigma_6) \tag{12}$$

The species E_1 and E_2 are doubly degenerate ones, which mean that each has two LGOs to be found. Therefore the first E_1 LGO is:

$$\text{First } \Psi(E_1) = \frac{1}{\sqrt{12}} (-\sigma_1 + \sigma_2 + 2\sigma_3 + \sigma_4 - \sigma_5 - 2\sigma_6) \qquad (13)$$

And the first E_2 LGO is:

$$\text{First } \Psi(E_2) = \frac{1}{\sqrt{12}} (-\sigma_1 - \sigma_2 + 2\sigma_3 - \sigma_4 - \sigma_5 + 2\sigma_6) \qquad (5)$$

The second E_1 LGO species can be found from the first E_1 LGO, by performing any suitable operation, such *C₆* operation, on it. The operation shifts individual basis functions as follows: $\sigma_1 \rightarrow \sigma_2$, $\sigma_2 \rightarrow \sigma_3$, $\sigma_3 \rightarrow \sigma_4$, $\sigma_4 \rightarrow \sigma_5$, $\sigma_5 \rightarrow \sigma_6$, $\sigma_6 \rightarrow \sigma_1$. Therefore, the first $\Psi(E_1)$ is transformed as:

$(-\sigma_1 + \sigma_2 + 2\sigma_3 + \sigma_4 - \sigma_5 - 2\sigma_6) \rightarrow (-2\sigma_1 - \sigma_2 + \sigma_3 + 2\sigma_4 + \sigma_5 - \sigma_6)$

The expected second E_1 LGO wave function will thus be:

$$\text{Second } \Psi(E_1) = \frac{1}{\sqrt{12}} (-2\sigma_1 - \sigma_2 + \sigma_3 + 2\sigma_4 + \sigma_5 - \sigma_6)$$

To be accepted, this LGO must be orthogonal to the other E_1 LGO. Testing for orthogonality shows that:

$$\frac{1}{\sqrt{12}} \bullet \frac{1}{\sqrt{12}} \int(-\sigma_1 + \sigma_2 + 2\sigma_3 + \sigma_4 - \sigma_5 - 2\sigma_6)\bullet(-2\sigma_1 - \sigma_2 + \sigma_3 + 2\sigma_4 + \sigma_5 - \sigma_6)d\tau =$$

$$\frac{1}{12} \bullet (2 - 1 + 2 + 2 - 1 + 2) \neq 0$$

The resulting second E_1 LGO is not orthogonal with the first counterpart, is thus unacceptable.

The correct second E_1 LGO could be obtained as follows:

Performing linear combination on the second (unacceptable) E_1 LGO and the first E_1 LGO gives:

$$\begin{array}{l}(-2)\times \text{second}\,\Psi(E_1)+(1)\times \text{first}\,\Psi(E_1)= \\ (-\sigma_1+\sigma_2+2\sigma_3+\sigma_4-\sigma_5-2\sigma_6)+ \\ (4\sigma_1+2\sigma_2-2\sigma_3-4\sigma_4-2\sigma_5+2\sigma_6) \\ -------------------- \\ \qquad 3\sigma_1+3\sigma_2-3\sigma_4-3\sigma_5\end{array}$$

Where the terms (-2) and (1) appearing in the first line are arbitrary terms chosen by trial and error so as to give results that satisfy orthogonality. The term values have specifically been chosen in this example in order to cancel off largest coefficients appearing in the first E_1 LGO.

The correct second E_1 LGO (orthogonal to all other LGOs) is thus:

$$\text{Second} \quad \Psi(E_1) = \frac{1}{\sqrt{4}}\,(\sigma_1+\sigma_2-\sigma_4-\sigma_5) \tag{6}$$

By using the same technique, the second E_2 LGO can be found as:

$$\text{Second} \quad \Psi(E_2) = \frac{1}{\sqrt{4}}\,(\sigma_1-\sigma_2+\sigma_4-\sigma_5) \tag{7}$$

The six wave functions for all LGOs are summarized in Figure (4.5).

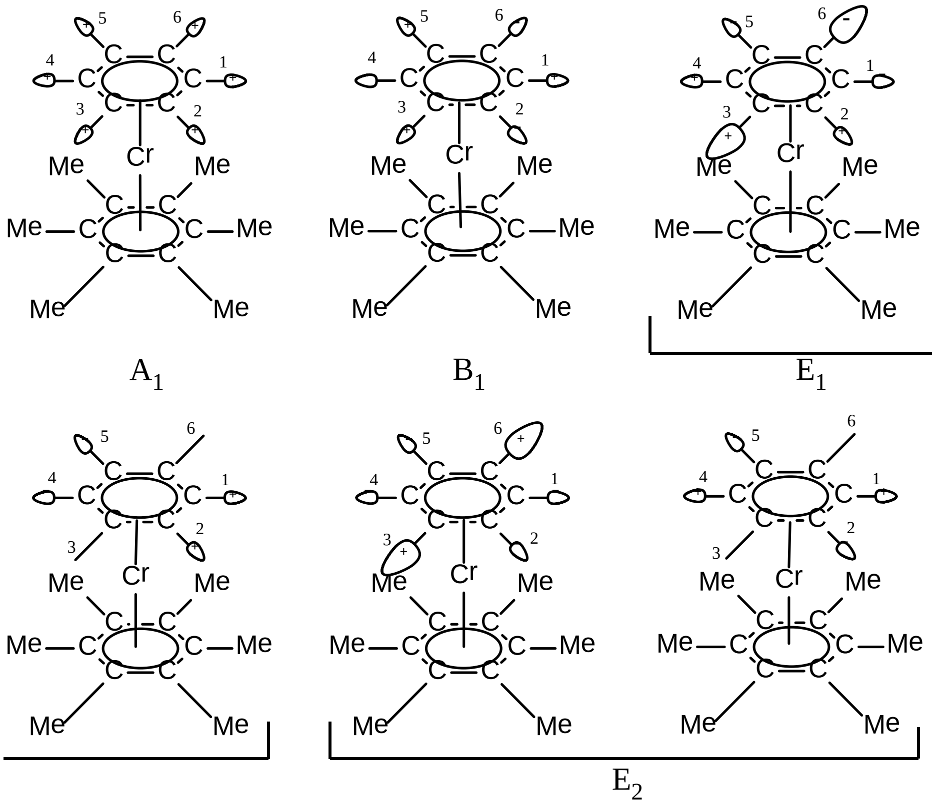
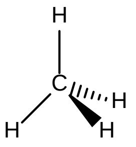


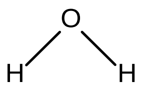
Figure (4.5): Schematics showing balloon representations for all six LGOs resulting from H-atomic orbitals in the C_{6v} molecule.

Exercises:

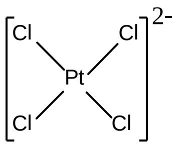
1) For each of the following species, use group theory to find out hybrid orbitals for the central metal atom.



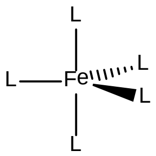
T_d



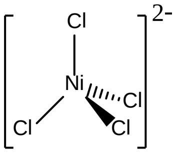
C_{2v}



D_{4h}



D_{3h}



T_d

2) Considering the BF$_3$ molecule with D_{3h} symmetry:

a) use group theory to find out symmetries for molecular orbitals involved in:

i) σ-bonding system.

ii) π-bonding system (out-of-plane)

b) Use the $\boldsymbol{D_{3h}}$ Character Table to find out which orbitals of B atom will be used in σ- and π-bonding systems in the BF_3 molecule.

c) Construct a schematic molecular orbital energy level diagram for BF_3molecule, showing both σ- and π-bonding systems together.

3) Consider the H_2O molecule with $\boldsymbol{C_{2v}}$ symmetry:

a) Use group theory to find out symmetries for LGOs used in σ-bonding for the molecule.

b) Construct a schematic molecular orbital energy level diagram for the H_2O molecule.

4) Find out symmetries for out-of-plane π-bonding molecular orbitals involved in each of the following cyclic systems:

$C_3H_3^+$ ($\boldsymbol{D_{3h}}$); C_4H_4 ($\boldsymbol{D_{4h}}$).

(Hint: In each cyclic system, use the set of p_z atomic orbitals for C atoms present as a starting basis, perform all symmetry operations on the basis to construct the suitable reducible representation and use the reduction formula to reduce the representation).

5) Use the projection operator method to find out wave functions and balloon shapes for:

a) LGOs used for σ-bonding system in H_2O molecule.

b) π-LGOs in a $\boldsymbol{D_{4h}}$ $M(CO)_4$ symmetry

c) σ- and out-of-plane π-LGOs used for M-CO bonding only in a $\boldsymbol{D_{2h}}$ trans-$M(CO)_2L_2$ compound.