PRINCIPLES OF INORGANIC CHEMISTRY

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Book: Principles of Inorganic Chemistry II (Nocera)

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CHAPTER OVERVIEW

1: Chapters

1.1: Symmetry Elements and Operations

Consider the symmetry properties of an object (e.g. atoms of a molecule, set of orbitals, vibrations). The collection of objects is commonly referred to as a basis set

- *classify* objects of the basis set into symmetry operations
- *symmetry* operations form a group
- *group* mathematically defined and manipulated by group theory

Definition: Symmetry Operation

A **symmetry operation** moves an object into an indistinguishable orientation

Definition: Symmetry Element

A **symmetry element** is a point, line or plane about which a symmetry operation is performed

There are five symmetry elements in 3D space, which will be defined relative to point with coordinate (x_1, y_1, z_1) :

1. **identity, E**

$$E\left(x_1, y_1, z_1\right) = \left(x_1, y_1, z_1\right) \tag{1.1.1}$$

2. **plane of reflection, σ**

3. **inversion, i**

$$\mathrm{i}\left(\mathrm{x}_1, \mathrm{y}_1, \mathrm{z}_1\right) = \left(-\mathrm{x}_1, -\mathrm{y}_1, -\mathrm{z}_1\right) \tag{1.1.2}$$

4. **proper rotation axis, $\mathbf{C_n}$** $\left(\text{where } \theta = \frac{2\pi}{n}\right)$

convention is a clockwise rotation of the point

$$\mathrm{C}_2(\mathrm{z})\left(\mathrm{x}_1, \mathrm{y}_1, \mathrm{z}_1\right) = \left(-\mathrm{x}_1, -\mathrm{y}_1, \mathrm{z}_1\right) \tag{1.1.3}$$

5. **improper rotation axis, $\mathbf{S_n}$**

two step operation: C_n followed by σ through plane ⊥ to C_n

$$\mathrm{S}_4(\mathrm{z})\left(\mathrm{x}_1, \mathrm{y}_1, \mathrm{z}_1\right) = \sigma(\mathrm{xy})\mathrm{C}_4(\mathrm{z})\left(\mathrm{x}_1, \mathrm{y}_1, \mathrm{z}_1\right) = \sigma(\mathrm{xy})\left(\mathrm{y}_1, -\mathrm{x}_1, \mathrm{z}_1\right) = \left(\mathrm{y}_1, -\mathrm{x}_1 - \mathrm{z}_1\right) \tag{1.1.4}$$

Note: rotation of pt is clockwise; Corollary is that axes rotate counterclockwise relative to fixed point

In the example above, we took the **direct product** of two operators:

$\sigma_\mathrm{h} \cdot \mathrm{C_n} = \mathrm{S_n}$ $\downarrow$ Horizontal mirror plane (normal to C_n)	for n even : $S_n^n = C_n^n \cdot \sigma_h^n = E \cdot E = E$ for n odd: $S_n^n = C_n^n \cdot \sigma_h^n = E \cdot \sigma_h = \sigma_h$ $S_n^{2n} = C_n^{2n} \cdot \sigma_h^{2n} = E \cdot E = \sigma_h$ for m even: $\mathrm{S_n^m} = \mathrm{C_n^m} \cdot \sigma_\mathrm{h}^\mathrm{m} = \mathrm{C_n^m}$ for m odd: $S_n^m = C_n^m \cdot \sigma_h^m = C_n^m \cdot \sigma_h = S_n^m$

Symmetry operations may be represented as matrices. Consider the vector $\overline{\mathbf{v}}$

1. identity: $E \begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix} = \begin{bmatrix} & ? & \end{bmatrix} \begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix} = \begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix}$

matrix satisfying this condition is:

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$\therefore \mathrm{E} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$ ... E is always the unit matrix

2. reflection: $\sigma(\mathrm{xy}) \begin{bmatrix} \mathrm{x}_1 \\ \mathrm{y}_1 \\ \mathrm{z}_1 \end{bmatrix} = \begin{bmatrix} \mathrm{x}_1 \\ \mathrm{y}_1 \\ -\mathrm{z}_1 \end{bmatrix} \quad \therefore \sigma(\mathrm{xy}) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$

similarly similarly $\sigma(\mathrm{xz}) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$ and $\sigma(\mathrm{yz}) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$

3. inversion: $\mathrm{i} \begin{bmatrix} \mathrm{x}_1 \\ \mathrm{y}_1 \\ \mathrm{z}_1 \end{bmatrix} = \begin{bmatrix} -\mathrm{x}_1 \\ -\mathrm{y}_1 \\ -\mathrm{z}_1 \end{bmatrix} \quad \therefore \quad \mathrm{i} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$

4. proper rotation axis:

because of convention, φ, and hence z_i, is not transformed under $C_n(\theta)$ ∴ projection into xy plane need only be considered… i.e., rotation of vector $v(x_i,y_i)$ through θ

$x_1 = \vec{v}\cos\alpha$ $y_1 = \vec{v}\sin\alpha$	$C_n(\theta)$	$\mathrm{x}_2 = \bar{\mathrm{v}}\cos[-(\theta-\alpha)] = \bar{\mathrm{v}}\cos(\theta-\alpha)$ $y_2 = \vec{v}\sin[-(\theta-\alpha)] = -\bar{v}\sin(\theta-\alpha)$

using identity relations:

$x_2 = \vec{v}\cos(\theta-\alpha) = \vec{v}\cos\theta\cos\alpha + \vec{v}\sin\theta\sin\alpha = x_1\cos\theta + y_1\sin\theta$

$y_2 = -\bar{v}\sin(\theta-\alpha) = -[\bar{v}\sin\theta\cos\alpha - \bar{v}\cos\theta\sin\alpha] = -x_1\sin\theta + y_1\cos\theta$

Reformulating in terms of matrix representation:

$$\mathrm{C_n}(\theta) \begin{bmatrix} \mathrm{x}_1 \\ \mathrm{y}_1 \\ \mathrm{z}_1 \end{bmatrix} = \begin{bmatrix} \mathrm{x}_1\cos\theta + \mathrm{y}_1\sin\theta \\ -\mathrm{x}_1\sin\theta + \mathrm{y}_1\cos\theta \\ \mathrm{z}_1 \end{bmatrix}$$

$$\therefore \mathrm{C_n}(\theta) = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \text{where } \theta = \frac{2\pi}{\mathrm{n}}$$

Note… the rotation above is clockwise, as discussed by HB (pg 39). Cotton on pg. 73 solves for the counterclockwise rotation… and presents the clockwise result derived above. To be consistent with HB (and math classes) we will rotate *clockwise* as the convention.

The above matrix representation is completely general for any rotation θ…

Example: $C_3, \theta = \frac{2\pi}{n}$

$$C_3 = \begin{bmatrix} \cos\frac{2\pi}{3} & \sin\frac{2\pi}{3} & 0 \\ -\sin\frac{2\pi}{3} & \cos\frac{2\pi}{3} & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{1.1.5}$$

5. improper rotation axis :

$\sigma_h \cdot \mathrm{C_n}(\theta) = \mathrm{S_n}(\theta)$

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \cdot \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & -1 \end{bmatrix} \tag{1.1.6}$$

Like operators themselves, matrix operations may be manipulated with simple matrix algebra…above direct product yields matrix representation for $\mathrm{S_n}$.

Another example:

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \cdot \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \tag{1.1.7}$$

σ_{xy} ($\equiv \sigma_h$) · C_2 (z) = i

1.2: Operator Properties and Mathematical Groups

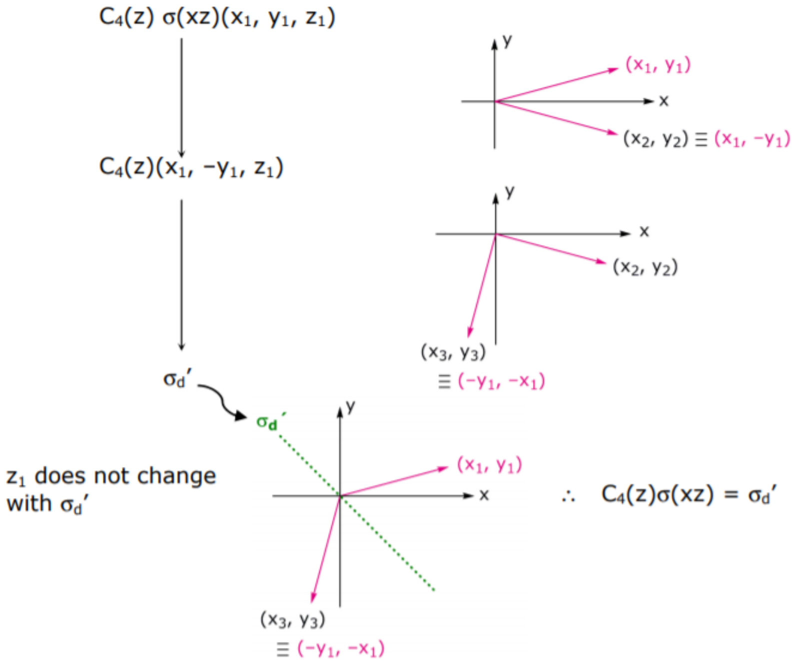
The **inverse** of A (defined as $(A)^{-1}$) is B if A · B = E

For each of the five symmetry operations:

$$(E)^{-1}=E\Longrightarrow(E)^{-1}\cdot E=E\cdot E=E$$
$$(\sigma)^{-1}=\sigma\Longrightarrow(\sigma)^{-1}\cdot\sigma=\sigma\cdot\sigma=E$$
$$(i)^{-1}=i\Longrightarrow(i)^{-1}\cdot i=i\cdot i=E$$
$$\left(C_n^m\right)^{-1}=C_n^{n-m}\Longrightarrow\left(C_n^m\right)^{-1}\cdot C_n^m=C_n^{n-m}\cdot C_n^m=C_n^n=E$$
$$\text{e.g. }\left(C_5^2\right)^{-1}=C_5^3\text{ since }C_5^2\cdot C_5^3=E$$
$$\left(S_n^m\right)^{-1}=S_n^{n-m}(n\text{ even })\Longrightarrow\left(S_n^m\right)^{-1}\cdot S_n^m=S_n^{n-m}\cdot S_n^m=S_n^n=C_n^n\cdot\sigma_h^n=E$$
$$\left(S_n^m\right)^{-1}=S_n^{2n-m}(n\text{ odd })\Longrightarrow\left(S_n^m\right)^{-1}\cdot S_n^m=S_n^{2n-m}\cdot S_n^m=S_n^{2n}=C_n^{2n}\cdot\sigma_h^{2n}=E$$

Two operators **commute** when A · B = B · A

Example: Do $C_4(z)$ and σ(xz) commute?

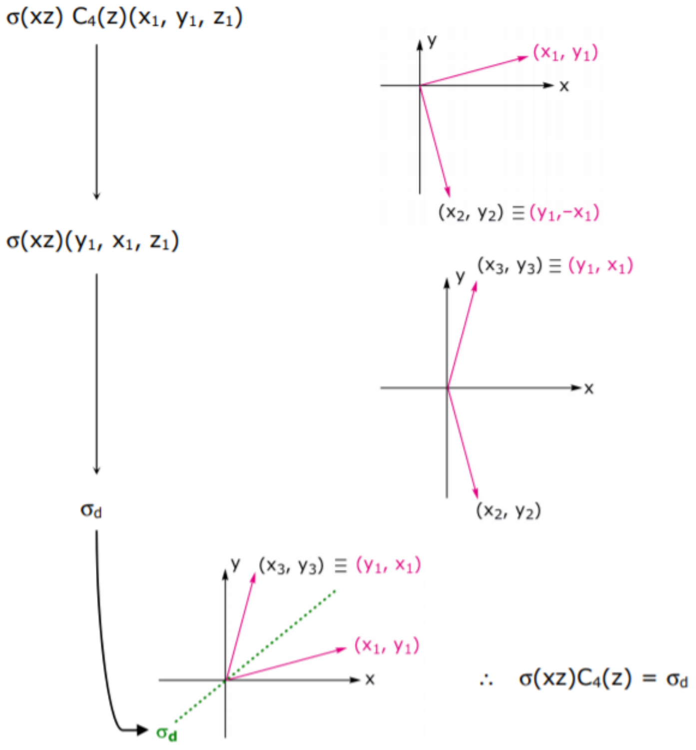


… or analyzing with matrix representations,

$$\begin{bmatrix}0&1&0\\-1&0&0\\0&0&1\end{bmatrix}\cdot\begin{bmatrix}1&0&0\\0&-1&0\\0&0&1\end{bmatrix}=\begin{bmatrix}0&-1&0\\-1&0&0\\0&0&1\end{bmatrix}$$

$C_4(z)\cdot\sigma_{xz}=\sigma_d{}'$

Now applying the operations in the inverse order,



… or analyzing with matrix representations,

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \cdot \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\sigma_{xz} \cdot C_4(z) = \sigma_d$$

$$\therefore \quad C_4(z)\sigma(xz) = \sigma'_d \neq \sigma(xz)C_4(z) = \sigma_d \Rightarrow \text{ so } C_4(z) \text{ does not commute with } \sigma(xz) \tag{1.2.1}$$

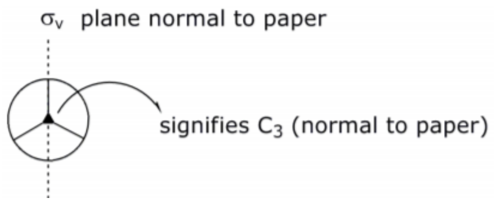
A collection of operations are a mathematical group when the following conditions are met:

- **closure**: all binary products must be members of the group
- **identity**: a group must contain the identity operator
- **inverse**: every operator must have an inverse
- **associativity**: associative law of multiplication must hold

$$(A \cdot B) \cdot C = A \cdot (B \cdot C \tag{1.2.2}$$

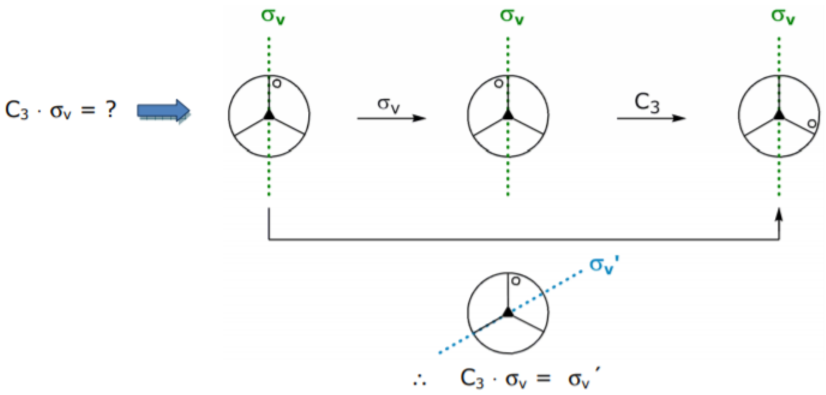
(note: commutation not required… groups in which all operators do commute are called **Abelian**)

Consider the operators C_3 and σ_v. These do not constitute a group because identity criterion is not satisfied. Do E, C_3, σ_v form a group? To address this question, a stereographic projection (featuring critical operators) will be used:



So how about closure?

$C_3 \cdot C_3 = C_3{}^2$ (so $C_3{}^2$ needs to be included as part of the group)



Thus E, C_3 and σ_v are not closed and consequently these operators do not form a group. Is the addition of $C_3{}^2$ and σ_v´ sufficient to define a group? In other terms, are there any other operators that are generated by C_3 and σ_v?

… the proper rotation axis, C_3:

$$\begin{gathered} C_3 \\ C_3 \cdot C_3 = C_3^2 \\ C_3 \cdot C_3 \cdot C_3 = C_3^2 \cdot C_3 = C_3 \cdot C_3^2 = E \\ C_3 \cdot C_3 \cdot C_3 \cdot C_3 = E \cdot C_3 = C_3 \end{gathered}$$

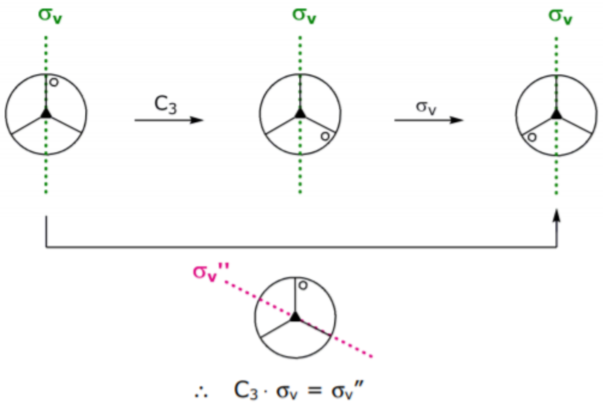
etc.

$\therefore C_3$ is the generator of E, C_3 and C_3^2, note: these three operators form a group

… for the plane of reflection, σ_v

$$\begin{gathered} \sigma_v \\ \sigma_v \cdot \sigma_v = E \\ \sigma_v \cdot \sigma_v \cdot \sigma_v = E \cdot \sigma_v = \sigma_v \end{gathered}$$

etc.
So we obtain no new information here. But there is more information to be gained upon considering C_3 and σ_v. Have already seen that $C_3 \cdot \sigma_v = \sigma_v$' … how about $\sigma_v \cdot C_3$



Will discover that no new operators may be generated. Moreover one finds

$$\begin{array}{ccccccc} & E^{-1} & C_3^{-1} & \left(C_3^2\right)^{-1} & \sigma_v^{-1} & \left(\sigma_v'\right)^{-1} & \left(\sigma_v''\right)^{-1} \\ \text{inverses} & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\ & E & C_3^2 & C_3 & \sigma_v & \sigma_v' & \sigma_v'' \end{array}$$

The above group is closed, i.e. it contains the identity operator and meets inverse and associativity conditions. Thus the above set of operators constitutes a mathematical group (note that the group is not Abelian).

Some definitions:

Operators C_3 and σ_v are called **generators** for the group since every element of the group can be expressed as a product of these operators (and their inverses).

The **order** of the group, designated h, is the number of elements. In the above example, h = 6.

Groups defined by a single generator are called **cyclic** groups.

Example: C_3 → E, C_3, $C_3^{\ 2}$

As mentioned above, E, C_3, and C_3^2 meet the conditions of a group; they form a cyclic group. Moreover these three operators are a **subgroup** of E, C_3, $C_3^{\ 2}$, σ_v, σ_v’,σ_v”. The order of a subgroup must be a divisor of the order of its parent group. (Example $h_{subgroup}$ = 3, h_{group} = 6 … a divisor of 2.)

A **similarity transformation** is defined as: $v^{-1} \cdot A \cdot v = B$ where B is designated the similarity transform of A by x and A and B are **conjugates** of each other. A complete set of operators that are conjugates to one another is called a **class** of the group.

Let’s determine the classes of the group defined by E, C_3, $C_3^{\ 2}$, σ_v, σ_v’,σ_v”… the analysis is facilitated by the construction of a multiplication table

$$\begin{array}{c|cccccc}
 & E & C_3 & C_3^2 & \sigma_v & \sigma_v' & \sigma_v'' \\
\hline
E & E & C_3 & C_3^2 & \sigma_v & \sigma_v' & \sigma_v'' \\
C_3 & C_3 & C_3^2 & E & \sigma_v' & \sigma_v'' & \sigma_v \\
C_3^2 & C_3^2 & E & C_3 & \sigma_v'' & \sigma_v & \sigma_v' \\
\sigma_v & \sigma_v & \sigma_v'' & \sigma_v' & E & C_3^2 & C_3 \\
\sigma_v' & \sigma_v' & \sigma_v & \sigma_v'' & C_3 & E & C_3^2 \\
\sigma_v'' & \sigma_v'' & \sigma_v' & \sigma_v & C_3^2 & C_3 & E
\end{array} \tag{1.2.3}$$

may construct easily using stereographic projections

$$\begin{gathered}
E^{-1} \cdot C_3 \cdot E = E \cdot C_3 \cdot E = C_3 \\
C_3^{-1} \cdot C_3 \cdot C_3 = C_3^2 \cdot C_3 \cdot C_3 = E \cdot C_3 = C_3 \\
\left(C_3^2\right)^{-1} \cdot C_3 \cdot C_3^2 = C_3 \cdot C_3 \cdot C_3^2 = C_3 \cdot E = C_3 \\
\sigma_v^{-1} \cdot C_3 \cdot \sigma_v = \sigma_v \cdot C_3 \cdot \sigma_v = \sigma_v \cdot \sigma_v' = C_3^2 \\
(\sigma_v')^{-1} \cdot C_3 \cdot \sigma_v' = \sigma_v' \cdot C_3 \cdot \sigma_v' = \sigma_v' \cdot \sigma_v'' = C_3^2 \\
(\sigma_v'')^{-1} \cdot C_3 \cdot \sigma_v'' = \sigma_v'' \cdot C_3 \cdot \sigma_v'' = \sigma_v'' \cdot \sigma_v = C_3^2
\end{gathered}$$

∴ C_3 and $C_3^{\ 2}$ from a class

Performing a similar analysis on σ_v will reveal that σ_v, σ_v’ and σ_v’’ form a class and E is in a class by itself. Thus there are three classes:

$$E, \left(C_3, C_3^2\right), \left(\sigma_v, \sigma_v', \sigma_v''\right)$$

Additional properties of transforms and classes are:

- no operator occurs in more than one class
- order of all classes must be integral factors of the group’s order
- in an Abelian group, each operator is in a class by itself.

1.3: Irreducible Representations and Character Tables

Similarity transformations yield **irreducible representations**, Γ_i, which lead to the useful tool in group theory – the **character table**. The general strategy for determining Γ_i is as follows: **A**, **B** and **C** are matrix representations of symmetry operations of an arbitrary basis set (i.e., elements on which symmetry operations are performed). There is some similarity transform operator such that

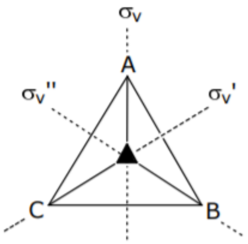
$$\begin{aligned} \boldsymbol{A}' &= v^{-1} \cdot \boldsymbol{A} \cdot v \\ \boldsymbol{B}' &= v^{-1} \cdot \boldsymbol{B} \cdot v \\ \boldsymbol{C}' &= v^{-1} \cdot \boldsymbol{C} \cdot v \end{aligned} \tag{1.3.1}$$

where *v* uniquely produces **block-diagonalized** matrices, which are matrices possessing square arrays along the diagonal and zeros outside the blocks

$$\mathbf{A}' = \begin{bmatrix} \mathrm{A}_1 & & \\ & \mathrm{A}_2 & \\ & & \mathrm{A}_3 \end{bmatrix} \quad \mathbf{B}' = \begin{bmatrix} \mathrm{B}_1 & & \\ & \mathrm{B}_2 & \\ & & \mathrm{B}_3 \end{bmatrix} \quad \mathbf{C}' = \begin{bmatrix} \mathrm{C}_1 & & \\ & \mathrm{C}_2 & \\ & & \mathrm{C}_3 \end{bmatrix} \tag{1.3.2}$$

Matrices **A**, **B**, and **C** are **reducible**. Sub-matrices A_i, B_i and C_i obey the same multiplication properties as **A**, **B** and **C**. If application of the similarity transform does not further block-diagonalize **A'**, **B'** and **C'**, then the blocks are **irreducible representations**. The **character** is the sum of the diagonal elements of Γ_i.

As an example, let's continue with our exemplary group: E, C_3, $C_3{}^2$, σ_v, σ_v', σ_v'' by defining an arbitrary basis … a triangle



The basis set is described by the triangles vertices, points A, B and C. The transformation properties of these points under the symmetry operations of the group are:

$$E \begin{bmatrix} A \\ B \\ C \end{bmatrix} = \begin{bmatrix} A \\ B \\ C \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} A \\ B \\ C \end{bmatrix} \qquad \sigma_V \begin{bmatrix} A \\ B \\ C \end{bmatrix} = \begin{bmatrix} A \\ C \\ B \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} A \\ B \\ C \end{bmatrix} \tag{1.3.3}$$

$$C_3 \begin{bmatrix} A \\ B \\ C \end{bmatrix} = \begin{bmatrix} B \\ C \\ A \end{bmatrix} = \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} A \\ B \\ C \end{bmatrix} \qquad \sigma_V' \begin{bmatrix} A \\ B \\ C \end{bmatrix} = \begin{bmatrix} B \\ A \\ C \end{bmatrix} = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} A \\ B \\ C \end{bmatrix} \tag{1.3.4}$$

$$C_3^2 \begin{bmatrix} A \\ B \\ C \end{bmatrix} = \begin{bmatrix} C \\ A \\ B \end{bmatrix} = \begin{bmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix} \begin{bmatrix} A \\ B \\ C \end{bmatrix} \qquad \sigma_V'' \begin{bmatrix} A \\ B \\ C \end{bmatrix} = \begin{bmatrix} C \\ B \\ A \end{bmatrix} = \begin{bmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{bmatrix} \begin{bmatrix} A \\ B \\ C \end{bmatrix} \tag{1.3.5}$$

These matrices are not block-diagonalized, however a suitable similarity transformation will accomplish the task,

$$v = \begin{bmatrix} \frac{1}{\sqrt{3}} & \frac{2}{\sqrt{6}} & 0 \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{2}} \end{bmatrix} \quad ; \quad v^{-1} = \begin{bmatrix} \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} \\ \frac{2}{\sqrt{6}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{6}} \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{bmatrix}$$

Applying the similarity transformation with C_3 as the example,

$$v^{-1}\cdot\boldsymbol{C}_3\cdot v=\begin{bmatrix}\frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}}\\ \frac{2}{\sqrt{6}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{6}}\\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}}\end{bmatrix}\cdot\begin{bmatrix}0 & 1 & 0\\ 0 & 0 & 1\\ 1 & 0 & 0\end{bmatrix}\cdot\begin{bmatrix}\frac{1}{\sqrt{3}} & \frac{2}{\sqrt{6}} & 0\\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & \frac{1}{\sqrt{2}}\\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{2}}\end{bmatrix}$$

$$\begin{bmatrix}\frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}}\\ \frac{2}{\sqrt{6}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{6}}\\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}}\end{bmatrix}\cdot\begin{bmatrix}\frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & \frac{1}{\sqrt{2}}\\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{2}}\\ \frac{1}{\sqrt{3}} & \frac{2}{\sqrt{6}} & 0\end{bmatrix}=\begin{bmatrix}1 & 0 & 0\\ 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2}\\ 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2}\end{bmatrix}=\boldsymbol{C}_3^*$$

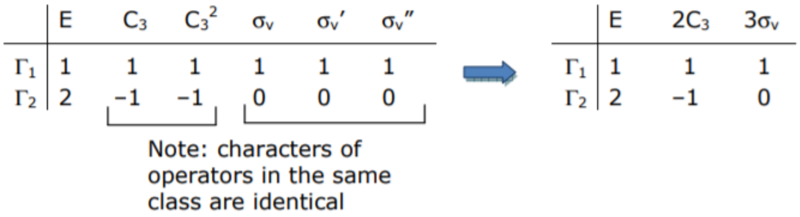
if $v^{-1}\cdot \mathbf{C_3^*}\cdot v$ is applied again, the matrix is not block diagonalized any further. The same diagonal sum is obtained *though off-diagonal elements may change). In this case, $\mathbf{C_3^*}$ is an irreducible representation, Γ_i.

The similarity transformation applied to other reducible representations yields:

$$\begin{gathered}v^{-1}\cdot\mathbf{E}\cdot v=\mathbf{E}^*=\left[\begin{array}{c:cc}1 & 0 & 0\\ \hdashline 0 & 1 & 0\\ 0 & 0 & 1\end{array}\right]\qquad v^{-1}\cdot\mathbf{C_3}^2\cdot v=\mathbf{C_3}^2*=\left[\begin{array}{c:cc}1 & 0 & 0\\ 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2}\\ 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2}\end{array}\right]\\ v^{-1}\cdot\boldsymbol{\sigma}_\mathrm{v}\cdot v=\boldsymbol{\sigma}_\mathrm{v}{}^*=\left[\begin{array}{c:cc}1 & 0 & 0\\ \hdashline 0 & 1 & 0\\ 0 & 0 & -1\end{array}\right]\qquad v^{-1}\cdot\boldsymbol{\sigma}_\mathrm{v}{}''\cdot v=\boldsymbol{\sigma}_\mathrm{v}{}'^*=\left[\begin{array}{c:cc}1 & 0 & 0\\ 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2}\\ 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2}\end{array}\right]\\ v^{-1}\cdot\sigma_v{}'\cdot v=\sigma_v{}^*=\left[\begin{array}{c:cc}1 & 0 & 0\\ \hdashline 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2}\\ 0 & \frac{\sqrt{3}}{2} & \frac{1}{2}\end{array}\right]\end{gathered}\tag{1.3.6}$$

As above, the block-diagonalized matrices do not further reduce under reapplication of the similarity transform. All are Γ_{irr} **s**.

Thus a 3 × 3 reducible representation, Γ_{red}, has been decomposed under a similarity transformation into a 1 (1 × 1) and 1 (2 × 2) block-diagonalized irreducible representations, Γi. The traces (i.e. sum of diagonal matrix elements) of the Γ_i's under each operation yield the **characters** (indicated by χ) of the representation. Taking the traces of each of the blocks:



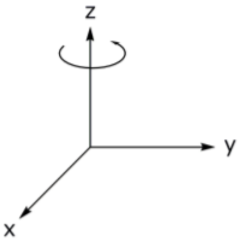
	E	C_3	$C_3{}^2$	σ_v	σ_v'	σ_v''
Γ_1	1	1	1	1	1	1
Γ_2	2	−1	−1	0	0	0

Note: characters of operators in the same class are identical

	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	2	−1	0

This collection of characters for a given irreducible representation, under the operations of a group is called a **character table**. As this example shows, from a completely arbitrary basis and a similarity transform, a character table is born.

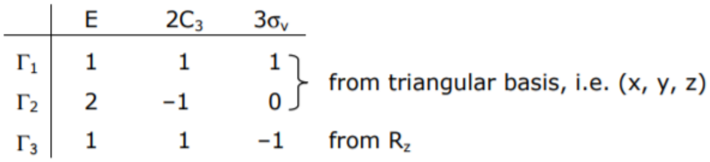
The triangular basis set does not uncover all Γ_{irr} of the group defined by {E, C_3, $C_3{}^2$, σ_v, σ_v', σ_v''}. A triangle represents Cartesian coordinate space (x,y,z) for which the Γ_is were determined. May choose other basis functions in an attempt to uncover other Γ_is. For instance, consider a rotation about the z-axis,



The transformation properties of this basis function, R_z, under the operations of the group (will choose only 1 operation from each class, since characters of operators in a class are identical):

$$\text{E: } R_z \rightarrow R_z \quad C_3 : R_2 \rightarrow R_2 \quad \sigma_v(xy) : R_2 \rightarrow \overline{R}_2$$

Note, these transformation properties give rise to a Γ_i that is not contained in a triangular basis. A new (1 x 1) basis is obtained, Γ_3, which describes the transform properties for R_z. A summary of the Γ_i for the group defined by E, C_3, $C_3{}^2$, σ_v, σ_v', σ_v'' is:



	E	$2C_3$	$3\sigma_v$	
Γ_1	1	1	1	from triangular basis, i.e. (x, y, z)
Γ_2	2	−1	0	
Γ_3	1	1	−1	from R_z

Is this character table complete? Irreducible representations and their characters obey certain algebraic relationships. From these 5 rules, we can ascertain whether this is a complete character table for these 6 symmetry operations.

Five important rules govern irreducible representations and their characters:

Rule 1

The sum of the squares of the dimensions, ℓ, of irreducible representation Γ_i is equal to the order, h, of the group,

$$\sum_i \underbrace{\ell_i{}^2}_{\text{order of matrix representation of } \Gamma_i \text{ (e.g. } \ell = 2 \text{ for a } 2 \times 2)} = \ell_1{}^2 + \ell_2{}^2 + \ell_3{}^2 + \ldots = h$$

Since the character under the identity operation is equal to the dimension of Γ_i (since E is always the unit matrix), the rule can be reformulated as,

$$\sum_i \Big[\underbrace{x_i(E)}_{\text{character under E}} \Big]^2 = h$$

Rule 2

The sum of squares of the characters of irreducible representation Γ_i equals h

$$\sum_R \Big[\underbrace{x_i(R)}_{\text{character of } \Gamma_i \text{ under operation R}} \Big]^2 = h$$

Rule 3

Vectors whose components are characters of two different irreducible representations are orthogonal

$$\sum_R [x_i(R)]\,[x_j(R)] = 0 \quad \text{for} \quad i \neq j$$

Rule 4

For a given representation, characters of all matrices belonging to operations in the same class are identical

Rule 5

The number of Γ_is of a group is equal to the number of classes in a group.

With these rules one can algebraically construct a character table. Returning to our example, let’s construct the character table in the absence of an arbitrary basis:

Rule 5: E (C_3, $C_3{}^2$) (σ_v, σ_v’, σ_v”) … 3 classes ∴ 3 Γ_is

Rule 1: $\ell_1^2+\ell_2^2+\ell_3^2=6 \quad \therefore \ell_1=\ell_2=1, \ell_2=2$

Rule 2: All character tables have a totally symmetric representation. Thus one of the irreducible representations, Γ_i, possesses the character set $\chi_1(E) = 1$, $\chi_1(C_3, C_3{}^2) = 1$, $\chi_1(\sigma_v, \sigma_v', \sigma_v'') = 1$. Applying Rule 2, we find for the other irreducible representation of dimension 1,

$$1\cdot\chi_1(E)\cdot\chi_2(E) + \overset{\swarrow}{2}\cdot\chi_1(C_3)\cdot\chi_2(C_3) + \overset{\nwarrow}{3}\cdot\chi_1(\sigma_v)\cdot\chi_2(\sigma_v) = 0$$

consequence of Rule 4

$$1\cdot 1\cdot x_2(E)+2\cdot 1\cdot x_2\left(C_3\right)+3\cdot 1\cdot x_2\left(\sigma_v\right)=0$$

Since $\chi_2(E) = 1$,

$$1+2\cdot x_2\left(C_3\right)+3\cdot x_2\left(\sigma_v\right)=0 \quad \therefore \quad \chi_2\left(C_3\right)=1, \chi_2\left(\sigma_v\right)=-1$$

For the case of Γ_3 ($\ell_3 = 2$) there is not a unique solution to Rule 2

$$2+2\cdot\chi_3\left(C_3\right)+3\cdot\chi_3\left(\sigma_v\right)=0$$

However, application of Rule 2 to Γ_3 gives us one equation for two unknowns. Have several options to obtain a second independent equation:

Rule 1: $1\cdot 2^2+2\left[\chi_3\left(C_3\right)\right]^2+3\left[\chi_3\left(\sigma_v\right)\right]^2=6$

Rule 3: $1\cdot 1\cdot 2+2\cdot 1\cdot x_3\left(C_3\right)+3\cdot 1\cdot x_3\left(\sigma_v\right)=0$
or
$1\cdot 1\cdot 2+2\cdot 1\cdot x_3\left(C_3\right)+3\cdot(-1)\cdot x_3\left(\sigma_v\right)=0$

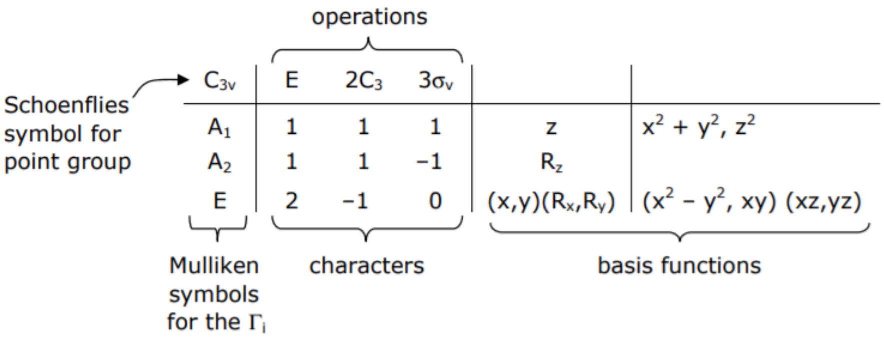
Solving simultaneously yields $\chi_3\left(C_3\right)=-1, \chi_3\left(\sigma_x\right)=0$

Thus the same result shown on pg 4 is obtained:

$$\begin{array}{c|ccc} & \mathrm{E} & 2\mathrm{C}_3 & 3\sigma_{\mathrm{v}} \\ \hline \Gamma_1 & 1 & 1 & 1 \\ \Gamma_2 & 2 & -1 & 0 \\ \Gamma_3 & 1 & 1 & -1 \end{array} \tag{1.3.7}$$

Note, the derivation of the character table in this section is based solely on the properties of characters; the table was derived algebraically. The derivation on pg 4 was accomplished from first principles.

The complete character table is:



C_{3v}	E	2C_3	3σ_v		
A_1	1	1	1	z	$x^2 + y^2$, z^2
A_2	1	1	−1	R_z	
E	2	−1	0	(x,y)(R_x,R_y)	($x^2 - y^2$, xy) (xz,yz)

- Γ_is of:

$\ell = 1 \Longrightarrow A$ or B $\ell = 2 \Longrightarrow E$ $\ell = 3 \Longrightarrow T$	A is symmetric (+1) with respect to C_n B is antisymmetric (–1) with respect to C_n

- subscripts 1 and 2 designate Γ_is that are symmetric and antisymmetric, respectively to $\perp C_2$s; if $\perp C_2$s do not exist, then with respect to σ_v
- primes (’) and double primes (”) attached to Γ_is that are symmetric and antisymmetric, respectively, to σ_h
- for groups containing i, g subscript attached to Γis that are symmetric to i whereas u subscript designates Γis that are antisymmetic to i

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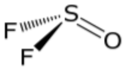
1.4: Molecular Point Groups 1

The symmetry properties of molecules (i.e. the atoms of a molecule form a basis set) are described by ***point groups***, since all the symmetry elements in a molecule will intersect at a common point, which is not shifted by any of the symmetry operations. There are also symmetry groups, called ***space groups***, which contain operators involving translational motion.

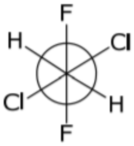
The point groups are listed below along with their distinguishing symmetry elements

C_1 : E (h = 1) $\Longrightarrow$ no symmetry

C_s : σ (h = 2) $\Longrightarrow$ only a mirror plane

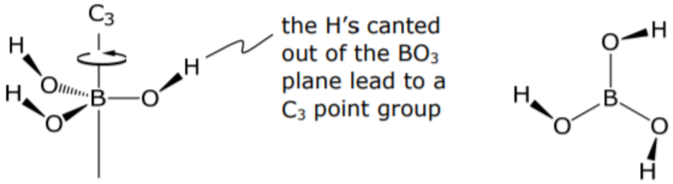


C_i : i (h = 2) $\Longrightarrow$ only an inversion center (rare point group)

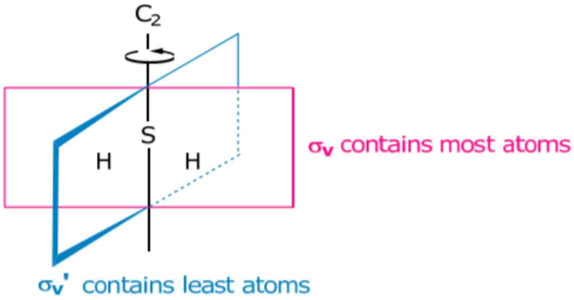


isomer of dichloro(difluoro)ethane

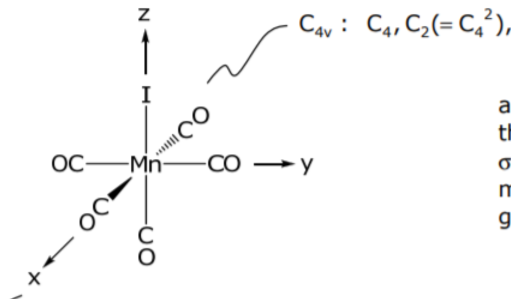
C_n : C_n and all powers up to $C_n{}^n = E$ (h = 2) $\Longrightarrow$ a cyclic point group



C_{nv} : C_n and $n\sigma_v$ (h = 2n) … by convention a σ_v contains C_n (as opposed to σ_h which is normal to C_n). For n even, there are $\frac{n}{2}\sigma_v$ and $\frac{n}{2}\sigma_{v_v}$ ' with the σ_v containing the most atoms and the σ_vs containing the least atoms



Consider a second example:

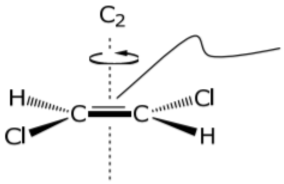


C_{4v} : $C_4, C_2(=C_4^{\,2}), C_4^{\,3}, 2\sigma_v, 2\sigma_d$

a dihedral mirror plane ... the σ_ds bisect the σ_vs (and σ_v'); the σ_d designation is more common in D point groups (see below)

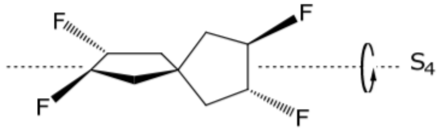
two σ_vs: the $\sigma(xz)$ and $\sigma(yz)$ mirror planes
two σ_ds bisect the $\sigma(xz)$ and $\sigma(yz)$ planes

C_{nh} : C_n and σ_h (normal to C_n) are generators of S_n operations as well (h = 2n)



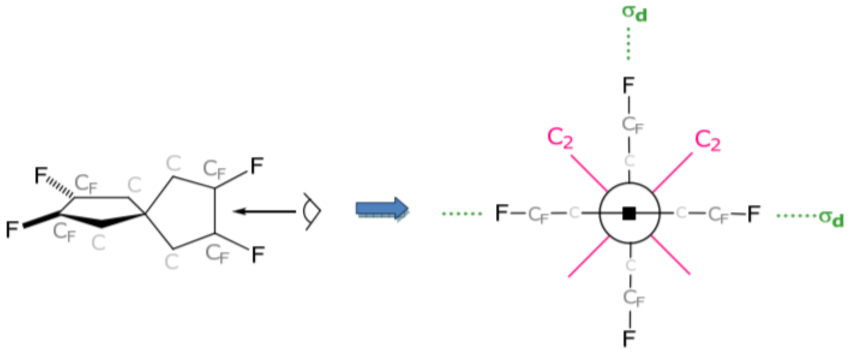
Note the inversion center;
generated from $C_2 \cdot \sigma_h = S_2 = i$

S_{2n} : S_{2n} and all powers up to $S_{2n}^{\;2n} = E$ (h = 2n).



S_{2n} is a generator; for this example, the generator S_4 gives rise to C_2 (= $S_4^{\,2}$), $S_4^{\,3}$, E(= $S_4^{\,4}$)

The F’s do not lie in the plane of the cyclopentane rings. If they did, then other symmetry operations arise; these are easiest to see by looking down the line indicated below:



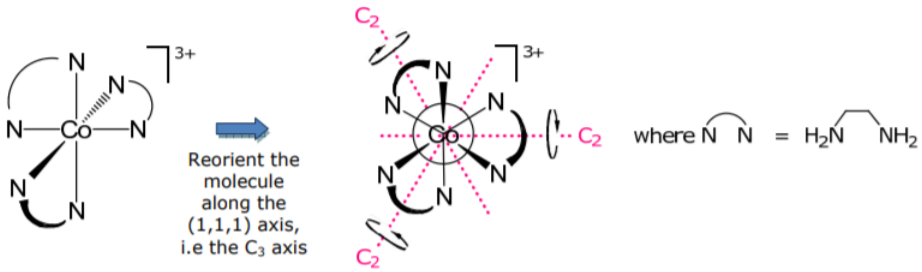
Note S_n, where n is odd, is redundant with C_{nh} because $S_n^{\;n} = \sigma_h$ for n odd. As an example consider a S_3 point group. S_3 is the generator for S_3, $S_3^{\;2}$ (= $C_3^{\;2}$) $S_3^{\;3}$ (= σ_h), $S_3^{\;4}$ (= C_3), $S_3^{\;5}$, $S_3^{\;6}$ (= E). The C_3’s and σ_h are the distinguishing elements of the C_{3h} point group.

1.5: Molecular Point Groups 2

The D point groups are distiguished from C point groups by the presence of rotation axes that are perpindicular to the principal axis of rotation.

D_n : C_n and $n\perp C_2$ ($h = 2n$)

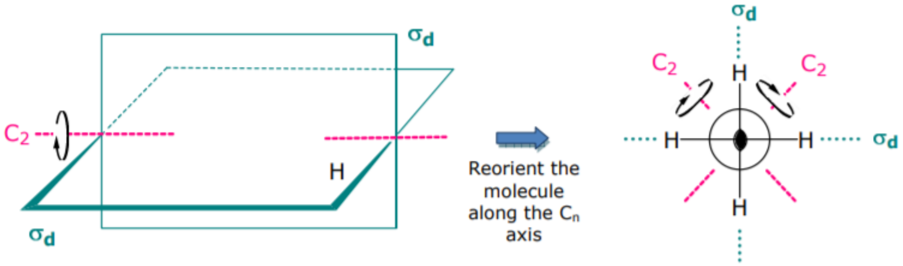
Example: $Co(en)_3{}^{3+}$ is in the D_3 point group,



In identifying molecules belonging to this point group, if a C_n is present and one $\perp C_2$ axis is identified, then there must necessarily be $(n–1)\perp C_2$s generated by rotation about C_n.

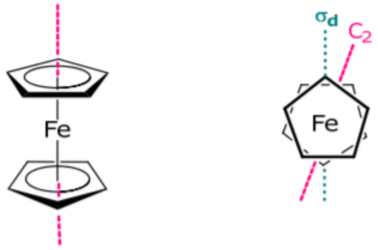
D_{nd} : C_n, $n\perp C_2$, $n\sigma_d$ (dihedral mirror planes bisect the $\perp C_2$s)

Example: allene is in the D_{2d} point group,



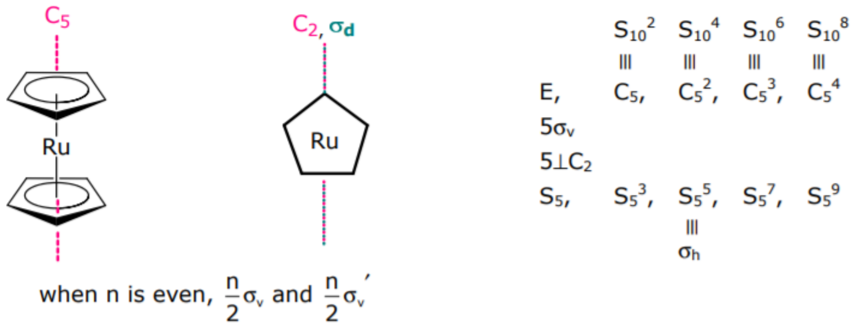
Two C_2s bisect σ_ds. The example on the bottom on pg 3 of the Lecture 4 notes was a harbinger of this point group. As indicated there, it is often easier to see these perpendicular C_2s by reorienting the molecule along the principal axis of rotation.

Note: D_{nd} point groups will contain i, when n is odd



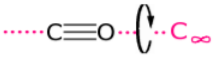
$S_{10}{}^2$ $S_{10}{}^4$ $S_{10}{}^6$ $S_{10}{}^8$
$\equiv$ $\equiv$ $\equiv$ $\equiv$
E C_5 $C_5{}^2$ $C_5{}^3$ $C_5{}^4$
$5\sigma_d$ (generated with C_5 axis)
$5\perp C_2$ (generated with C_5 axis)
S_{10}, $S_{10}{}^3$, $S_{10}{}^5$, $S_{10}{}^7$, $S_{10}{}^9$
$\equiv$
i

D_{nh} : C_n, $n\perp C_2$, $n\sigma_v$, σ_h ($h = 4n$)



$C_{\infty v}$: C_∞ and $\infty\sigma_v$ ($h = \infty$)

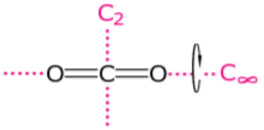
linear molecules without an inversion center



a σ_v is easily identified as the plane of the paper, by virtue of the C_∞, $\infty\sigma_v$s are generated

$D_{\infty h}$: C_∞, $\infty\perp C_2$, $\infty\sigma_v$, σ_h, i ($h = \infty$)

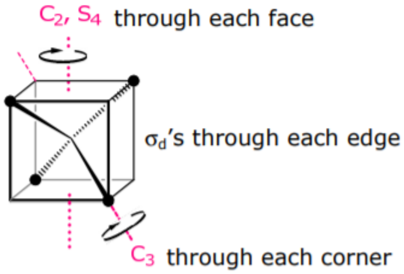
linear molecules with an inversion center



the C_∞, generates $\infty\sigma_v$ and ∞C_2

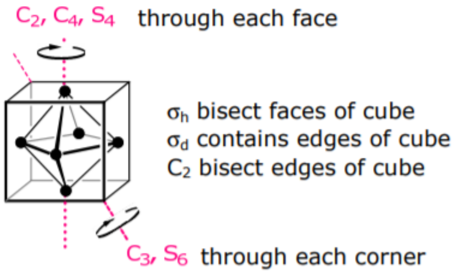
when working with this point group, it is often convenient to drop to D_{2h} and then correlate up to $D_{\infty h}$

T_d : E, $8C_3$, $3C_2$, $6S_4$, $6\sigma_d$ ($h = 24$)



a cubic point group; the cubic nature of the point group is easiest to visualize by inscribing the tetrahedron within a cube

O_h : E, $8C_3$, $6C_2$, $6C_4$, $3C_2$ ($=C_4^{\,2}$), i, $6S_4$, $8S_6$, $3\sigma_h$, $6\sigma_d$ ($h = 48$)



a cubic point group; an octahedron inscribed within a cube

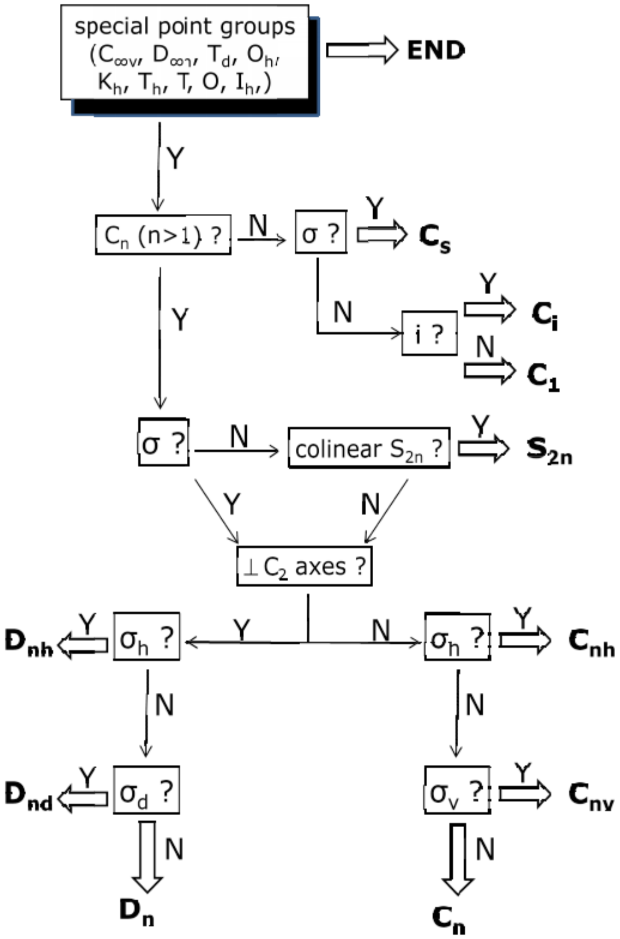
O : E, 8C_3, 6C_2, 6C_4, 3C_2 (=$C_4{}^2$)
A pure rotational subgroup of O_h, contains only the C_n's of O_h point group
T : E, 8C_3, 3C_2
A pure rotational subgroup of T_d, contains only the C_n's of T_d point group

O and T are rare point groups; whereas few molecules possess this symmetry, they are mathematically useful for molecules of O_h and T_d, respectively

I_h : generators are C_3, C_5, i (h = 120) ⟹ the icosahedral point group

K_h : generators are C_φ, C_φ', i (h = ∞) ⟹ the spherical point group

Flow chart for assigning molecular point groups:



1.6: LCAO and Hückel Theory 1 (Eigenfunctions)

A common approximation employed in the construction of molecular orbitals (MOs) is the **linear combination of atomic orbitals (LCAOs)**. In the LCAO method, the kth molecular orbital, ψ_k, is expanded in an atomic orbital basis,

$$|\psi_k\rangle = c_a\phi_a + c_b\phi_b + \ldots c_i\phi_i \tag{1.6.1}$$

where the ϕ_is are normalized atomic wavefunctions and . Solving Schrödinger's equation and substituting for ψ_k yields,

$$H\psi_k = E\psi_k$$
$$|H - E|\psi_k\rangle = 0$$

Substitute Equation 1.6.1

$$|H - E|c_a\phi_a + c_b\phi_b + \ldots + c_i\phi\rangle = 0 \tag{1.6.2}$$

Left-multiplying by each ϕ_i yields a set of i linear homogeneous equations,

$$\begin{aligned} \mathrm{c_a}\,\langle\phi_\mathrm{a}|\mathrm{H}-\mathrm{E}|\phi_\mathrm{a}\rangle + \mathrm{c_b}\,\langle\phi_\mathrm{a}|\mathrm{H}-\mathrm{E}|\phi_\mathrm{b}\rangle + \ldots + \mathrm{c}_i\,\langle\phi_\mathrm{a}|\mathrm{H}-\mathrm{E}|\phi_i\rangle &= 0 \\ c_a\,\langle\phi_b|H-E|\phi_a\rangle + c_b\,\langle\phi_b|H-E|\phi_b\rangle + \ldots + c_i\,\langle\phi_b|H-E|\phi_i\rangle &= 0 \\ &\vdots \\ c_a\,\langle\phi_i|H-E|\phi_a\rangle + c_b\,\langle\phi_i|H-E|\phi_b\rangle + \ldots + c_i\langle\phi_i|H-E|\phi_i\rangle &= 0 \end{aligned}$$

Solving the secular determinant,

$$\begin{matrix} \mathrm{H_{aa}-ES_{aa}} & \mathrm{H_{ab}-ES_{ab}} & \cdots & \cdots & \mathrm{H_{ai}-ES_{ai}} \\ \mathrm{H_{ba}-ES_{ba}} & \mathrm{H_{bb}-ES_{bb}} & \cdots & \cdots & \mathrm{H_{bi}-ES_{bi}} \\ \vdots & & \ddots & & \vdots \\ \vdots & & & \ddots & \vdots \\ \mathrm{H_{ia}-ES_{ia}} & \mathrm{H_{ib}-ES_{ib}} & \cdots & \cdots & \mathrm{H_{ii}-ES_{ii}} \end{matrix} \quad | = 0$$

where $H_{ij} = \int \phi H \phi d\tau$; $S_{ii} = \int \phi\phi d\tau = 1$; $H_{ij} = \int \phi H \phi_j d\tau$; $S_{ij} = \int \phi\phi_j d\tau$

In the Hückel approximation,

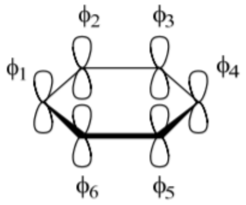
- $H_{iv} = \alpha$
- $H_{ij} = 0$ for ϕ_i not adjacent to ϕ_j
- $H_{ij} = \beta$ for ϕ_i not adjacent to ϕ_j
- $S_{ij} = 1$
- $S_{ij} = 0$

The foregoing approximation is the simplest. Different computational methods treat these integrals differently. Extended Hückel Theory (EHT) includes all valence orbitals in the basis (as opposed to the highest energy atomic orbitals), all $\mathrm{S_{ij}}$s are calculated, the Hiis are estimated from spectroscopic data (as opposed to a constant, α) and $\mathrm{H_{ij}}$s are estimated from a simple function of S_{ii}, H_{ii} and H_{ij} (zero differential overlap approximation).

The EHT (and other Hückel methods) are termed **semi–empirical** because they rely on experimental data for quantification of parameters. Other semi-empirical methods include CNDO, MINDO, INDO, etc. in which more care is taken in evaluating $\mathrm{H_{ij}}$ (these methods are based on self-consistent field procedures). Still higher level computational methods calculate the pertinent energies from first principles – *ab initio* and DFT. Here core potentials must be included and high order basis sets are used for the valence orbitals.

Benzene

As an example of the Hückel method, we will examine the frontier orbitals (i.e. determine eigenfunctions) and their associated orbital energies (i.e. eigenvalues) of benzene. The highest energy atomic orbitals of benzene are the C pπ orbitals. Hence, it is reasonable to begin the analysis by assuming that the frontier MO's will be composed of LCAO of the C 2pπ orbitals:



The matrix representations for this orbital basis in D_{6h} is,

$$E\cdot\begin{bmatrix}\phi_1\\\phi_2\\\phi_3\\\phi_4\\\phi_5\\\phi_6\end{bmatrix}=\begin{bmatrix}1&0&0&0&0&0\\0&1&0&0&0&0\\0&0&1&0&0&0\\0&0&0&1&0&0\\0&0&0&0&1&0\\0&0&0&0&0&1\end{bmatrix}\begin{bmatrix}\phi_1\\\phi_2\\\phi_3\\\phi_4\\\phi_5\\\phi_6\end{bmatrix}=\begin{bmatrix}\phi_1\\\phi_2\\\phi_3\\\phi_4\\\phi_5\\\phi_6\end{bmatrix}\qquad x_{\text{trace}}=6$$

$$C_6\cdot\begin{bmatrix}\phi_1\\\phi_2\\\phi_3\\\phi_4\\\phi_5\\\phi_6\end{bmatrix}=\begin{bmatrix}0&1&0&0&0&0\\0&0&1&0&0&0\\0&0&0&1&0&0\\0&0&0&0&1&0\\0&0&0&0&0&1\\1&0&0&0&0&0\end{bmatrix}\begin{bmatrix}\phi_1\\\phi_2\\\phi_3\\\phi_4\\\phi_5\\\phi_6\end{bmatrix}=\begin{bmatrix}\phi_2\\\phi_3\\\phi_4\\\phi_5\\\phi_6\\\phi_1\end{bmatrix}\qquad x_{\text{trace}}=0$$

$$C_2'\cdot\begin{bmatrix}\phi_1\\\phi_2\\\phi_3\\\phi_4\\\phi_5\\\phi_6\end{bmatrix}=\begin{bmatrix}-1&0&0&0&0&0\\0&0&0&0&0&-1\\0&0&0&0&-1&0\\0&0&0&-1&0&0\\0&0&-1&0&0&0\\0&-1&0&0&0&0\end{bmatrix}\begin{bmatrix}\phi_1\\\phi_2\\\phi_3\\\phi_4\\\phi_5\\\phi_6\end{bmatrix}=\begin{bmatrix}\bar{\phi}_1\\\bar{\phi}_6\\\bar{\phi}_5\\\bar{\phi}_4\\\bar{\phi}_3\\\bar{\phi}_2\end{bmatrix}\qquad x_{\text{trace}}=-2$$

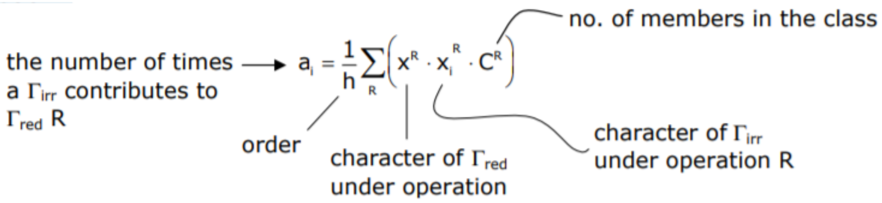
The only orbitals that contribute to the trace are those that transform into +1 or –1 themselves (i.e. in phase or with opposite phase, respectively). Thus the trace of the remaining characters of the pπ basis may be determined by inspection:

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_v$	$3\sigma_d$
$\Gamma_{p\pi}$	6	0	0	0	−2	0	0	0	0	−6	2	0

(1.6.3)

The $\Gamma_{p\pi}$ representation is a reducible basis that must be decomposed into irreducible representations.

Decomposition of reducible representations may be accomplished with the following relation:



Returning to the above example,

$$a_{A_{19}}=\frac{1}{24}[6\cdot1\cdot1+0\cdot0\cdot0+(-2)(1)(3)+0+0+0+0+(-6)(1)(1)+2\cdot1\cdot3+0]=0$$

thus A_{1g} does not contribute to $\Gamma_{p\pi}$

How about $a_{A_{2u}}$?

$$a_{A_{2u}}=\frac{1}{24}[6\cdot1\cdot1+0\cdot0\cdot0+(-2)(-1)(3)+0+0+0+0+(-6)(1)(-1)+2\cdot1\cdot3+0]=1$$

Continuing the procedure, one finds,

$$\Gamma_{p\pi} = A_{2u} + B_{29} + E_{19} + E_{2u} \tag{1.6.4}$$

these are the symmetries of the MO's formed by the LCAO of pπ orbitals in benzene.

With symmetries established, LCAOs may be constructed by "projecting out" the appropriate linear combination. A projection operator, $P^{(i)}$, allows the linear combination of the i^{th} irreducible representation to be determined,

$$P^{(i)} = \frac{\overset{\text{dimension of } \Gamma_i}{\ell_i}}{\underset{\text{order}}{h}} \sum_R \left[\underset{\text{character of } \Gamma_i \text{ under operator R}}{\chi^{(i)}(R)} \right] \bullet \overset{\text{operator}}{R}$$

A drawback of projecting out of the D_{6h} point group is the large number of operators. The problem can be simplified by dropping to the pure rotational subgroup, C_6. In this point group, the full extent of mixing among ϕ_1 through ϕ_6 is maintained; however the inversion center, and hence u and g symmetry labels are lost. Thus in the final analysis, the Γ_is in C_6 will have to be correlated to those in D_{6h}. Reformulating in C_6,

C_6	E	C_6	C_3	C_2	C_3^2	C_3^5
$\Gamma_{p\pi}$	6	0	0	0	0	0

$$\begin{array}{cccccccccl} \Gamma_{p\pi} = & A & + & B & + & E_1 & + & E_2 & & \\ & \Downarrow & & \Downarrow & & \Downarrow & & \Downarrow & & \text{in } D_{6h} \\ & A_{2u} & & B_{2g} & & E_{1g} & & E_{2u} & & \end{array}$$

The projection of the SALC that from ϕ_1 transforms as A is,

$$\begin{aligned} P^{(A)}\phi_1 &= \frac{1}{6}\left[1 \cdot E \cdot \phi_1 + 1 \cdot C_6 \cdot \phi_1 + 1 \cdot C_6^{\,2} \cdot \phi_1 + 1 \cdot C_6^{\,3} \cdot \phi_1 + 1 \cdot C_6^{\,4} \cdot \phi_1 + 1 \cdot C_6^{\,5} \cdot \phi_1\right] \\ &\underset{\text{drop constant since LCAO will be normalized}}{\cong} \phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6 \end{aligned}$$

Continuing,

- $P^{(B)}\phi_1 = \phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6$
- $P^{(E_{1a})}\phi_1 = \phi_1 + \varepsilon\phi_2 - \varepsilon^*\phi_3 - \phi_4 - \varepsilon\phi_5 + \varepsilon^*\phi_6$
- $P^{(E_{16})}\phi_1 = \phi_1 + \varepsilon^*\phi_2 - \varepsilon\phi_3 - \phi_4 - \varepsilon^*\phi_5 + \varepsilon\phi_6$
- $P^{(E_{22})}\phi_1 = \phi_1 - \varepsilon^*\phi_2 - \varepsilon\phi_3 + \phi_4 - \varepsilon^*\phi_5 - \varepsilon\phi_6$
- $P^{(E_{26})}\phi_1 = \phi_1 - \varepsilon\phi_2 - \varepsilon^*\phi_3 + \phi_4 - \varepsilon\phi_5 - \varepsilon^*\phi_6$

The projections contain imaginary components; the real component of the linear combination may be realized by taking ± linear combinations:

For $\psi(E_{1a})$ SALC's:

$$\begin{gathered} \psi_3'(E_{1a}) + \psi_4'(E_{1b}) = 2\phi_1 + (\varepsilon + \varepsilon^*)\phi_2 - (\varepsilon + \varepsilon^*)\phi_3 - 2\phi_4 - (\varepsilon + \varepsilon^*)\phi_5 + (\varepsilon + \varepsilon^*)\phi_6 \\ \psi_3'(E_{1a}) - \psi_4'(E_{1b}) = (\varepsilon - \varepsilon^*)\phi_2 + (\varepsilon - \varepsilon^*)\phi_3 + (\varepsilon^* - \varepsilon)\phi_5 + (\varepsilon^* - \varepsilon)\phi_6 \end{gathered}$$

where in the C_6 point group,

$$\begin{gathered} \varepsilon = \exp\left(\frac{2\pi}{6}\right)i = \cos\frac{2\pi}{6} - i\sin\frac{2\pi}{6} \\ \therefore \varepsilon + \varepsilon^* = \cos\frac{2\pi}{6} - i\sin\frac{2\pi}{6} + \cos\frac{2\pi}{6} + i\sin\frac{2\pi}{6} = 2\cos\frac{2\pi}{6} = 1 \\ \varepsilon^* - \varepsilon = -\cos\frac{2\pi}{6} + i\sin\frac{2\pi}{6} - \cos\frac{2\pi}{6} + i\sin\frac{2\pi}{6} = 2i\sin\frac{2\pi}{6} = i\sqrt{3} \\ \varepsilon - \varepsilon^* = \cos\frac{2\pi}{6} - i\sin\frac{2\pi}{6} - \left(\cos\frac{2\pi}{6} + i\sin\frac{2\pi}{6}\right) = -2i\sin\frac{2\pi}{6} = -i\sqrt{3} \end{gathered}$$

∴ the E_{1a} LCAO's reduce to (again ignoring the constant prefactor),

$$\begin{gathered} \psi_3(E_1) = \psi_3'(E_{1a}) + \psi_4'(E_{1b}) = 2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_5 + \phi_6 \\ \psi_4(E_1) = \psi_3'(E_{1a}) - \psi_4'(E_{1b}) = \phi_2 + \phi_3 - \phi_5 - \phi_6 \end{gathered}$$

Similarly for the $\psi_5(E_2)$ and $\psi_6(E_2)$ LCAO's… normalizing the SALC's

$$\psi_1(A)=\frac{1}{\sqrt{6}}(\phi_1+\phi_2+\phi_3+\phi_4+\phi_5+\phi_6) \qquad \psi_2(B)=\frac{1}{\sqrt{6}}(\phi_1-\phi_2+\phi_3-\phi_4+\phi_5+\phi_6)$$

$$\psi_3\left(E_1\right)=\frac{1}{\sqrt{12}}(2\phi_1+\phi_2-\phi_3-2\phi_4-\phi_5+\phi_6) \qquad \psi_4\left(E_1\right)=\frac{1}{2}(\phi_2+\phi_3-\phi_5-\phi_6)$$

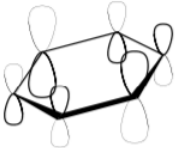
$$\psi_5\left(E_2\right)=\frac{1}{\sqrt{12}}(2\phi_1-\phi_2-\phi_3+2\phi_4-\phi_5-\phi_6) \qquad \psi_6\left(E_2\right)=\frac{1}{2}(\phi_2-\phi_3+\phi_5-\phi_6)$$

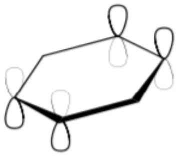
The pictorial representation of the SALC's are,

$\Psi(A_{2u})$

$\Psi(B_{2g})$

$\Psi(E_{1g}{}^{a})$





$\Psi(E_{1g}{}^{b})$

$\Psi(E_{2u}{}^{a})$

$\Psi(E_{2u}{}^{b})$

1.7: Hückel Theory 2 (Eigenvalues)

The energies (eigenvalues) may be determined by using the Hückel approximation.

$$\psi_{A_{1g}} = \frac{1}{\sqrt{6}}(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)$$

$$\begin{aligned} E\left(\psi_{A_{1g}}\right) &= \int \psi_{A1g}\, H\, \psi_{A1g}\, d\tau = \left\langle \psi_{A_{1g}} \,|\, H \,|\, \psi_{A_{1g}} \right\rangle \\ &= \left\langle \frac{1}{\sqrt{6}}(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6) \right| H \left| \frac{1}{\sqrt{6}}(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6) \right\rangle \\ &= \frac{1}{6}\Big(\underset{\alpha}{\underset{\downarrow}{H_{11}}} + \underset{\beta}{\underset{\downarrow}{H_{12}}} + H_{13} + H_{14} + H_{15} + \underset{\beta}{\underset{\downarrow}{H_{16}}} + \underset{\beta}{\underset{\downarrow}{H_{21}}} + \underset{\alpha}{\underset{\downarrow}{H_{22}}} + \underset{\beta}{\underset{\downarrow}{H_{23}}} + H_{24} + H_{25} + H_{26} \\ &\quad + \underset{\alpha+2\beta}{\underset{\downarrow}{H_{3i}(i=1-6)}} + \underset{\alpha+2\beta}{\underset{\downarrow}{H_{4i}(i=1-6)}} + \underset{\alpha+2\beta}{\underset{\downarrow}{H_{5i}(i=1-6)}} + \underset{\alpha+2\beta}{\underset{\downarrow}{H_{6i}(i=1-6)}} \Big) \end{aligned}$$

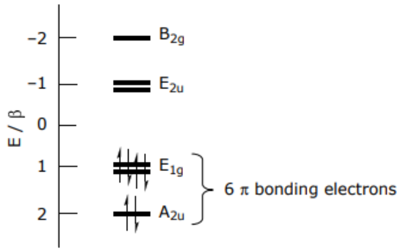
$$E\left(\psi_{B_{2g}}\right) = \frac{1}{6}(6)(\alpha - 2\beta) = \alpha - 2\beta \tag{1.7.1}$$

The energies of the remaining LCAO's are:

$$E\left(\psi^a_{E_{1g}}\right) = \left(\psi^b_{E_{1g}}\right) = \alpha + \beta \tag{1.7.2}$$

$$E\left(\psi^a_{E_{2u}}\right) = \left(\psi^b_{E_{2u}}\right) = \alpha - \beta \tag{1.7.3}$$

Note the energies of the E orbitals are degenerate. Constructing the energy level diagram, we set α = 0 and β as the energy parameter (a negative quantity, so an MO whose energy is positive in units of β has an absolute energy that is negative),

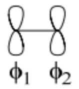


The energy of benzene based on the Hückel approximation is

$$E_{total} = 2(2\beta) + 4(\beta) = 8\beta \tag{1.7.4}$$

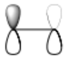
What is the delocalization energy (i.e. π **resonance energy**)?

To determine this, we consider cyclohexatriene, which is a six-membered cyclic ring with 3 localized π bonds; in other terms, cyclohexatriene is the product of three condensed ethylene molecules. For ethylene,



Following the procedures outlined above, we find,

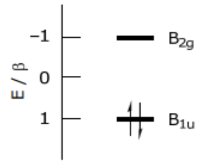
$$\psi_1(A) = \frac{1}{\sqrt{2}}(\phi_1 + \phi_2)$$



$$\psi_2(B) = \frac{1}{\sqrt{2}}(\phi_1 - \phi_2)$$

$$\mathrm{E}\left(\psi_1\right)=\left\langle\frac{1}{\sqrt{2}}\left(\phi_1+\phi_2\right)|\mathrm{H}| \frac{1}{\sqrt{2}}\left(\phi_1+\phi_2\right)\right\rangle=\frac{1}{2}(2 \alpha+2 \beta)=\beta$$
$$\mathrm{E}\left(\psi_2\right)=\left\langle\frac{1}{\sqrt{2}}\left(\phi_1-\phi_2\right)|\mathrm{H}| \frac{1}{\sqrt{2}}\left(\phi_1-\phi_2\right)\right\rangle=\frac{1}{2}(2 \alpha-2 \beta)=-\beta$$

The above was determined in the C_2 point group. Correlating to D_{2h} point group gives A in C2 → B_{1u} in D_{2h} and B in C_2 → B_{2g} in D_{2h}:



The Hückel energy of ethylene is,

$$E_{total}=2(\beta)=2\beta \tag{1.7.5}$$

Therefore, the energy of cyclohexatriene is 3(2β) = 6β. The resonance energy is therefore,

$$E_{res}(C_6H_6) = \underset{\substack{\downarrow \\ E_{total} \\ \text{benzene}}}{8\beta} - \underset{\substack{\downarrow \\ E_{total} \\ \text{cyclohexatriene}}}{6\beta} = 2\beta$$

The **bond order** is given by,

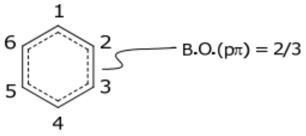
$$\text{B.O.} = \sum_{i,j} \underset{\text{orbital } e^- \text{ occupancy}}{n_e} \overset{\text{coefficients of electron i and electron j in a given bond}}{c_i c_j}$$

Consider the B.O. between the C_1 and C_2 carbons of benzene

$$[\psi_1(A_{2u})]=2(\frac{1}{\sqrt{6}})(\frac{1}{\sqrt{6}})=\frac{1}{3} \tag{1.7.6}$$

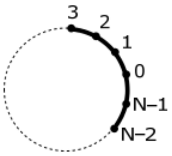
$$[\psi_3(E^a_{1g})]=2(\frac{1}{\sqrt{12}})(\frac{1}{\sqrt{12}})=\frac{1}{3} \tag{1.7.7}$$

$$[\psi_4(E^b_{1g})]=\frac{1}{2}(0)(\frac{1}{2})=\frac{0}{\frac{2}{3}} \tag{1.7.8}$$



1.8: N-dimensional cyclic systems

This lecture will provide a derivation of the LCAO eigenfunctions and eigenvalues of N total number of orbitals in a cyclic arrangement. The problem is illustrated below:



There are two derivations to this problem.

Polynomial Derivation

The Hückel determinant is given by,

$$D_N(x)=\begin{vmatrix} x & 1 & & & & & & & \\ 1 & x & 1 & & & & & & \\ & 1 & x & \ddots & & & & & \\ & & 1 & \ddots & \ddots & & & & \\ & & & \ddots & \ddots & \ddots & & & \\ & & & & \ddots & \ddots & \ddots & & \\ & & & & & \ddots & \ddots & 1 & \\ & & & & & & \ddots & x & 1 \\ & & & & & & 1 & x & \end{vmatrix}=0 \tag{1.8.1}$$

where

$$x=\frac{\alpha-E}{\beta} \tag{1.8.2}$$

From a Laplace expansion one finds,

$$D_N(x)=xD_{n-1}(x)-D_{N-2}(x) \tag{1.8.3}$$

Where

$$\begin{aligned} D_1(x)&=x \\ D_2(x)&=\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix}=x^2-1 \end{aligned}$$

With these parameters defined, the polynomial form of $D_N(x)$ for any value of N can be obtained,

$$\begin{gathered} D_3(x)=xD_2(x)-D_1(x)=x\left(x^2-1\right)-x=x\left(x^2-2\right) \\ D_4(x)=xD_3(x)-D_2(x)=x^2\left(x^2-2\right)-\left(x^2-1\right) \\ \vdots \\ \text{and so on} \end{gathered}$$

The expansion of DN(x) has as its solution,

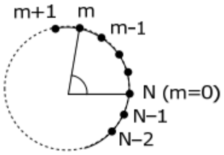
$$x=-2\cos\frac{2\pi}{N}j(j=0,1,2,3\ldots N-1)$$

and substituting for x,

$$E=\alpha+2\beta\cos\frac{2\pi}{N}j(j=0,1,2,3\ldots N-1)$$

Standing Wave Derivation

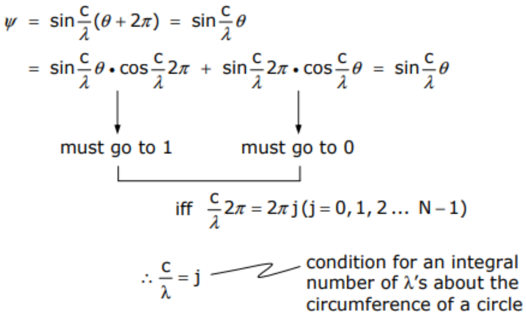
An alternative approach to solving this problem is to express the wavefunction directly in an angular coordinate, θ



For a standing wave of λ about the perimeter of a circle of circumference c,

$$\psi_j=\sin\frac{c}{\lambda}\theta$$

The solution to the wave function must be single valued ∴ a single solution must be obtained for ψ at every 2nπ or in analytical terms,



$$\psi = \sin\frac{c}{\lambda}(\theta+2\pi) = \sin\frac{c}{\lambda}\theta$$

$$= \sin\frac{c}{\lambda}\theta\cdot\underbrace{\cos\frac{c}{\lambda}2\pi}_{\text{must go to 1}} + \underbrace{\sin\frac{c}{\lambda}2\pi}_{\text{must go to 0}}\cdot\cos\frac{c}{\lambda}\theta = \sin\frac{c}{\lambda}\theta$$

$$\text{iff}\quad \frac{c}{\lambda}2\pi = 2\pi j\,(j=0,1,2\ldots\ N-1)$$

$$\therefore \frac{c}{\lambda}=j$$

condition for an integral number of λ's about the circumference of a circle

Thus the amplitude of ψ_j at atom m is, (where c/λ = j and θ = (2π/N)m)

$$\psi_j(m)=\sin 2m\pi Nj(j=0,1,2,3\ldots N-1)$$

Within the context of the LCAO method, ψ_j may be rewritten as a linear combination in φ_m with coefficients c_{jm}. Thus the amplitude of ψ_j at m is equivalent to the coefficient of φ_m in the LCAO expansion,

$$\psi_j=\sum_{k=1}^{N}C_{jm\phi m} \tag{1.8.4}$$

Where

$$C_{jm}=\sin 2\pi mNj(j=0,1,2,3\ldots N-1)$$

The energy of each MO, ψ_j, may be determined from a solution of Schrödinger's equation,

$$\begin{aligned}\mathrm{H}\psi_j&=\mathrm{E}_j\psi_j\\ |\mathrm{H}-\mathrm{E_j}|\,\psi_j\rangle&=0\\ |\mathrm{H}-\mathrm{E}_j|\textstyle\sum_m^{\mathrm{N}}\mathrm{c}_{jm}\phi_m\Big\rangle&=0\end{aligned}$$

The energy of the φ_m orbital is obtained by left–multiplying by φ_m,

$$\left\langle\phi_m\,|H-E_j|\sum_m^N c_{jm}\phi_m\right\rangle=0$$

but the Hückel condition is imposed; the only terms that are retained are those involving φ_m, φ_{m+1}, and φ_{m-1}. Expanding,

$$\left[c_{jm}\langle\phi_m|\overset{\alpha}{\cancel{H}}|\phi_m\rangle - c_{jm}E_j\overset{1}{\cancel{\langle\phi_m|\phi_m\rangle}}\right] + \left[c_{j(m+1)}\langle\phi_m|\overset{\beta}{\cancel{H}}|\phi_{m+1}\rangle - c_{j(m+1)}E_j\overset{0}{\cancel{\langle\phi_m|\phi_{m+1}\rangle}}\right]$$
$$+ \left[c_{j(m-1)}\langle\phi_m|\underset{\beta}{\cancel{H}}|\phi_{m-1}\rangle - c_{j(m-1)}E_j\underset{0}{\cancel{\langle\phi_m|\phi_{m-1}\rangle}}\right] = 0$$

Evaluating the integrals,

$$\begin{aligned} \alpha \mathrm{c}_{jm} - \mathrm{c}_{jm}\mathrm{E}_\mathrm{j} + \beta\left\lfloor \mathrm{c}_{\mathrm{j(m+1)}} + \mathrm{c}_{j(\,\mathrm{m}-1)}\right\rfloor = 0 \\ \alpha \mathrm{c}_{jm} + \beta\left\lfloor \mathrm{c}_{j(m+1)} + \mathrm{c}_{\mathrm{j(m-1)}}\right\rfloor = \mathrm{c}_{jm}\mathrm{E}_\mathrm{j} \end{aligned} \quad \backslash\text{no}tag \tag{1.8.5}$$

Substituting for c_{jm},

$$\alpha \sin\frac{2\pi m}{N}j + \beta\left(\sin\frac{2\pi(m+1)}{N}j + \sin\frac{2\pi(m-1)}{N}j\right) = E_j \sin\frac{2\pi m}{N}j$$

Dividing by $\sin\frac{2\pi m}{N}j$,

$$\alpha + \frac{\beta\left(\sin\frac{2\pi(m+1)}{N}j + \sin\frac{2\pi(m-1)}{N}j\right)}{\sin\frac{2\pi m}{N}j} = E_j$$

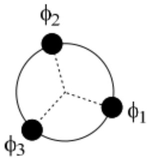
Making the simplifying substitution, $\kappa = \frac{2\pi}{N}j$

$$\mathrm{E}_\mathrm{j} = \alpha + \beta\left(\frac{\sin\kappa\mathrm{m}\cdot\cos\kappa + \sin\kappa\cdot\cos\kappa\mathrm{m} + \sin\kappa\mathrm{m}\cdot\cos\kappa - \sin\kappa\cdot\cos\kappa\mathrm{m}}{\sin\kappa\mathrm{m}}\right)$$

$$E_j = \alpha + 2\beta\cos k$$

$$E_j = \alpha + 2\beta\cos\frac{2\pi}{N}j(j = 0, 1, 2, 3 \ldots N-1)$$

Let’s look at the simplest cyclic system, N = 3



$$\mathrm{N} = 3, \text{ so } \mathrm{E}_\mathrm{j} = \alpha + 2\beta\cos\frac{2\pi}{\mathrm{N}}\mathrm{j} \text{ where } \mathrm{j} = 0, 1, 2$$

$$\begin{aligned} \mathrm{E}_0 &= \alpha + 2\beta \\ \mathrm{E}_1 &= \alpha + 2\beta\cos\frac{2\pi}{3} = \alpha - \beta \\ \mathrm{E}_2 &= \alpha + 2\beta\cos\frac{4\pi}{3} = \alpha - \beta \end{aligned}$$

Continuing with our approach (LCAO) and using Ej to solve for the eigenfunction, we find…

$$\psi_j = \sum_m e^{ij\theta}\phi_m \quad \text{for } j = 0, \pm1, \pm2 \ldots \begin{cases} \pm\frac{N}{2} \text{ for } N \text{ even} \\ \pm\frac{(N-1)}{2} \text{ for } N \text{ odd} \end{cases} \tag{1.8.6}$$

Using the general expression for ψj, the eigenfunctions are:

$$\psi_0 = e^{i(0)0}\phi_1 + e^{i(0)\frac{2\pi}{3}}\phi_2 + e^{i(0)\frac{4\pi}{3}}\phi_3$$

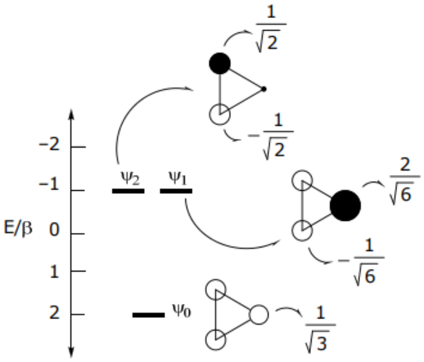
$$\psi_1 = e^{i(1)0}\phi_1 + e^{i(1)\frac{2\pi}{3}}\phi_2 + e^{i(1)\frac{4\pi}{3}}\phi_3$$

$$\psi_{-1} = e^{i(-1)0}\phi_1 + e^{i(-1)\frac{2\pi}{3}}\phi_2 + e^{i(-1)\frac{4\pi}{3}}\phi_3$$

Obtaining real components of the wavefunctions and normalizing,

$$\begin{aligned} \psi_0 = \phi_1 + \phi_2 + \phi_3 \rightarrow \qquad & \psi_0 = \frac{1}{\sqrt{3}}(\phi_1 + \phi_2 + \phi_3) \\ \psi_{+1} + \psi_{-1} = 2\phi_1 - \phi_2 - \phi_3 \rightarrow \qquad & \psi_1 = \frac{1}{\sqrt{6}}(2\phi_1 - \phi_2 - \phi_3) \\ \psi_{+1} - \psi_{-1} = \phi_2 - \phi_3 \rightarrow \qquad & \psi_2 = \frac{1}{\sqrt{2}}(\phi_2 - \phi_3) \end{aligned} \tag{1.8.7}$$

Summarizing on a MO diagram where α is set equal to 0,



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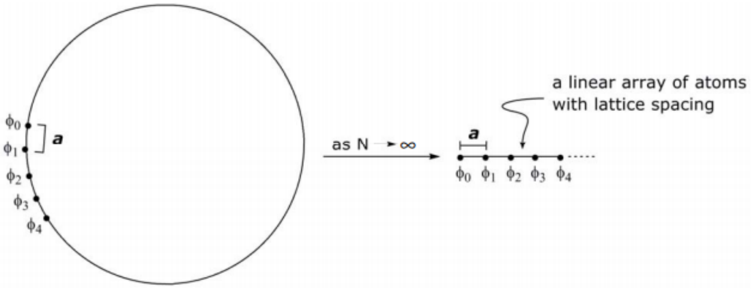
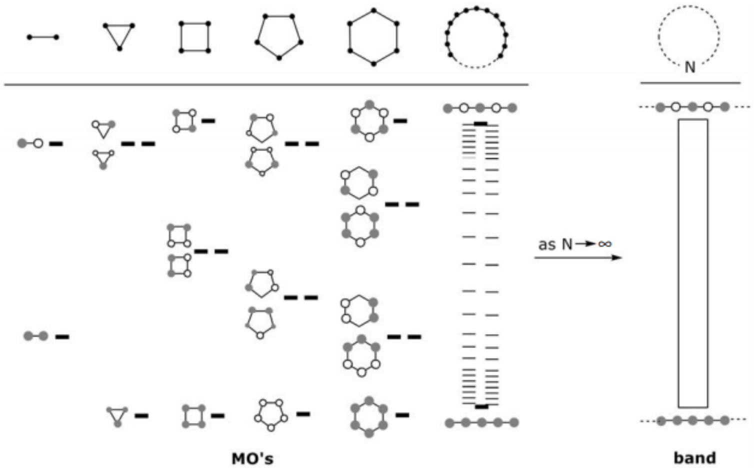
1.9: Band Theory in Solids

The LCAO method for cyclic systems provides a convenient starting point for the development of the electronic structure of solids.

At very large N, as the circumference of the circle approaches ∞, the cyclic problem converges to a linear one,



Qualitatively, from a MO energy level perspective,



More quantitatively, in moving from cyclic to linear systems, instead of describing orbital (atom) positions angularly, the position of an atom is described by m**a**, where m is the number of the atom in the array and **a** is the distance between atoms. Thus, the θ of the N-cyclic derivation becomes m**a**,

$$\psi_j = \sum_m e^{ij\theta}\phi_m \quad\Rightarrow\quad \psi_k = \sum_m e^{ik(m\boldsymbol{a})}\phi_m$$

$$E_j = \alpha + 2\beta\cos\frac{2\pi j}{N} \quad\Rightarrow\quad E_k = \alpha + 2\beta\cos\frac{2\pi j\boldsymbol{a}}{N\boldsymbol{a}} \longleftarrow \text{multiplied by } \boldsymbol{a}/\boldsymbol{a}$$

$$= \alpha + 2\beta\cos k\boldsymbol{a}$$

$$\uparrow$$

$$\text{where } k = \frac{2\pi j}{N\boldsymbol{a}}$$

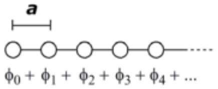
A few words about k. It is:

- a measure of the number of nodes
- an index of wavefunction and accordingly symmetry of wavefunction
- a “quantum number” for a given ψ_k
- a measure of length, related to wavelength λ^{-1}
- from DeBroglie’s relation, λ = (h/p) , therefore k is also a wave vector that measures momentum

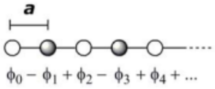
Returning to the foregoing discussion, note that k parametrically depends on **a**. Since a is **a** lattice parameter of the unit cell, there are as many k’s as there are unit cells in the crystal. In the linear case, the unit cell is the distance between adjacent atoms: there are n atoms ∴ n unit cells or in other terms – there are as many k’s as atoms in the 1-D chain.

Let’s determine the energy values of limits, k = 0 and k = (π/**a**) :

$$\textbf{at } \boldsymbol{k} = \textbf{0:} \quad \psi_0 = \sum_m e^{i0(m\boldsymbol{a})}\phi_m = \sum_m \phi_m$$



$$\textbf{at } \boldsymbol{k} = \frac{\pi}{\boldsymbol{a}}: \quad \psi_{\frac{\pi}{a}} = \sum_n e^{i\left(\frac{\pi}{a}\right)(m\boldsymbol{a})}\phi_m = \sum_m e^{im\pi}\phi_m = \sum_m (-1)^m \phi_m$$

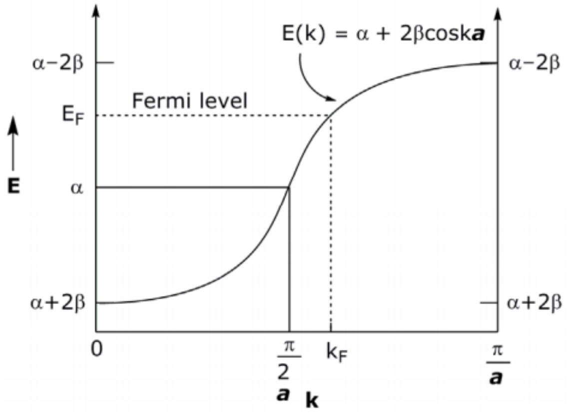


The energies for these band structures at the limits of k are:

$$E_0 = \alpha + 2\beta\cos(0)a = \alpha + 2\beta \tag{1.9.1}$$

$$E_{\frac{\pi}{a}} = \alpha + 2\beta\cos\left(\frac{\pi}{a}\right)a = \alpha - 2\beta \tag{1.9.2}$$

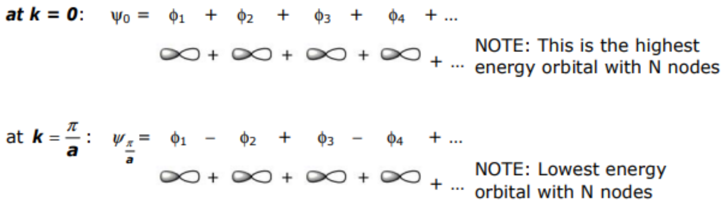
Note that k is quantized; so there are a finite number of values between α+2β and α–2β but for a very large number (~10^{23} atoms) between the limits of k. Thus, the energy is a continuous and smoothly varying function between these limits.

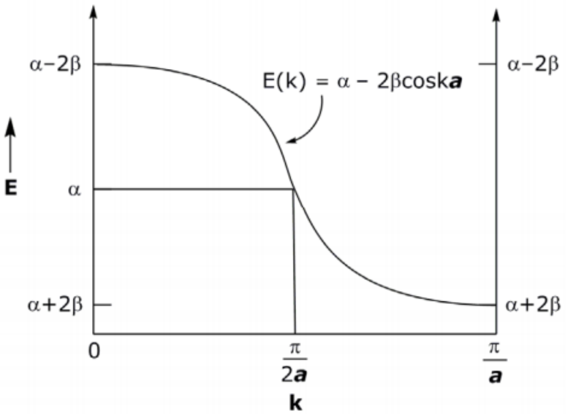


The range - π/**a** ≤ k ≤ π/**a** or |k| ≤ π/**a** is unique because the function repeats itself a a a outside these limits. This unique range of k values is called the Brillouin zone. The first Brillouin zone is plotted above from 0 to π/**a** (symmetric reflection from − π/**a** to 0).

With a given number of e^{-} s in the solid, the levels will be filled to a certain energy called the Fermi level, which corresponds to a certain value of k (= k_F). In the k above example, there are more electrons than there are orbitals, so k_F > k/2**a**. If each atomic orbital contributed $1e^{-}$ to the system, then E_F would occur for k_F = π/2**a**.

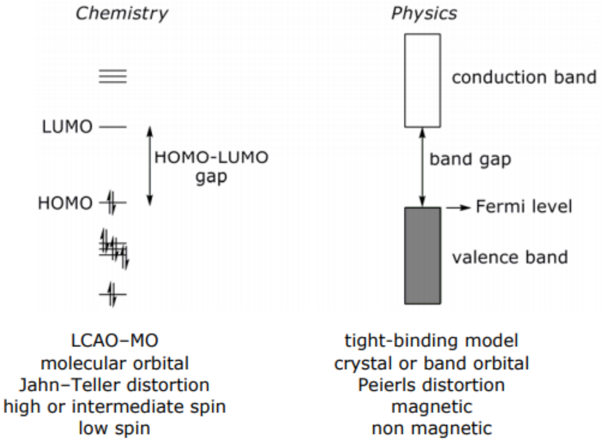
The symmetry of the individual atomic orbitals determines much about band structure. Consider p-orbitals overlapping in a linear array (vs the 1s orbitals of the above treatment). Analyzing limiting forms:





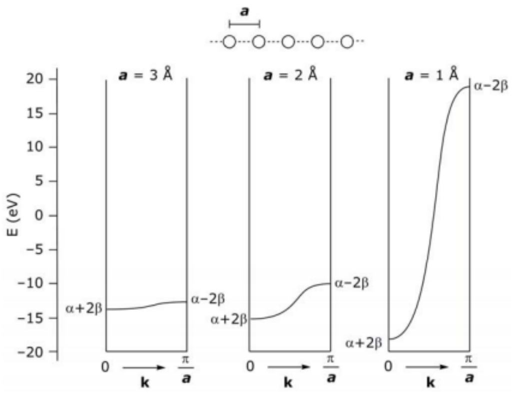
The energy band is opposite of that for the sσ orbital LCAO because the (+) LCAO for a pσ orbital is antibonding.

Thus, molecules are easily related to solids via Hückel theory. Not surprisingly, there is a language of chemistry describing the electronic structure of molecules that is related to the language of physics describing the electronic structure of solids. Below are some of the terms that chemists and physicists use to describe similar phenomena in molecules and solids:



Band Width or Dispersion

What determines the width or dispersion of a band? As for the HOMO-LUMO gap in a molecule, the overlap of neighboring orbitals determines the energy dispersion of a band – the greater the overlap, the greater the dispersion. Note how the band dispersion of a linear chain of H atoms varies as the 1s orbitals of the H atoms are spaced 1, 2, 3 Å apart (E of an isolated H atom is –13.6 eV):



Density of States

The total energy of the system is,

normalization constant

$$E_{total} = \frac{N\mathbf{a}}{2\pi}\int_{-k_F}^{k_F} 2E(k)dk = \frac{2N\mathbf{a}}{\pi}\int_0^{k_F} E(k)dk$$

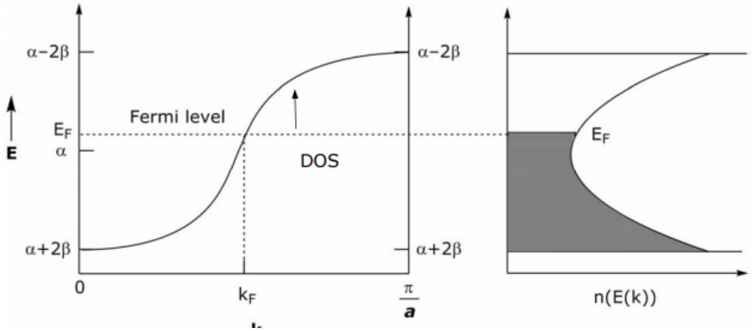
or in other words, it is the area under the curve to kF. Another useful quantity is the number of orbitals between E(k) + dE(k), called the **density of states** (DOS). For a 1-D system,

DOS

$$n(E(k)) \propto \left(\frac{\partial E(k)}{\partial k}\right)^{-1}$$

inversely proportional to slope of E(k) curve at given k. Since slope at k = 0 and k = π/**a** approaches 0, n(E(k)) is large

A plot of the above equations is,

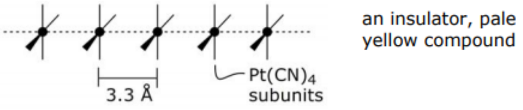


In the above DOS diagram, no energy gap separates the filled and empty bands, i.e. there is a continuous density of states – this property is characteristic of a metal. If an energy gap between filled and empty orbitals is present and it can be thermally surmounted, then it is **semiconductor**; an energy gap that cannot be surmounted is an **insulator**.

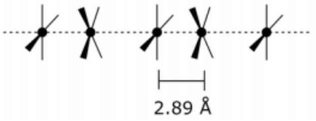
A 1-D Example

Arguably the best known 1-D system in inorganic chemistry is $K_2Pt(CN)_4$ and its partially oxidized compound (e.g. $K_2Pt(CN)_4Br_{0.3}$).

Normal platinocyanide, $K_2Pt(CN)_4$:



Partially oxidized platinocyanide, $K_2Pt(CN)_4Br_{0.3}$•$3H_2O$:

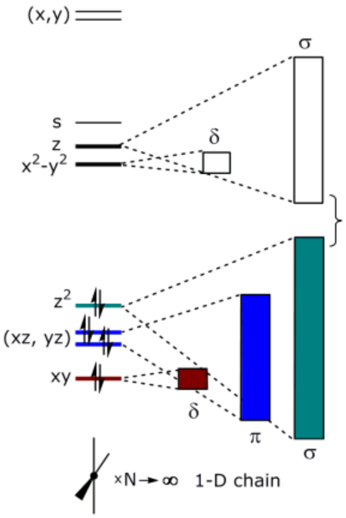


along chain: a conductor (500-1000 Ω^{-1} cm^{-1}) a copper-colored with metallic luster

⊥ to chain: an insulator (0.05-0.01 Ω^{-1} cm^{-1}), a yellow compound

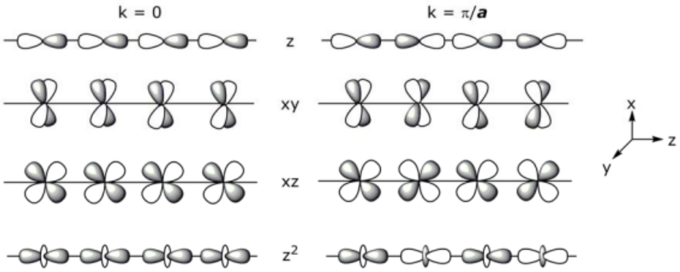
Note: d(Pt-Pt) = 2.78 Å in Pt metal

To explain these disparate properties of the 1-D compounds, consider the molecular subunit $Pt(CN)_4^{2-}$:

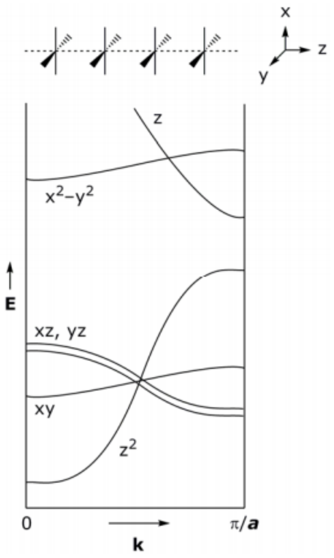


for d^8 system valence bonds completely filled … the energy gap between the M-Lσ derived valence band and the M-Lσ* derived conduction band is too large to be thermally populated, thus an insulator

The dispersion of the bands is due to the different overlaps of the dσ, dπ and dδ orbitals.

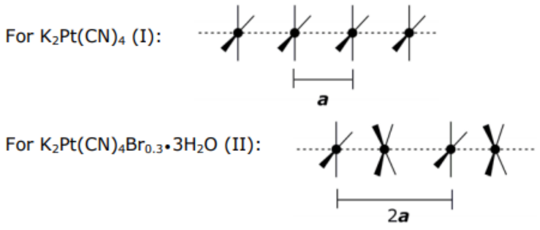


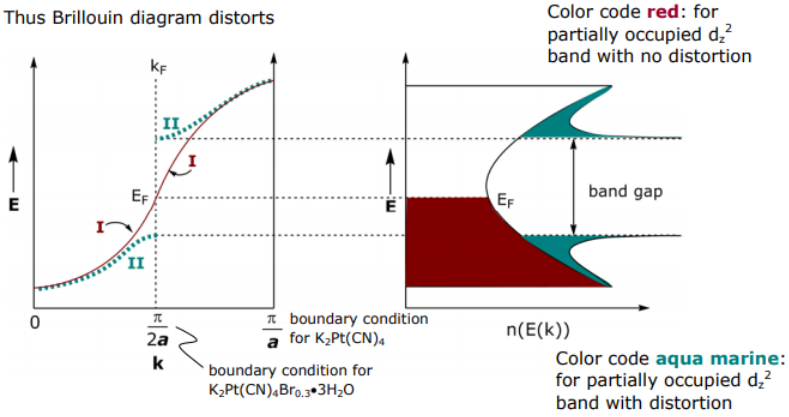
Band structure (or first Brillouin zones) derived from the frontier MO’s is:

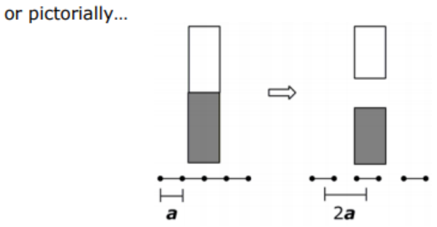


For partially oxidized system, the σ bond derived from dz^2 should be partially filled and thus metallic, but it is not, partially oxidized $K_2Pt(CN)_4Br_x$ is a semiconductor. To explain this anomaly, consider how the band structure is perturbed upon partial oxidation:

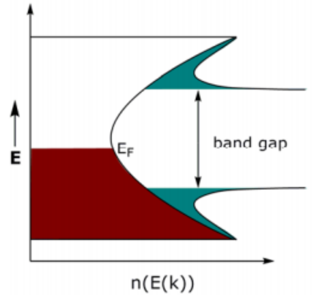
Isolating on the d_{z^2} band in $K_2Pt(CN)_4$, the Pt atoms are evenly spaced with lattice dimension **a** (I). Upon oxidation, the Pt chain can distort to give a lattice dimension 2**a** (II). In the case of the $K_2Pt(CN)_4Br_{0.3}$•$3H_2O$ the distortion is a rotation of Pt subunits and formation of dimers within chain, thus the unit cell dimension is pinned to every other Pt atom.



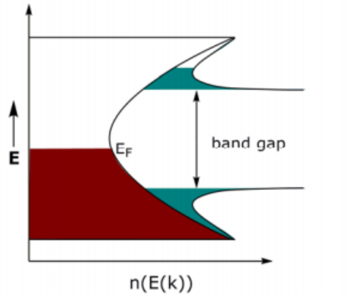




The Brillouin diagram above is for a distorted $K_2Pt(CN)_4$ but filled d_{z^2} orbital. Hence both aqua marine bands are filled and the material that thus possesses the electronic structure shown below is insulating, despite the distortion

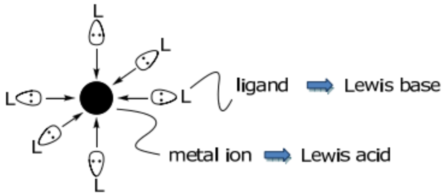


Upon partial oxidation of $K_2Pt(CN)_4$ to produce $K_2Pt(CN)_4Br_{0.3}$•$3H_2O$, the d_{z^2} band is now partially filled. Hence a conductive material results. The conductivity is along the Pt-Pt axis, explaining the electrical anisotropy of the material

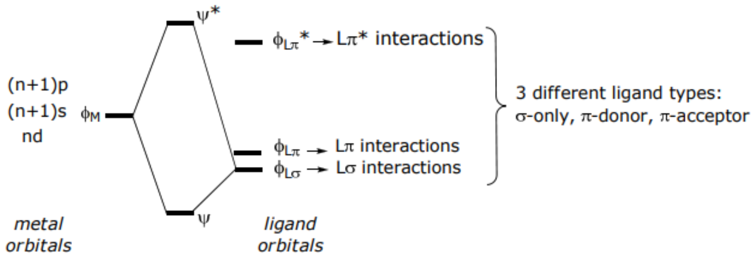


1.10: General electronic considerations of metal-ligand complexes

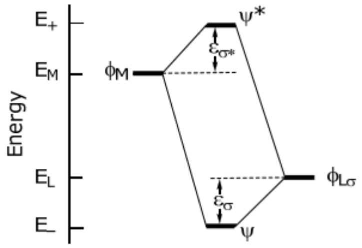
Metal complexes are Lewis acid-base adducts formed between metal ions (the acid) and ligands (the base).



The interaction of the frontier atomic (for single atom ligands) or molecular (for many atom ligands) orbitals of the ligand and metal lead to bond formation,



More quantitatively, the interaction energy of stabilization and destabilization, ε_σ and ε_{σ^*}, respectively, is defined on the following energy level diagram,



Treating this problem within the LCAO framework comprising metal and ligand orbitals yields,

$$\psi = c_M \varphi_M + c_L \varphi_L$$

and solving for the Hamiltonian,

$$\begin{gathered} \mathrm{H}\psi = \mathrm{E}\psi \\ |\mathrm{H}-\mathrm{E}|\psi\rangle = |\mathrm{H}-\mathrm{E_j}|\,\mathrm{c_M}\phi_\mathrm{M} + \mathrm{c_L}\phi\rangle = 0 \end{gathered}$$

Left-multiplying by φM and φL yields the set of linear homogeneous equations,

$$\begin{gathered} c_M\,\langle\phi_M|H-E|\phi_M\rangle + c_L\,\langle\phi_M|H-E|\phi\rangle = 0 \\ c_M\,\langle\phi_L|H-E|\phi_M\rangle + c_L\langle\phi|H-E|\phi\rangle = 0 \end{gathered}$$

which furnishes the secular determinant,

$$\begin{vmatrix} \mathrm{H}_{MM}-\mathrm{E} & \mathrm{H}_{ML}-\mathrm{ES}_{ML} \\ \mathrm{H}_{ML}-\mathrm{ES}_{ML} & \mathrm{H}_{LL}-\mathrm{E} \end{vmatrix} = \begin{vmatrix} \mathrm{E}_M-\mathrm{E} & \mathrm{H}_{ML}-\mathrm{ES}_{ML} \\ \mathrm{H}_{ML}-\mathrm{ES}_{ML} & \mathrm{E}_L-\mathrm{E} \end{vmatrix} = 0 \tag{1.10.1}$$

Solving the above secular determinant, using the expansion $\sqrt{1+x} = 1 + \frac{1}{2}x - \ldots$,

and realizing that $H_{MM} = E_M$ and $H_{LL} = E_L$

$$E_{+} = \underset{\substack{\downarrow \\ H_{MM}}}{E_{M}} + \underset{\substack{\downarrow \\ \varepsilon_{\sigma*}}}{\frac{\left(H_{ML} - E_{M}S_{ML}\right)^{2}}{\Delta E_{ML}}} \qquad E_{-} = \underset{\substack{\downarrow \\ H_{LL}}}{E_{L}} - \underset{\substack{\downarrow \\ \varepsilon_{\sigma}}}{\frac{\left(H_{ML} - E_{M}S_{ML}\right)^{2}}{\Delta E_{ML}}}$$

The Wolfsberg-Hemholz approximation provides a value for H_{ML}, defined as

$$H_{ML} = S_{ML}\,(E_L + E_M)$$

Substituting H_{ML} in the above expressions for E_+ and $E_–$ yields,

$$\varepsilon_{\sigma} = \frac{{E_M}^2{S_{ML}}^2}{\Delta E_{ML}} \quad \varepsilon_{\sigma*} = \frac{{E_L}^2{S_{ML}}^2}{\Delta E_{ML}} \tag{1.10.2}$$

The derivation highlights the following general rules for the construction of MO diagrams,

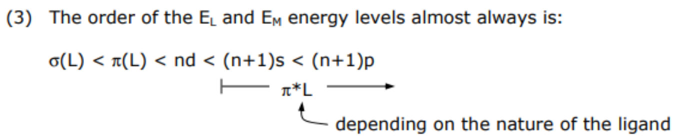
(1) M—L atomic orbital mixing is proportional to the overlap of the metal and ligand orbital, i.e., S_{ML}

> corollary A: only orbitals of correct symmetry can mix and ∴ give a nonzero interaction energy (i.e. $S_{ML} \neq 0$)
>
> corollary B: σ interactions typically give rise to larger interaction energies than those resulting from π interactions and π interactions are greater than δ interactions owing to more directional bonding along the series $S_{ML}(\sigma) > S_{ML}(\pi) > S_{ML}(\delta)$

(2) M–L atomic orbital mixing is inversely proportional to energy difference of mixing orbitals (i.e. ΔE_{ML}).

Another issue of interest for the construction of MOs is,

(3) The order of the EL and EM energy levels almost always is:



(3) The order of the E_L and E_M energy levels almost always is:

$\sigma(L) < \pi(L) < nd < (n+1)s < (n+1)p$

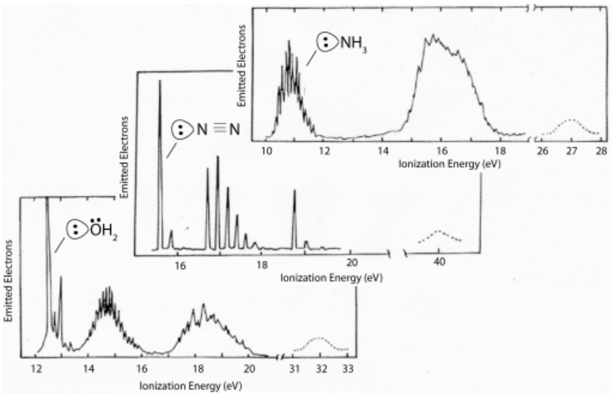
This energy ordering comes directly from Valence Orbital Ionization Energies (VOIE) of metal and main group atoms and PES spectra of molecular ligands.

	$3d^{n-1}4s \rightarrow 3d^{n-2}4s$	$\mathbf{3d^{n-1}4s \rightarrow 3d^{n-1}}$	$3d^{n-1}4p \rightarrow 3d^{n-1}$
Atom	3 d	4 s	4p
Sc	4.7	5.7	3.2
Ti	5.6	6.1	3.3
V	6.3	6.3	3.5
Cr	7.2	6.6	3.5
Mn	7.9	6.8	3.6
Fe	8.7	7.1	3.7
Co	9.4	7.3	3.8
Ni	10	7.6	3.8
Cu	10.7	7.7	4

Atom	**1 s**	**2 s**	2p	**3 s**	3p	**4 s**	4p
H	13.6						

Atom	1 s	2 s	2p	3 s	3p	4 s	4p
C		19.4	10.6				
N		25.6	13.2				
O		32.3	15.8				
F		40.2	18.6				
Si				14.9	7.7		
P				18.8	10.1		
S				20.7	11.6		
Br						24.1	12.5

PES energies of ligands are in eVs (note: a VOIE is simply the opposite of the ionization energy)



General observations:

(1) The s orbitals are generally too low in energy to participate in bonding ($\Delta E_{ML(\sigma)}$ is very large)

(2) Filled p orbitals are the frontier orbitals, and they have VOIEs that place them below the metal orbitals

(3) For molecular ligands, since the frontier orbitals comprise s and p orbitals, here too filled ligand orbitals have energies that are stabilized relative to the metal orbitals

---

1.11: Frontier molecular orbitals of σ-donor, π-donor and π-acceptor ligands

Before tackling the business of the complex, the nature of the ligand frontier orbitals must be considered. There are three general classes of ligands, as defined by their frontier orbitals: σ-donor ligands, π-donor ligands and π-acceptor ligands.

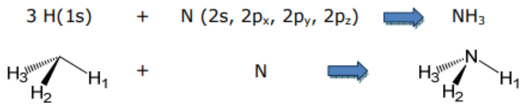
σ-donor ligands

These ligands donate two e– s from an orbital of σ-symmetry:

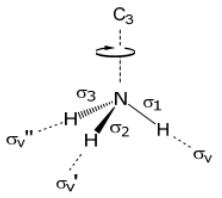
H^{-} ($1s^2$), NH_3 ($2a_1$ lp), PR_3 ($2a_1$ lp), CH_3^- ($2a_1$ lp), OH_2 (b_1 lp)

Note, some of these ligands are atomic, while others are LCAO-MOs. The frontier orbitals for bonding to the metal are thus are either atomic or molecular orbitals, depending on the nature of the ligand.

As an example of a molecular ligand, consider the ammonia ligand. Ammonia is formed from the LCAO between the valence orbitals of a central nitrogen and the three 1s orbitals of three hydrogens,



To begin this problem, the symmetry-adapted linear combinations of the three 1s orbitals must be determined. Hence, the basis will be derived from the H orbitals. Because the H(1s) orbitals can only form σ bonds, the choice of 3 σ N–H bonds is an appropriate basis set,



The transformation properties of the σ bonds (in C3v symmetry) are as follows:

$$E\begin{bmatrix}\sigma_1\\ \sigma_2\\ \sigma_3\end{bmatrix}\rightarrow\begin{bmatrix}\sigma_1\\ \sigma_2\\ \sigma_3\end{bmatrix}\rightarrow\begin{bmatrix}0&1&0\\ 0&0&1\\ 1&0&0\end{bmatrix}\tag{1.11.1}$$

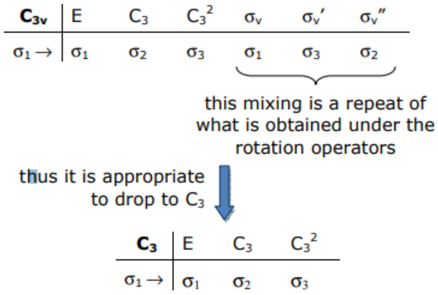
$$C_3\begin{bmatrix}\sigma_1\\ \sigma_2\\ \sigma_3\end{bmatrix}\rightarrow\begin{bmatrix}\sigma_1\\ \sigma_2\\ \sigma_3\end{bmatrix}\rightarrow\begin{bmatrix}1&0&0\\ 0&1&0\\ 0&0&1\end{bmatrix}\tag{1.11.2}$$

$$\sigma_v\begin{bmatrix}\sigma_1\\ \sigma_2\\ \sigma_3\end{bmatrix}\rightarrow\begin{bmatrix}\sigma_1\\ \sigma_2\\ \sigma_3\end{bmatrix}\rightarrow\begin{bmatrix}1&0&0\\ 0&0&1\\ 0&1&0\end{bmatrix}\tag{1.11.3}$$

These representation of this basis may be quickly ascertained by realizing that only bonds (or H(1s) orbitals) that do not move will contribute to the trace of the matrix representation,

$$\begin{array}{c|ccc}\mathrm{C_{3v}} & \mathrm{E} & \mathrm{2C_3} & 3\sigma_{\mathrm{v}}\\ \hline \Gamma_\sigma & 3 & 0 & 1\end{array}\rightarrow a_1+e\tag{1.11.4}$$

Projecting out the a1 and e SALCs of the 3H orbitals, we realize that the transformation properties of the H orbitals are preserved in the C3 rotational subgroup,



C_{3v}	E	C_3	C_3^2	σ_v	σ_v'	σ_v''
$\sigma_1 \rightarrow$	σ_1	σ_2	σ_3	σ_1	σ_3	σ_2

this mixing is a repeat of what is obtained under the rotation operators

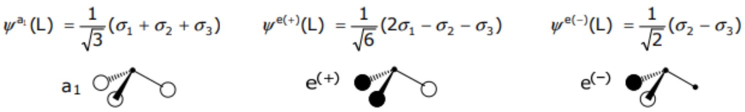
thus it is appropriate to drop to C_3

C_3	E	C_3	C_3^2
$\sigma_1 \rightarrow$	σ_1	σ_2	σ_3

Application of the projection operator in the cyclic C3 point group is an easy task – can simply read out the projections,

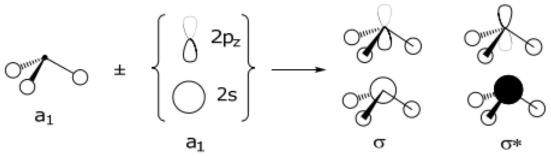
$$\mathrm{P}^{a_1}\left(\sigma_1\right) \rightarrow 1 \cdot \mathrm{E}\sigma_1 + 1 \cdot \mathrm{C}_3\sigma_1 + 1 \cdot \mathrm{C}_3^2\sigma_1 = \sigma_1 + \sigma_2 + \sigma_3$$
$$\mathrm{P}^{e(1)}\left(\sigma_1\right) \rightarrow 1 \cdot \mathrm{E}\sigma_1 + \left(\varepsilon^*\right)\mathrm{C}_3\sigma_1 + \varepsilon\mathrm{C}_3^2\sigma_1 = \sigma_1 + \varepsilon^*\sigma_2 + \varepsilon\sigma_3$$
$$\mathrm{P}^{e(2)}\left(\sigma_1\right) \rightarrow 1 \cdot \mathrm{E}\sigma_1 + \varepsilon\mathrm{C}_3\sigma_1 + \left(\varepsilon^*\right)\mathrm{C}_3^2\sigma_1 = \sigma_1 + \varepsilon\sigma_2 + \varepsilon^*\sigma_3$$

Taking appropriate linear combinations and normalizing,

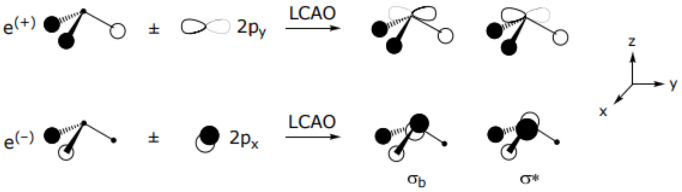


$$\psi^{a_1}(L) = \frac{1}{\sqrt{3}}(\sigma_1 + \sigma_2 + \sigma_3) \qquad \psi^{e(+)}(L) = \frac{1}{\sqrt{6}}(2\sigma_1 - \sigma_2 - \sigma_3) \qquad \psi^{e(-)}(L) = \frac{1}{\sqrt{2}}(\sigma_2 - \sigma_3)$$

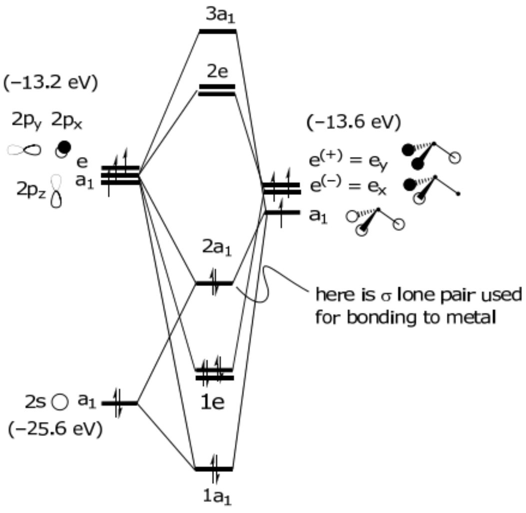
Only orbitals of the same symmetry can form a LCAO; thus the a1 SALC of the 3H(1s) orbitals can only combine with the a1 orbitals of the central N (i.e., the 2s and $2p_z$ valence orbitals),



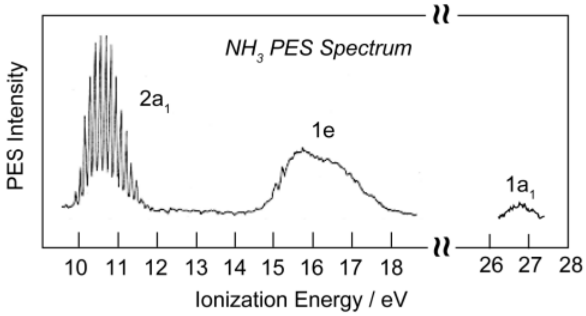
he $2p_y$ orbital combines with $e^{(+)}$, it is orthogonal to $e^{(-)}$, whereas the opposite is true for $2p_x$ orbital,



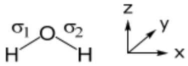
The MO is constructed by overlapping orbitals of the same symmetry. The greater the overlap, the greater the splitting between the orbitals. Note that the a_1 SALC participates in two types of σ interactions, one with the 2s orbital and one with the $2p_z$ orbital of nitrogen. The highest energy orbital, the ligand HOMO orbital, is used for bonding to the metal. This orbital too is composed of two types of interactions: (i) it is Lσ(a_1)–N(2s) antibonding and (ii) Lσ(a_1)–N($2p_z$) bonding in character. The energy of the atomic orbitals are shown in parenthesis.



Simple hybridization arguments predict two different of bond energies for NH_3: (1) the lone pair and (2) the σ N–H bond. The MO diagram on the other hand predicts three different energies. The photoelectron spectrum of NH_3 exhibits three ionization energies, thus verifying the MO bonding model.



A second molecular ligand is water. The ligand has two lone pairs, but only one is used in bonding to the metal. The reason for this electronic asymmetry and why only one lone pair is only available for bonding becomes evident from the electronic structure of the water molecule.



The basis set for water is the 2H(1s) orbitals and the O(2s, $2p_z$, $2p_x$, $2p_y$) atomic orbitals. The proper symmetry adapted linear combination for the 2H(1s) orbitals may be ascertained using the above σ bonds.

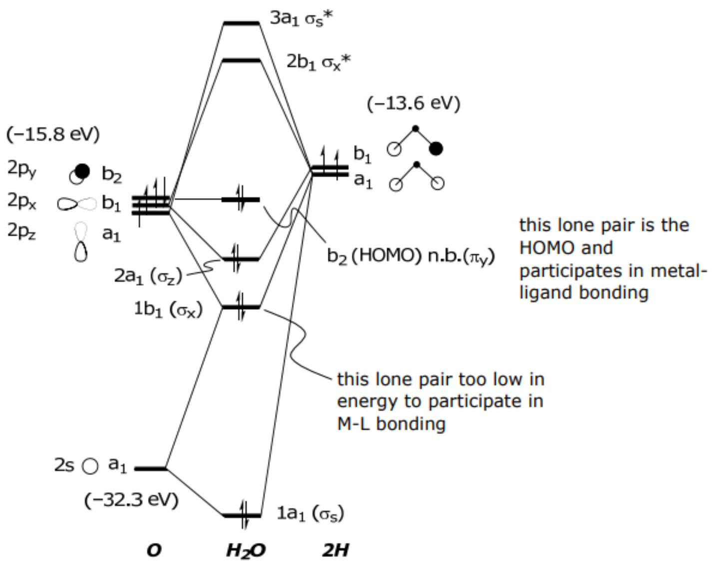
$\mathbf{C_{2v}}$	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$	
Γ_σ	2	0	2	0	$\rightarrow a_1 + b_1$
$\sigma_1 \rightarrow$	σ_1	σ_2	σ_1	σ_2	

Applying the projection operator,

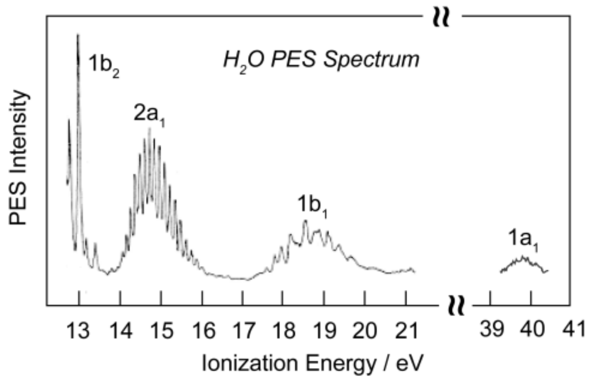
$$P^{a_1}(\sigma_1) \rightarrow 1\cdot\overbrace{E\sigma_1}^{\sigma_1} + 1\cdot\overbrace{C_2\sigma_1}^{\sigma_2} + 1\cdot\overbrace{\sigma(xz)\cdot\sigma_1}^{\sigma_1} + 1\cdot\overbrace{\sigma(yz)\cdot\sigma_1}^{\sigma_2} \rightarrow \psi_{a_1} = \frac{1}{\sqrt{2}}(\sigma_1+\sigma_2)$$

$$P^{b_1}(\sigma_1) \rightarrow 1\cdot E\sigma_1 + (-1)\cdot C_2\sigma_1 + 1\cdot\sigma(xz)\cdot\sigma_1 + (-1)\cdot\sigma(yz)\cdot\sigma_1 \rightarrow \psi_b = \frac{1}{\sqrt{2}}(\sigma_1-\sigma_2)$$

The s and pz orbitals on O have a1 symmetry and thus will mix with the Lσ(a_1), the p_x has b_1 symmetry and will mix with Lσ(b_1) and the p_y orbital is rigorously nonbonding, i.e., does not have a symmetry counterpart of the O atom, and hence no LCAO is formed using this orbital.

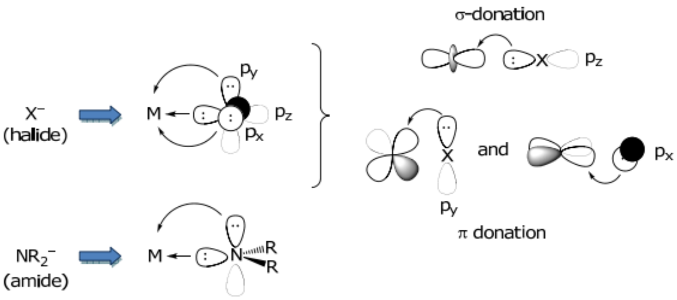


Again, the simple hybridization picture of bonding is shown to be incorrect, and the MO bonding model is corroborated.

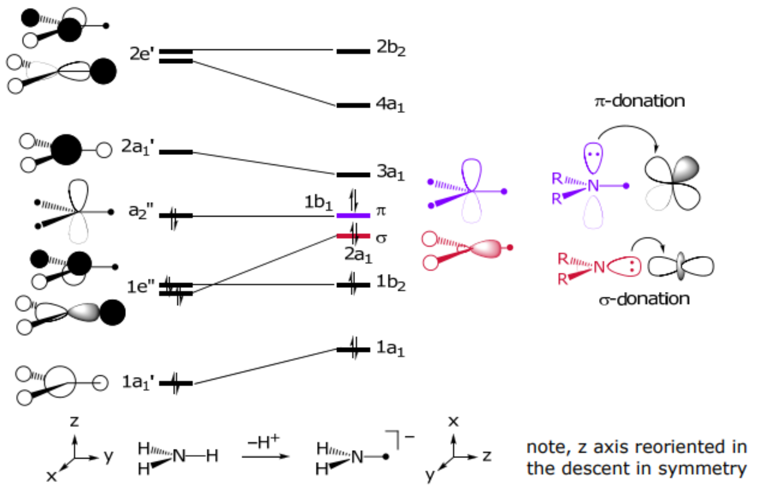


π-donors

π-donors In addition to donating electron density to a metal via a σ-bond, e⁻s may be provided to the metal via a π-symmetry interaction. π-donor ligands include X^- (halide), amide (NR_2^-), sulfide (S^{2-}), oxide (O^{2-}), alkoxide (RO^-).

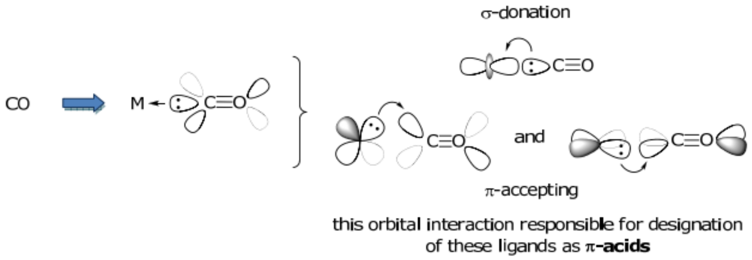


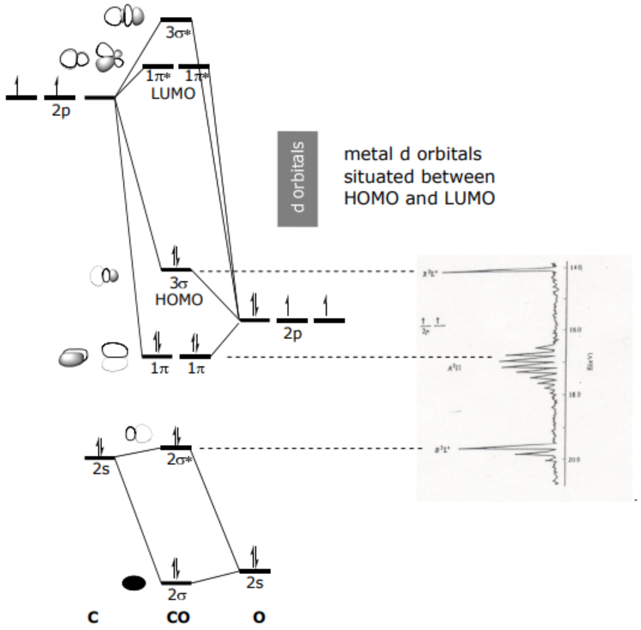
The amide MO may be constructed by beginning with the MO of “planar” NH_3, followed by its perturbation upon removal of H^+,



π-acceptors

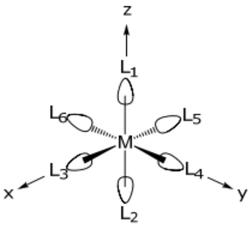
This class of ligands donate e^-s from a σ orbital and they accept e^-s from the metal into an empty π* orbital. CO is the archetype of this ligand class. Other π-acceptors are NO$^+$, CN$^-$, CNR. Consider the MO diagram of CO below; the HOMO is filled and of σ-symmetry, the LUMO is empty and of π* symmetry.





1.12: Octahedral ML_6 Sigma Complexes

An octahedral complex comprises a central metal ion and six terminal ligands. If the ligands are exclusively σ-donors, then the basis set for the ligands is defined as follows,



Ligands that move upon the application of an operation, R, cannot contribute to the diagonal matrix element of the representation. Since the σ bond is along the internuclear axis that connects the ligand and metal, the transformation properties of the ligand are correspondent with that of the M–L σ bond. Moreover, a σ bond has no phase change within the internuclear axis, hence the bond can only transform into itself (+1) or into another ligand (0).

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2\ (=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
$\Gamma_{L\sigma}$	6	0	0	2	2	0	0	0	4	2

(1.12.1)

$$\Gamma_{L\sigma} = a_{1g} + t_{1u} + e_g \tag{1.12.2}$$

Need now to determine the SALCs of the Lσ basis set. Three different methods will deliver the SALCs.

Method 1

As we have done previously, the SALCs of Lσ may be determined using the projection operator. Note that the ligand mixing in O_h is retained in the pure rotational subgroup, O. Can thus drop from O_h → O, thereby saving 24 operations.

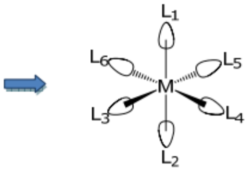
O	E	C_3	C_3	C_3	C_3	C_3	C_3	C_3	C_3	C_2	C_2	C_2	C_2	C_2	C_2	C_4	C_4	C_4	C_4	C_4	C_4	C_2	C_2	C_2
$L_1 \rightarrow$	L_1	L_3	L_4	L_4	L_5	L_6	L_5	L_6	L_3	L_2	L_2	L_6	L_5	L_4	L_3	L_1	L_1	L_5	L_3	L_4	L_6	L_1	L_2	L_2

The A_1 irreducible representation is totally symmetric. Hence the projection is simply the sum of the above ligand transformations.

$$P^{A_1}(L1) \sim 4(L1 + L2 + L3 + L4 + L5 + L6)$$

and normalizing yields,

$$\boldsymbol{\psi_{a_{1g}} = \frac{1}{\sqrt{6}}(L_1 + L_2 + L_3 + L_4 + L_5 + L_6)} \tag{1.12.3}$$

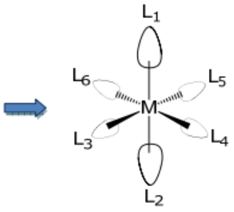


The application of the projection operator for the E irreducible representation furnishes the E_g SALCs.

$$\begin{aligned} P^E(L_1) &\rightarrow (2L_1 - L_3 - L_4 - L_4 - L_5 - L_6 - L_5 - L_6 - L_3 + 2L_1 + 2L_2 + 2L_2) \\ &\rightarrow (4L_1 + 4L_2 - 2L_3 - 2L_4 - 2L_5 - 2L_6) \end{aligned}$$

and normalizing yields,

$$\psi_{e_g}^{(1)} = \frac{1}{\sqrt{12}}\left(2L_1 + 2L_2 - L_3 - L_4 - L_5 - L_6\right)$$



But E_g is a doubly degenerate representation, and therefore there is a another SALC. As is obvious from above, the projection operator only yields one of the two SALCs. How do we obtain the other?

Method 2

The **Schmidt orthogonalization** procedure can extract SALCs from a nonorthogonal linear combination of an appropriate basis. Suppose we have a SALC, $\mathbf{v_1}$, then there exists a $\mathbf{v_2}$ that meets the following condition,

$$\mathbf{v_2} = a\mathbf{v_1} + \mathbf{u}$$

where $\mathbf{u}$ is the non-orthogonal linear combination. Multiplying the above equation by $\mathbf{v_1}$ gives,

$$\cancelto{0}{\mathbf{v_2 v_1}} = a\cancelto{1}{\mathbf{v_1 v_1}} + \mathbf{uv_1}$$

$$\therefore a = -\mathbf{uv_1}$$

What is the nature of $\mathbf{u}$? Consider using the projection operator on L_3 instead of L_1,

$$P^{e_g}(L_3) = \frac{1}{\sqrt{12}}(2L_3 + 2L_5 - L_1 - L_2 - L_4 - L_6) \tag{1.12.4}$$

Note, this does not yield any new information, i.e., the atomic orbitals on one axis are twice that and out-of-phase from the atomic orbitals in the equatorial plane. However, this new wavefunction is not $\psi_{eg}^{(2)}$ because it is not orthogonal to $\psi_{eg}^{(1)}$.

Thus the projection must yield a wavefunction that is a linear combination of $\psi_{eg}^{(1)}$ and $\psi_{eg}^{(2)}$, i.e., the wavefunction obtained from the projection is a viable $\mathbf{u}$. Applying the Schmidt orthogonalization procedure,

$$\begin{aligned} a &= -\mathbf{uv}_1 = -\left\langle \frac{1}{\sqrt{12}}(2L_3 + 2L_5 - L_1 - L_2 - L_4 - L_6) \mid \frac{1}{\sqrt{12}}(2L_1 + 2L_2 - L_3 - L_4 - L_5 - L_6) \right\rangle \\ &= -\frac{1}{12}[-6] = +\frac{1}{2} \end{aligned}$$

so,

$$\begin{aligned} \mathbf{v}_2 &= \frac{1}{2}\frac{1}{\sqrt{12}}(2L_1 + 2L_2 - L_3 - L_4 - L_5 - L_6) + \frac{1}{\sqrt{12}}(2L_3 + 2L_5 - L_1 - L_2 - L_4 - L_6) \\ &= \frac{1}{\sqrt{12}}\left[\left(\frac{3}{2}L_3 + \frac{3}{2}L_5\right) - \left(\frac{3}{2}L_4 + \frac{3}{2}L_6\right)\right] \approx (L_3 + L_5) - (L_4 + L_6) \end{aligned}$$

$$\therefore \psi_{e_g}^{(2)} = \frac{1}{2}(L_3 - L_4 + L_5 - L_6) \Rightarrow$$

$\psi_{eg}^{(2)}$ is orthogonal to $\psi_{eg}^{(1)}$, thus it is the other SALC.

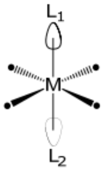
The T_{1g} SALCs must now be determined. The projection operator yields,

$$P^{T_1}(L_1) \rightarrow (3L_1 - L_2 - L_2 - L_6 - L_5 - L_4 - L_3 + L_1 + L_1 + L_5 + L_3 + L_4 + L_6 - L_1 - L_1 - L_2)$$

$$P^{T_1}(L_1) \sim 3(L_1 - L_2)$$

and normalizing yields,

$$\psi_{t_{1u}}^{(1)} = \frac{1}{\sqrt{2}}(L_1 - L_2) \Rightarrow$$



Applying the Schmidt orthogonalization method,

$$P^{T_1}(L_3) \sim 3(L_3 - L_5) \rightarrow \psi_{t_{1u}} = \frac{1}{\sqrt{2}}(L_3 - L_5) \tag{1.12.5}$$

This wavefunction is orthogonal to $\psi_{t_{1u}}^{(1)}$, hence it is likely a SALC. Can prove this by t1u applying the Schmidt orthogonalization process and setting this to be u. Solving for a,

$$\begin{aligned} a &= -\mathbf{u}\mathbf{v}_1 = -\left\langle \frac{1}{\sqrt{2}}(\mathrm{L}_1 - \mathrm{L}_2) \mid \frac{1}{\sqrt{2}}(\mathrm{L}_3 - \mathrm{L}_5)\right\rangle \\ &= -\frac{1}{2}(0) = 0 \end{aligned}$$

and

$$v_2 = av_1 + u = 0 \cdot \frac{1}{\sqrt{2}}(L_1 - L_2) + \frac{1}{\sqrt{2}}(L_3 - L_5) \tag{1.12.6}$$

so, as suspected, this is a SALC. And the third SALC of T_{1u} symmetry is the (L_4,L_6) pair.

Method 3

For those SALCs with symmetries that are the same as s, p or d orbitals, may adapt the symmetry of the ligand set to the symmetry of the metal orbitals.

Consider the dz2 orbital, which is more accurately defined as $2z^2 - x^2 - y^2$. Thus the coefficient of the z axis is twice that of x and y and out of phase with x and y. The ligands on the z-axis, L_1 and L_2, should therefore be twice that and of opposite sign to the equatorial ligands, L_3,L_4,L_5,L_6. This leads naturally to,

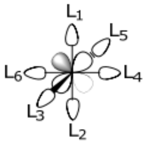
$$\begin{aligned} \psi_{\mathrm{e_9}}^{(1)} &\approx 2\,\mathrm{L}_1 + 2\,\mathrm{L}_2 - \mathrm{L}_3 - \mathrm{L}_4 - \mathrm{L}_5 - \mathrm{L}_6 \\ \psi_{\mathrm{e_9}}^{(1)} &= \frac{1}{\sqrt{12}}(2\,\mathrm{L}_1 + 2\,\mathrm{L}_2 - \mathrm{L}_3 - \mathrm{L}_4 - \mathrm{L}_5 - \mathrm{L}_6) \end{aligned}$$

The other SALC of this degenerate set is given by $d_{x^2-y^2}$, which has no coefficient on z, and x and y coefficients that are equal but of opposite sign. By symmetry matching to the orbital,

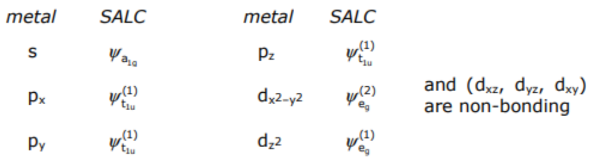
$$\begin{aligned} \psi_{\mathrm{e_9}}^{(2)} &\approx \mathrm{L}_3 - \mathrm{L}_4 + \mathrm{L}_5 - \mathrm{L}_6 \\ \psi_{\mathrm{e_9}}^{(2)} &= \frac{1}{2}(\mathrm{L}_3 - \mathrm{L}_4 + \mathrm{L}_5 - \mathrm{L}_6) \end{aligned}$$

The other SALCs follow suit.

The t_{2g} d-orbital set (i.e. d_{xy}, d_{xz}, d_{yz}) is of incorrect symmetry to interact with the Lσ ligand set and thus is non-bonding. This can be seen from the orbital picture. The Lσ orbitals are directed between the lobes of the t_{2g} d-orbitals,

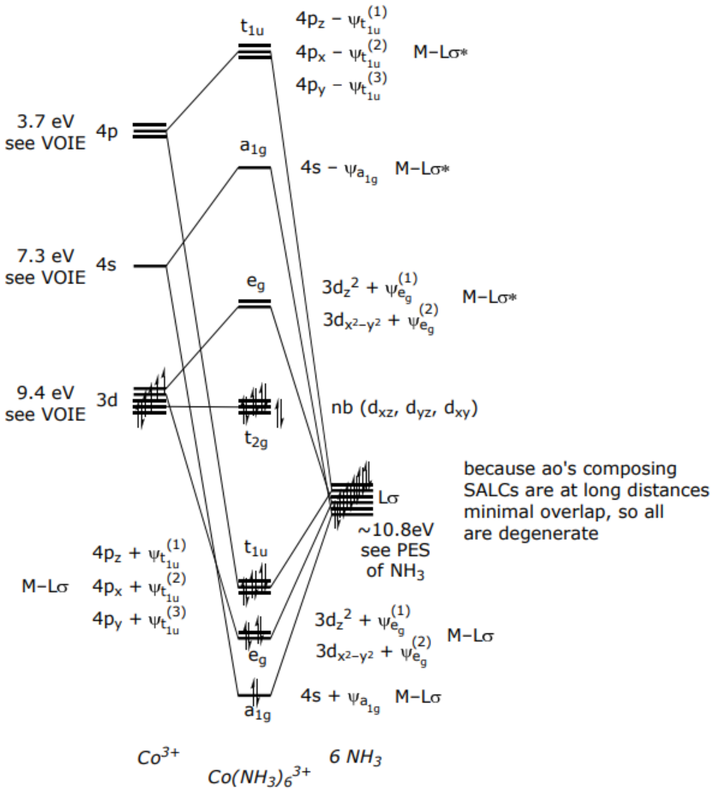


Only metal orbitals and SALCs of the same symmetry can overlap. In the case of the octahedral ML_6 σ-complex,



metal	SALC	metal	SALC	
s	$\psi_{a_{1g}}$	p_z	$\psi_{t_{1u}}^{(1)}$	
p_x	$\psi_{t_{1u}}^{(1)}$	$d_{x^2-y^2}$	$\psi_{e_g}^{(2)}$	and (d_{xz}, d_{yz}, d_{xy}) are non-bonding
p_y	$\psi_{t_{1u}}^{(1)}$	d_{z^2}	$\psi_{e_g}^{(1)}$	

With above considerations of ΔE_{ML} and S_{ML} in mind, the MO diagram for $M(L\sigma)_6$ is constructed with $Co(NH_3)_6{}^{3+}$ as the exemplar,



Interaction energies ε_σ and $\varepsilon_{\sigma*}$ (i.e., the off-diagonal matrix elements, H_{ML}) are smaller than the difference in energies of the metal and ligand atomic orbitals (i.e., the diagonal matrix elements, H_{MM} and H_{LL}), so molecular orbitals stay within their energy “zones”.

1.13: Octahedral ML$_6$ π complexes

The basis set needs to be expanded for metal complexes with ligands containing π orbitals. An appropriate basis for ligands with two orthogonal π orbitals, e.g. CO, CN$^-$, O^{2-}, X$^-$, to the σ bond is shown below.

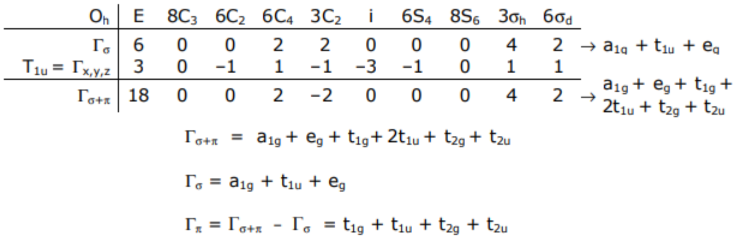
The arrow is indicative of the directional phase of the pπ orbitals. Owing to their ungerade symmetry, in constructing the pπ representation

- a p orbital, i.e. arrow, that transforms into itself contributes +1
- a p orbital that transforms into minus itself contributes –1
- a p orbital that moves, contributes 0

$$\begin{array}{c|cccccccccc} O_h & E & 8C_3 & 6C_2 & 6C_4 & 3C_2 & i & 6\,S_4 & 8\,S_6 & 3\sigma_h & 6\sigma_d & \\ \hline \Gamma_\sigma & 6 & 0 & 0 & 2 & 2 & 0 & 0 & 0 & 4 & 2 & \rightarrow a_{19}+t_{1u}+e_g \\ \Gamma_\pi & 12 & 0 & 0 & 0 & -4 & 0 & 0 & 0 & 0 & 0 & \rightarrow t_{1\,g}+t_{1u}+t_{2\,g}+t_{2u} \end{array} \tag{1.13.1}$$

There is a second method to derive the pπ basis. The Cartesian coordinate systems on each ligand contains the σ and π basis sets. Thus the $\Gamma_{x,y,z}$ irreducible representation (which is the sum of Γ_x + Γ_y + Γ_z or Γ_z + $\Gamma_{x,y}$ for irreducible representations for which x,y,z are not triply degenerate) defines the 1σ and 2pπ bonds of each ligand. Since the bond is coincident with the ligand, an unmoved atom is approximated by Γσ. On the basis of geometrical considerations, the following is true,

$$\Gamma_{\underset{\text{atomoved}}{\text{atoms}}} = \Gamma_\sigma$$
$$\Gamma_{\sigma+\pi} = \Gamma_{x,y,z}\cdot\Gamma_\sigma$$
$$\Gamma_\pi = \Gamma_{\sigma+\pi} - \Gamma_\sigma$$



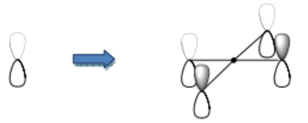
O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	
Γ_σ	6	0	0	2	2	0	0	0	4	2	$\rightarrow a_{1g} + t_{1u} + e_g$
$T_{1u} = \Gamma_{x,y,z}$	3	0	−1	1	−1	−3	−1	0	1	1	
$\Gamma_{\sigma+\pi}$	18	0	0	2	−2	0	0	0	4	2	$\rightarrow a_{1g} + e_g + t_{1g} + 2t_{1u} + t_{2g} + t_{2u}$

$$\Gamma_{\sigma+\pi} = a_{1g} + e_g + t_{1g} + 2t_{1u} + t_{2g} + t_{2u}$$

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

$$\Gamma_\pi = \Gamma_{\sigma+\pi} - \Gamma_\sigma = t_{1g} + t_{1u} + t_{2g} + t_{2u}$$

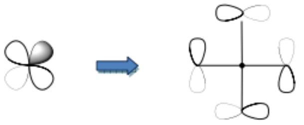
The σ SALCs have already been derived in Lecture 12. Methods 1-3 of Lecture 12 can be employed to determine the pπ SALCs. For the orbitals that transform as t_{1u} and t_{2g}, Method 3 (mirror the metal atomic orbital symmetry) is convenient. For the t_{1u} SALC,



and 2 others (in the xz and yz planes as defined by the symmetries of the p_y and p_x orbitals)

p_z $$\psi^{(1)}_{t_{1u}} = \frac{1}{2}\left(L\pi_3 + L\pi_4 + L\pi_5 + L\pi_6\right)$$

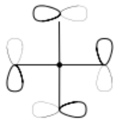
The t_{2g} SALCs have the mirrored symmetry of the (d_{xy},d_{xz},d_{yz}) orbital set,



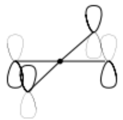
and 2 others (in the xy and xz planes as defined by the symmetries of the d_{xy} and d_{xz} orbitals)

d_{yz} $$\psi^{(1)}_{t_{2g}} = \frac{1}{2}\left(L\pi_1 - L\pi_2 - L\pi_4 + L\pi_6\right)$$

Non-bonding SALCs must be ascertained from projection operators and Schmidt orthogonalization methods.

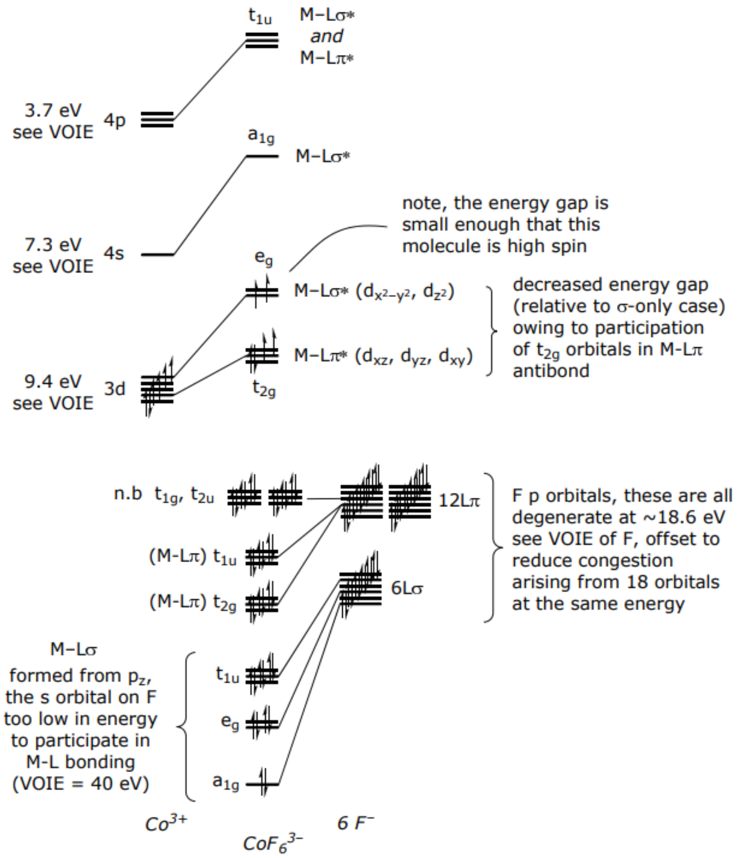


t_{1g} (and 2 others in the xz and xy planes)

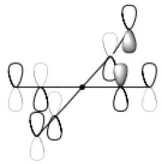


t_{2u} (and 2 others in the xz and yz planes)

For a π donor complex such as $CoF_6{}^{3-}$,

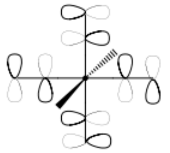


For a π-accepting ligand set, orbitals have the same form (or symmetry) as π donors,



t_{1u}

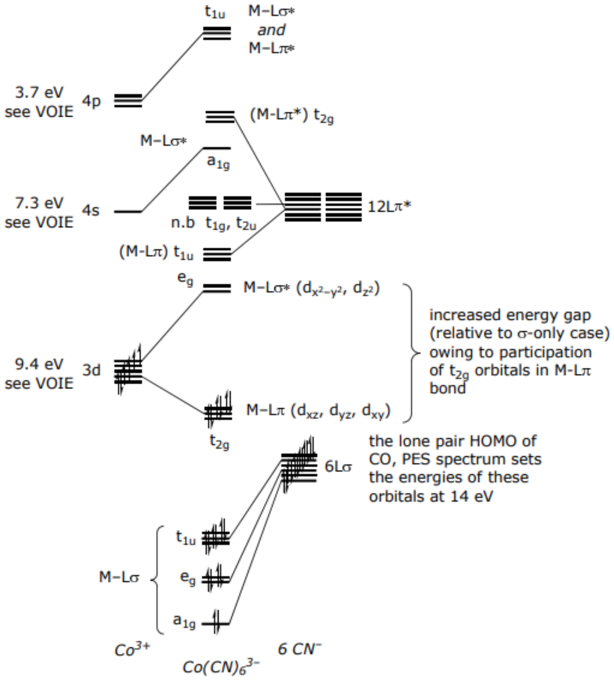
$$\psi_{t_{1u}}^{(1)}=\frac{1}{2}\left(L\pi_3{}^{*}+L\pi_4{}^{*}+L\pi_5{}^{*}+L\pi_6{}^{*}\right)$$



t_{2g}

$$\psi_{t_{2g}}^{(1)}=\frac{1}{2}\left(L\pi_1{}^{*}-L\pi_2{}^{*}-L\pi_4{}^{*}+L\pi_6{}^{*}\right)$$

The only difference between the π-donor and π-acceptor MO diagrams is the relative placement of the π* orbitals relative to the metal atomic orbitals; for $Co(CN)_6{}^{3-}$,


t1u
M–Lσ*
and
M–Lπ*
3.7 eV
see VOIE
4p
(M-Lπ*) t2g
M–Lσ*
a1g
7.3 eV
see VOIE
4s
n.b
t1g, t2u
12Lπ*
(M-Lπ) t1u
eg
M–Lσ* (dx²−y², dz²)
increased energy gap
(relative to σ-only case)
owing to participation
of t2g orbitals in M-Lπ
bond
9.4 eV
see VOIE
3d
M–Lπ (dxz, dyz, dxy)
t2g
6Lσ
the lone pair HOMO of
CO, PES spectrum sets
the energies of these
orbitals at 14 eV
t1u
M–Lσ
eg
a1g
Co3+
Co(CN)6 3−
6 CN−

1.14: Angular Overlap Method and M-L Diatomics

The Wolfsberg-Hemholtz approximation (Lecture 10) provided the LCAO-MO energy between metal and ligand to be,

$$\varepsilon_{\sigma} = \frac{\mathrm{E}_{\mathrm{M}}^{2}\,\mathrm{S}_{\mathrm{ML}}^{2}}{\Delta \mathrm{E}_{\mathrm{ML}}} \quad \varepsilon_{\sigma^{*}} = \frac{\mathrm{E}_{\mathrm{L}}^{2}\,\mathrm{S}_{\mathrm{ML}}^{2}}{\Delta \mathrm{E}_{\mathrm{ML}}} \tag{1.14.1}$$

Note that E_M, E_L and ΔE_{ML} in the above expressions are constants. Hence, the MO within the Wolfsberg-Hemholtz framework scales directly with the overlap integral, S_{ML}

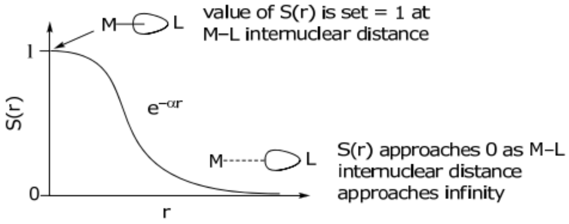
$$\varepsilon_{\sigma} = \frac{\mathrm{E_M}^{2}\,\mathrm{S}_{\mathrm{ML}}^{2}}{\Delta \mathrm{E}_{\mathrm{ML}}} = \beta' \mathrm{S}_{\mathrm{ML}}^{2} \quad \varepsilon_{\sigma^{*}} = \frac{\mathrm{E}_{\mathrm{L}}^{2}\,\mathrm{S}_{\mathrm{ML}}^{2}}{\Delta \mathrm{E}_{\mathrm{ML}}} = \beta \mathrm{S_{ML}}^{2} \tag{1.14.2}$$

where β and β´are constants. Thus by determining the overlap integral, S_{ML}, the energies of the MOs may be ascertained relative to the metal and ligand atomic orbitals.

The **Angular Overlap Method** (AOM), provides a measure of S_{ML} and hence MO energy levels. In AOM, the overlap integral is also factored into a radial and angular product,

$$S_{ML}=S(r)F(\theta,\Phi)$$

Analyzing S(r) as a function of the M–L internuclear distance,

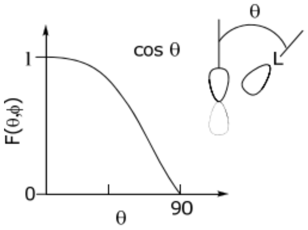


Under the condition of a fixed M-L distance, S(r) is invariant, and therefore the overlap integral, S_{ML}, will depend only on the angular dependence, i.e., on F(θ,φ).

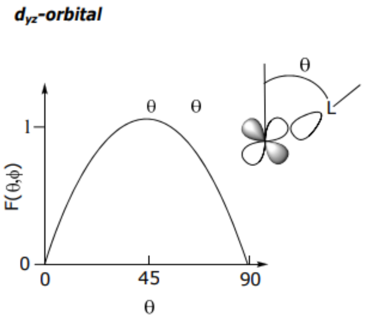
Because the σ orbital is symmetric, the angular dependence, F(θ,φ), of the overlap integral mirrors the angular dependence of the central orbital.

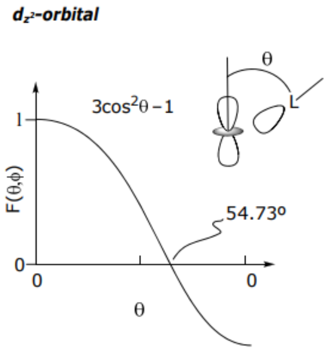
p-orbital

…is defined angularly by a cos θ function. Hence, the angular dependence of a σ orbital as it angularly rotates about a p-orbital reflects the cos θ angular dependence of the p-orbital.



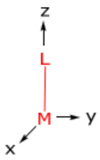
Similarly, the other orbitals take on the angular dependence of the central metal orbital. Hence, for a



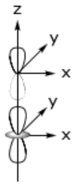


ML Diatomic Complexes

To begin, let’s determine the energy of the d-orbitals for a M-L diatomic defined by the following coordinate system,



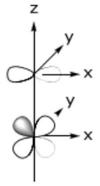
There are three types of overlap interactions based on σ, π and δ ligand orbital symmetries. For a σ orbital, the interaction is defined as,

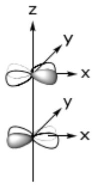


$$E\left(d_{z^2}\right) = S^2_{ML}(\sigma) = \beta \cdot F_\sigma{}^2(\theta, \phi) = \beta \cdot 1 = e\sigma \tag{1.14.3}$$

The energy for maximum overlap, at θ = 0 (see above) is set equal to 1. This energy is defined as eσ. The metal orbital bears the antibonding interaction, hence d_{z^2} is destablized by eσ (the corresponding L orbital is stabilized by (β’)2 • 1 = eσ’).

For orbitals of π and δ symmetry, the same holds…maximum overlap is set equal to 1, and the energies are eπ and eδ, respectively.



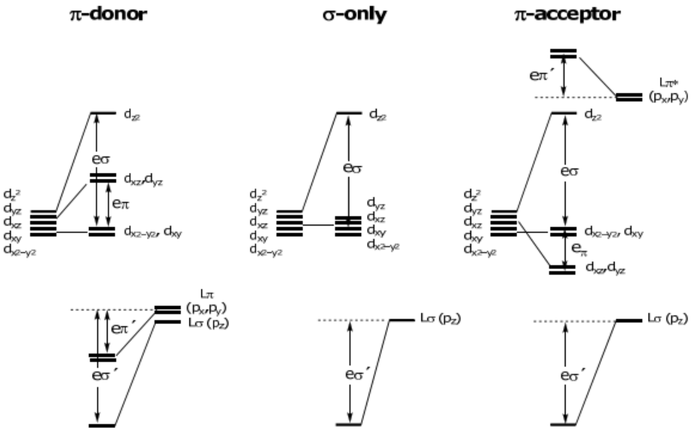


$E(d_{yz})=E(d_{xz})=S_{ML}{}^2(\pi)=e\pi$ $E(d_{xy})=E(d_{x^2-y^2})=S_{ML}{}^2(\delta)=e\delta$

As with the σ interaction, the (M-Lπ)* interaction for the d-orbitals is de-stabilizing and the metal-based orbital is destablized by eπ, whereas the Lπ ligands are stabilized by eπ. The same case occurs for a ligand possessing a δ orbital, with the only difference being an energy of stabilization of eδ for the Lδ orbital and the energy of de-stabilization of eδ for the δ metal-based orbitals.

$S_{ML}(\delta)$ is small compared to $S_{ML}(\pi)$ or $S_{ML}(\sigma)$. Moreover, there are few ligands with δ orbital symmetry (if they exist, the δ symmetry arises from the pπ-systems of organic ligands). For these reasons, the $S_{ML}(\delta)$ overlap integral and associated energy is not included in most AOM treatments.

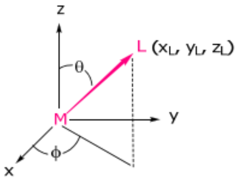
Returning to the problem at hand, the overall energy level diagrams for a M-L diatomic molecule for the three ligand classes are:



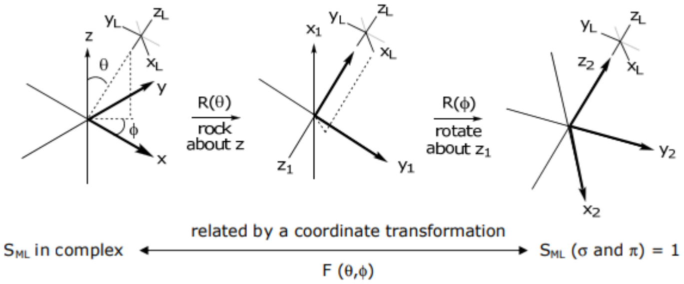
ML$_6$ Octahedral Complexes

Of course, there is more than 1 ligand in a typical coordination compound. The power of AOM is that the eσ and eπ (and eδ), energies are additive. Thus, the MO energy levels of coordination compounds are determined by simply summing eσ and eπ for each M(d)-L interaction.

Consider a ligand positioned arbitrarily about the metal,

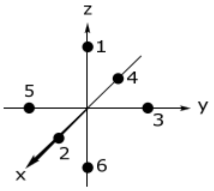


We can imagine placing the ligand on the metal z axis (with x and y axes of M and L also aligned) and then rotate it on the surface of a sphere (thus maintaining M-L distance) to its final coordinate position. Within the reference frame of the ligand,



Note, the coordinate transformation lines up the ligand of interest on the z axis so that the normalized energies, eσ and eπ (and eδ) may be normalized to 1. The transformation matrix for the coordinate transformation is:

$$\begin{array}{c|ccccc} & \mathbf{z_2}^2 & \mathrm{y}_2\mathbf{z}_2 & \mathrm{x}_2 z_2 & \mathrm{x}_2\mathrm{y}_2 & \mathrm{x_2}^2-\mathrm{y_2}^2 \\ \hline \mathbf{z^2} & \frac{1}{4}(1+3\cos 2\theta) & 0 & -\frac{\sqrt{3}}{2}\sin 2\theta & 0 & \frac{\sqrt{3}}{4}(1-\cos 2\theta) \\ \mathbf{yz} & \frac{\sqrt{3}}{2}\sin\phi\sin 2\theta & \cos\phi\cos\theta & \sin\phi\cos 2\theta & -\cos\phi\sin\theta & -\frac{1}{2}\sin\phi\sin 2\theta \\ \mathbf{xz} & \frac{\sqrt{3}}{2}\cos\phi\sin 2\theta & -\sin\phi\cos\theta & \cos\phi\cos 2\theta & \sin\phi\sin\theta & -\frac{1}{2}\cos\phi\sin 2\theta \\ \mathbf{xy} & \frac{\sqrt{3}}{4}\sin 2\phi(1-\cos 2\theta) & \cos 2\phi\sin\theta & \frac{1}{2}\sin 2\phi\sin 2\theta & \cos 2\phi\cos\theta & \frac{1}{4}\sin 2\phi(3+\cos 2\theta) \\ \mathbf{x^2-y^2} & \frac{\sqrt{3}}{4}\cos 2\phi(1-\cos 2\theta) & -\sin 2\phi\sin\theta & \frac{1}{2}\cos 2\phi\sin 2\theta & -\sin 2\phi\cos\theta & \frac{1}{4}\cos 2\phi(3+\cos 2\theta) \end{array} \tag{1.14.4}$$



Ligand	1	2	3	4	5	6
θ	0	90	90	90	90	180°
ϕ	0	0	90	180	270	0

Consider the overlap of Ligand 2 in the transformed coordinate space; the contribution of the overlap of Ligand 2 with each metal orbital must be considered. This orbital interaction is given by the transformation matrix above. By substituting the θ = 90 and φ = 0 for Ligand 2 into the above transformation matrix, one finds,

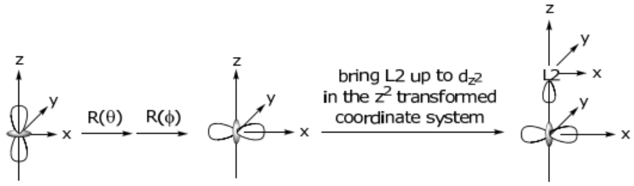
for d_{z^2} for L_2

$$\begin{aligned} \mathrm{d}_{z^2} &= \frac{1}{4}(1+3\cos 2\theta)d_{z_2{}^2} + 0d_{y_2z_2} - \frac{\sqrt{3}}{2}\sin 2\theta d_{x_2z_2} + 0d_{x_2y_2} + \frac{\sqrt{3}}{4}(1-\cos 2\theta)d_{x_2^2-y_2^2} \\ &= -\frac{1}{2}d_{z_2^2} + 0d_{y_2z_2} + 0d_{x_2z_2} + 0d_{x_2y_2} + \frac{\sqrt{3}}{2}d_{x_2^2-y_2^2} \end{aligned}$$

Thus the d_{z^2} orbital in the transformed coordinate, d_{z2^2}, has a contribution from d_{z^2} and $d_{x^2-y^2}$. Recall that energy of the orbital is defined by the square of the overlap integral. Thus the above coefficients are squared to give the energy of the d_{z^2} orbital as a result of its interaction with Ligand 2 to be,

$$\mathrm{E}(\mathrm{d}_{z^2})^{\mathrm{L2}} = \mathrm{S_{ML}}^2(\sigma) = \beta\cdot \mathrm{F}_\sigma^2(\theta,\phi) = \tfrac{1}{4}\ \mathrm{d}_{\mathrm{z_2}^2} + \tfrac{3}{4}\ \mathrm{d}_{\mathrm{x_2}^2-\mathrm{y_2}^2} = \tfrac{1}{4}\mathrm{e}\sigma + \tfrac{3}{4}\mathrm{e}\delta$$

Visually, this result is logical. In the coordinate transformation, a σ ligand residing on the z-axis (of energy eσ) is overlapping with d_{z^2}. This is the energy for L1. The normalized energy for L2 is its overlap with the coordinate transformed d_{z^2} 2:



Note, the d_{z^2} orbital is actually $2z^2 - x^2 - y^2$, which is a linear combination of $z^2 - x^2$ and $z^2 - y^2$. Thus in the coordinate transformed system, L2, as compared to L1, is looking at the x^2 contribution of the wavefunction to σ bonding. Since it is ½ the electron density of that on the z-axis, it is ¼ the energy (i.e., the square of the coefficient) on the σ-axis, hence ¼ eσ. The δ component of the transformation comes from the $2z^2 - (x^2 + y^2)$ orbital functional form. Thus if L2 has an orbital of δ symmetry, then it will have an energy of ¾ eδ.

The transformation properties of the other d-orbitals, as they pertain to L2 orbital overlap, may be ascertained by completing the transformation matrix for θ = 90 and φ = 0,

$$\begin{bmatrix} \mathrm{d_{z^2}} \\ \mathrm{d_{yz}} \\ \mathrm{d_{xz}} \\ \mathrm{d_{xy}} \\ \mathrm{d}_{\mathrm{x}^2-y^2} \end{bmatrix} = \begin{bmatrix} -\frac{1}{2} & 0 & 0 & 0 & \frac{\sqrt{3}}{2} \\ 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & -1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ \frac{\sqrt{3}}{2} & 0 & 0 & 0 & \frac{1}{2} \end{bmatrix} \begin{bmatrix} \mathrm{d}_{z_2{}^2} \\ \mathrm{d}_{\mathrm{y}_2 z_2} \\ \mathrm{d_{x_2z_2}} \\ \mathrm{d}_{\mathrm{x}_2 y_2} \\ \mathrm{d}_{\mathrm{x}_2^2-\mathrm{y}_2{}^2} \end{bmatrix} \tag{1.14.5}$$

The energy contribution from L2 to the d-orbital levels as defined by AOM is,

$$\mathrm{E}\left(\mathrm{d_{yz}}\right) = \mathrm{e}\delta; \quad \mathrm{E}\left(\mathrm{d_{xz}}\right) = \mathrm{e}\pi; \quad \mathrm{E}\left(\mathrm{d_{xy}}\right) = \mathrm{e}\pi; \quad \mathrm{E}\left(\mathrm{d}_{x^2-y^2}\right) = \tfrac{3}{4}\mathrm{e}\sigma + \tfrac{1}{4}\mathrm{e}\delta$$

Until this point, only the L2 ligand has been treated. The overlap of the d-orbitals with the other five ligands also needs to be determined. The elements of the transformation matrices for these ligands are,

$$L_1:\begin{bmatrix}1&0&0&0&0\\0&1&0&0&0\\0&0&1&0&0\\0&0&0&1&0\\0&0&0&0&1\end{bmatrix}\quad L_3:\begin{bmatrix}-\frac{1}{2}&0&0&0&\frac{\sqrt{3}}{2}\\0&0&-1&0&0\\0&0&0&1&0\\0&-1&0&0&0\\-\frac{\sqrt{3}}{2}&0&0&0&-\frac{1}{2}\end{bmatrix}\quad L_4:\begin{bmatrix}-\frac{1}{2}&0&0&0&\frac{\sqrt{3}}{2}\\0&0&0&1&0\\0&0&1&0&0\\0&1&0&0&0\\\frac{\sqrt{3}}{2}&0&0&0&\frac{1}{2}\end{bmatrix}$$

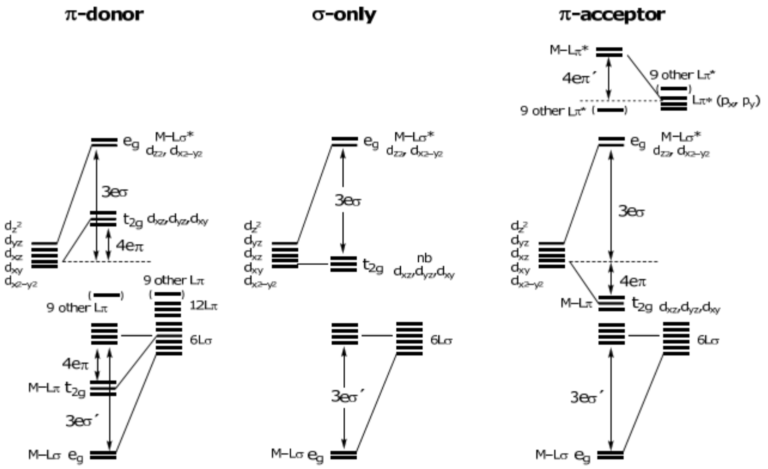
$$\mathrm{L}_5:\begin{bmatrix}-\frac{1}{2}&0&0&0&\frac{\sqrt{3}}{2}\\0&0&1&0&0\\0&0&0&-1&0\\0&-1&0&0&0\\-\frac{\sqrt{3}}{2}&0&0&0&-\frac{1}{2}\end{bmatrix}\quad L_6:\begin{bmatrix}1&0&0&0&0\\0&-1&0&0&0\\0&0&1&0&0\\0&0&0&-1&0\\0&0&0&0&1\end{bmatrix}$$

Squaring the coefficients for each of the ligands and then summing the total energy of each d-orbital,

	L1	L2	L3	L4	L5	L6	E_TOTAL
$\mathbf{E}(\mathbf{d}_{\mathbf{z}^2})$	eo	$\frac{1}{4}e\sigma+\frac{3}{4}e\delta$	$\frac{1}{4}e\sigma+\frac{3}{4}e\delta$	$\frac{1}{4}e\sigma+\frac{3}{4}e\delta$	$\frac{1}{4}e\sigma+\frac{3}{4}e\delta$	$e\sigma$	$=3e\sigma+3e\delta$
$\mathbf{E}(\mathbf{d}_{\mathrm{yz}})$	$e\pi$	$e\delta$	$e\pi$	$e\delta$	$e\pi$	$e\pi$	$=4e\pi+2e\delta$
$\mathbf{E}(\mathbf{d}_{\mathrm{xz}})$	$e\pi$	$e\pi$	$e\delta$	$e\pi$	$e\delta$	$e\pi$	$=4e\pi+2e\delta$
$\mathbf{E}(\mathbf{d}_{\mathrm{xy}})$	$e\delta$	$e\pi$	$e\pi$	$e\pi$	$e\pi$	$e\delta$	$=4e\pi+2e\delta$
$\mathbf{E}(\mathbf{d}_{\mathbf{x}^2-\mathbf{y}^2})$	$e\delta$	$\frac{3}{4}e\sigma+\frac{1}{4}e\delta$	$\frac{3}{4}e\sigma+\frac{1}{4}e\delta$	$\frac{3}{4}e\sigma+\frac{1}{4}e\delta$	$\frac{3}{4}e\sigma+\frac{1}{4}e\delta$	$e\delta$	$=3e\sigma+3e\delta$

(1.14.6)

As mentioned above, eδ << e_σ or e_π… thus e_δ may be ignored. The O_h energy level diagram is:



Note the d-orbital splitting is the same result obtained from the crystal field theory (CFT) model taught in freshman chemistry. In fact the energy parametrization scales directly between CFT and AOM

$$10\ \mathrm{Dq} = \Delta 0 = 3e\sigma - 4e\pi$$

CHAPTER OVERVIEW

2: Assignments

2.1: Problem set 1

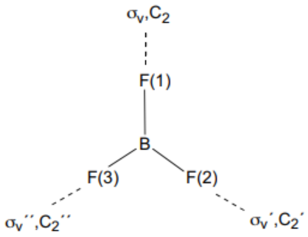
1. Determine the general matrix rep for a σ_v at angle from the xz plane on a point (x_1,y_1,z_1) at angle from the xz plane. Provide matrix reps for the $3\sigma_v$ in C_{3v}.

2. Consider the generators C5 and h.

a. What group is generated from these two operations?
b. Construct a multiplication table.
c. Determine the classes in the group.
d. Do C_5 and σ_h commute? Show both by matrix algebra and by operating on a vector (x_1,y_1,z_1).

3. Do the following problems in Cotton (3rd edition): A3.2, A3.4, 4.4 and 4.7.

4. Consider the trigonal planar molecule, BF_3. Use the three fluorine atoms as an arbitrary basis set to describe the matrix representation for each of the operations in the point group (relying on the methods employed above, solve the appropriate eigenvalue problem).



a. Construct the matrix representations for the operations in the D3h point group.
b. Find the three eigenvalues λ_i and normalize the eigenvectors for the C3 matrix representation (Hint: The eigenvectors are orthogonal to each other. For complex eigenvectors, remember that the normalization is defined as A*A where A* is the complex conjugate).
c. Construct the similarity transformation matrix $\boldsymbol{\theta}$ from the eigenvectors and determine $\boldsymbol{\theta}^{-1}$. For the case where the eigenvectors are complex, take linear combinations to yield eigenvectors in real space. $\boldsymbol{\theta}^{-1}$ is the adjoint of $\boldsymbol{\theta}$ divided by the determinant. See pg 424 in Cotton for the definition of an adjoint.
d. Using $\boldsymbol{\theta}$ and $\boldsymbol{\theta}^{-1}$ block-diagonalize the matrices in Part (a) and calculate the characters of the irreducible representations for the given basis.
e. To what irreducible representations do the F atom basis functions belong?
f. Complete the D_{3h} character table using the algebraic rules governing irreducible representations. Show work.

5. Assign point groups to the following molecules. Sketch the molecule and the symmetry elements present in each.

a. ethane (staggered)
b. ethane (eclipsed)
c. cyclohexane (chair)
d. cyclohexane (boat)
e. adamantane
f. ferrocene (staggered)
g. ferrocene (eclipsed)
h. P_4
i. S_8

6. Draw a molecule (not found in the texts or lecture notes) that exemplifies each of the following point groups. Please use molecules that actually exist.

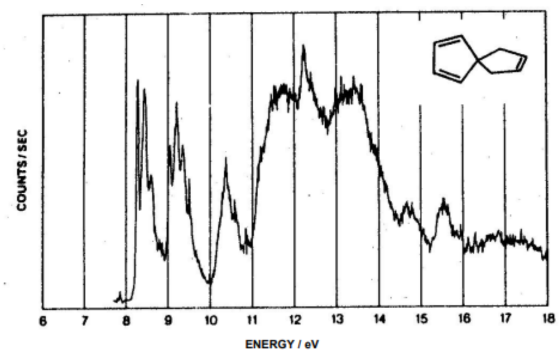
a. C_{2h}
b. D_{8h}
c. D_{2d}
d. C_S
e. C_{6v}

2.2: Problem Set 2

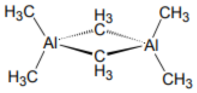
1. Do Problem 7.1, p. 201 in Cotton (3rd ed).

2. Do Problem 6.1, p. 129 in Cotton (3rd ed), and then solve the appropriate secular determinant to find the energies of the 10 MOs spanned by the SALCs you have derived.

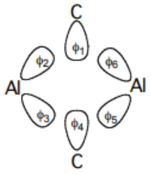
3. Construct the MO diagram for the molecule shown below and assign the photoelectron spectrum.



4. A Hückel analysis may also be used to describe σ-bonding. Consider the three center bond of the $Al_2(\mu\text{-}CH_3)_2$ unit in "trimethyl aluminum" which exists as the dimer $[Al(CH_3)_3]_2$ in the gas phase and nonpolar solvents.



a. Using the 6 σ orbitals shown below, determine the basis for the four Al σ-bonds.



b. Construct the SALC's using the projection operator method.

c. Follow the same procedure for the carbon σ-bonds.

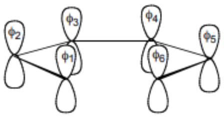
d. Determine the energy levels of the molecular orbital diagram.

e. Give the explicit expressions for the six molecular orbitals of the $Al_2(\mu\text{-}CH_3)_2$ unit.

5. Consider 1,3,5-hexatriene and benzene.

a. For the former construct the MO diagram; calculate the delocalization energy; and construct the molecular orbital eigenfunctions.

b. 1,3,5-hexatriene and benzene are limiting cases for a more general molecular orbital system in which the interaction energy for the terminal orbitals, $\beta_{1,6}$, is finite and not equal to the interaction energy between adjacent orbitals.



c. Determine the molecular orbital energies of the general C6 system (i.e. $\beta_{1,6} \neq \beta_{i,j}$ (i,j ≠ 1,6) and show that in the limiting regimes of this general case, the MO diagrams. For 1,3,5- hexatriene and benzene are obtained.

d. Draw a correlation diagram.

2.3: Problem Set 3

1. The octahedral molecular orbital (MO) diagram provides the starting point for the construction of the electronic structure of several metal complexes. But not all complexes are conveniently referenced to octahedral geometry. Other important geometries include tetrahedral, square planar, trigonal bipyramidal and pyramidal. Construct MO diagrams for each in the σ-only ligand framework. For the tetrahedral complex, also show the MO diagram for π^{-} and π*-bonding ligands.

2. Derive the MO diagram for trigonal prismatic WH_6. The $ReH_9{}^{2-}$ complex has hydride ligands capping the trigonal prismatic faces. Construct the MO diagram for The $ReH_9{}^{2-}$.

a. Make a LCAO of two H_3 molecules interacting face-to-face.

b. Place W between the two H_3 faces and then perturb the orbitals.

c. Mix another set of H_3 orbitals into the MO diagram you made in (b) to arrive at the MO diagram for.

3. Consider a one-dimensional chain of orbitals, for example polyacetylene.

(a) Use Hückel theory to generate the energy bands for a geometry in which all C–C distances are equal.

(b) Now generate the energy bands a geometry with alternating long and short C–C bonds. Use β for the H_{ij} across short bonds and β/2 across long bonds.

(c) Will polyacetylene in either one or both geometries be a metal or an insulator?

2.4: Problem Set 4

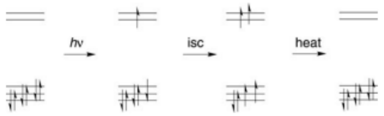
1. The raising and lowering operators are:

$$\mathrm{L}_t\Psi\left(\mathrm{L},\mathrm{M_L},\mathrm{S},\mathrm{M}\right)=\hbar\left[\left(\mathrm{L}\pm\mathrm{M_L}+1\right)\left(\mathrm{L}\mp\mathrm{M_L}\right)\right]^{1/2}\Psi\left(\mathrm{L},\mathrm{M_L}\pm1,\ \mathrm{S},\mathrm{M_S}\right)$$
$$\mathrm{S}_\pm\Psi\left(\mathrm{L},\mathrm{M_L},\mathrm{S},\mathrm{M}\right)=\hbar\left[\left(\mathrm{S}\pm\mathrm{M_S}+1\right)\left(\mathrm{S}\mp\mathrm{M_S}\right)\right]^{1/2}\Psi\left(\mathrm{L},\mathrm{M_L},\mathrm{S},\mathrm{M_S}\pm1\right)$$
$$\mathrm{L}_t\Phi\left(\mathrm{m}_{\boldsymbol{l}_1},\ \mathrm{m}_{\mathrm{s}_1};\ldots\mathrm{m}_{\boldsymbol{l}_\mathrm{N}},\mathrm{m}_{\mathrm{s}_\mathrm{N}}\right)=\hbar\sum_{\mathrm{i}=1}^{\mathrm{N}}\ \left[\left(\boldsymbol{\zeta}_1\pm\mathrm{m}_{\boldsymbol{\xi}}+1\right)\left(\boldsymbol{\zeta}_1\mp\mathrm{m}_{\boldsymbol{\ell}}\right)\right]^{1/2}\Phi\left(\mathrm{m}_{\boldsymbol{l}_1},\ \mathrm{m}_{\mathrm{s}_1};\ldots\mathrm{m}_{\boldsymbol{\xi}_1}\pm1,\ \mathrm{m}_{\mathrm{s}_\mathrm{i}};\ldots\mathrm{m}_{\boldsymbol{\zeta}_\mathrm{N}},\mathrm{m}_{\mathrm{s}_\mathrm{N}}\right)$$
$$\mathrm{S}_\pm\Phi\left(\mathrm{m}_{\boldsymbol{f}_1},\ \mathrm{m}_{\mathrm{s}_1};\ldots\mathrm{m}_{\boldsymbol{k}},\mathrm{m}_{\mathrm{s}_\mathrm{N}}\right)=\hbar\sum_{i=1}^{\mathrm{N}}\ \left[\left(\tfrac{3}{2}\pm\mathrm{m_s}\right)\left(\tfrac{1}{2}\mp\mathrm{m}_{\mathrm{s}_\mathrm{i}}\right)\right]^{1/6}\Phi\left(\mathrm{m}_{\boldsymbol{f}_1},\ \mathrm{m}_{\mathrm{s}_1};\ldots\mathrm{m}_{\boldsymbol{l}},\mathrm{m}_{\mathrm{s}_\mathrm{i}}\pm1;\ldots\mathrm{m}_{\boldsymbol{f}_\mathrm{N}},\mathrm{m}_{\mathrm{s}_\mathrm{N}}\right)$$

(a) For the p 2 configuration, we found that Ψ(L = 1, M_L = 1, S = 1, M_S = 1) for the ^{3}P state was defined by a unique configuration (1^+, 0^+). Similarily, Ψ(L = 1, M_L = 0, S = 1, M_S = 1) of the ^{3}P state is defined by the unique configuration, (1^+, -1^+). Using the angular momentum operator on Ψ(L = 1, M_L = 1, S = 1, M_S = 1) = (1^+, 0^+), show that you obtain the result, Ψ(L = 1, M_L = 0, S = 1, M_S = 1) = (1^+, -1^+).

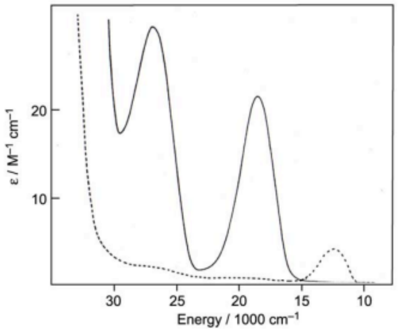
(b) The states encompassed by Ψ(L, M_L = 0, S, M_S = 0) are defined by three configurations, (0^+, 0^+), (1^+, -1^-), (1^-, -1^+). . Beginning with your result for Ψ(L = 1, M_L = 0, S = 1, M_S = 1) of the ^{3}P state, determine the linear combination that defines Ψ(L = 1, M_L = 0, S = 1, M_S = 0).

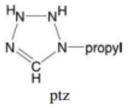
2. LIESST (Light Induced Electronic Spin State Trapping) is a method of changing the electronic spin state of a compound by means of irradiation with light. The overall effect is represented schematically with regard to configurations as follows,



The low spin state is slightly more stable than the high spin state by only a few cm^{-1}. Thus, the complex will exhibit low spin behavior only at very low temperatures (< 10 K). Excitation produces excited states corresponding to the low spin complex. From these low spin excited states, intersystem crossing (isc) occurs to produce the high spin complex. At low temperatures the high spin complex is trapped indefinitely owing to an Arrenhius barrier of ~800 cm^{-1}. Upon warming the barrier is surmounted and the complex converts back to the low spin state. This overall process has been called the Light-Induced Excited Spin State Trapping (LIESST).

A compound displaying LIESST is $[Fe(ptz)_6](BF_4)_2$. Shown below are the absorption spectra responsible for the effect.





(a) The solid line is the low temperature spectrum of the low spin complex. The energies of the transitions are 18,400 and 26,650 cm^{-1} , respectively. Using the appropriate TS diagram (from ant standard text), assign the two transitions.

(b) Upon irradiation, the dashed spectrum is produced. This is the absorption spectrum for the high spin complex, which features only a single band at 12,250 cm^{-1} . Assign this transition. Using the B value obtained from part a, determine Dq for the high spin system.

(c) On the basis of the Tanabe-Sugano diagram, explain the LIESST effect.

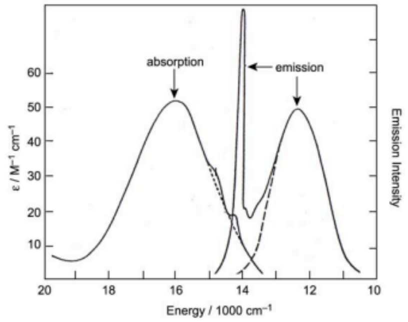
3. The spectroscopy and photochemistry of Cr(III) has spanned four decades of spectroscopic and photochemical research. The spectroscopy of Cr(III) in the solid state is the underpinning for the invention in the 1960's of the first solid state laser, the ruby

laser. The photochemistry of these complexes continues to be pursued by a number of research programs around the world. Consider the following.

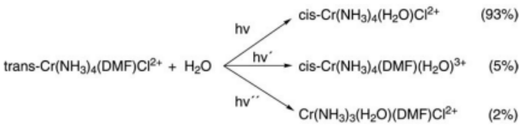
(a) Ruby is a gemstone composed of Cr(III) embedded in the octahedral oxide environment of Al_2O_3. The electronic spectrum of the octahedral Cr(III) exhibits three spin-allowed (strong = s) transitions and a number of so called ‘ruby’ lines, spin-forbidden (quartet-doublet) transitions (weak = w), which are extremely narrow and 10^{-3} times weaker than d-d transitions.

(i) The absorption bands in the electronic spectrum of Cr^{3+} /Al_2O_3 system are 14430(w), 18000(s), 21000(w), 24600(s) and 39000(s) cm^{-1} . Use a d^3 Tanabe-Sugano diagram to assign the transitions and calculate Dq.

(ii) The absorption and emission spectra of the lowest energy transitions of Cr(III) are given below. On the basis of your above work, assign the emission and absorption bands to the appropriate transitions. Why is the one transition broad and the other sharp? Why are the absorption and emission maxima of the sharp transition nearly overlapped whereas the absorption and emission maxima of the broad transition so far removed from each other?



(b) Trans-$Cr(NH_3)_4(DMF)Cl^{2+}$ cation is a high spin chromium(III) complex. The spectroscopy of this complex is intriguing because it is one of the few systems in which three different simultaneous photoreactions have been fully characterized. A complete scheme of the photoreactions is given below:



Because Cr(III) is in a C_{4v} environment, the octahedral Tanabe-Sugano diagram is invalid. In this case, spectroscopic assignments are achieved by using a descent in symmetry method, where the splitting of the t_{2g} and e_g manifolds are analyzed in the desired symmetry field as follows:

(i) The wavelengths (nm) and the extinction coefficients (M^{-1} cm^{-1}) of the complex are 555 (20), 468 (18) and 384 (42). Assign the quartet transitions and give the state symmetries of the excited states by qualitatively considering the splitting of the d-orbital manifold. For determining the states of the $(e)^2$ electronic configuration, you will need the equations given in the lecture notes and reproduced here:

$$\chi^{+} = 1/2\left\{[\chi(R)]^2 + \chi\left(R^2\right)\right\}$$
$$\chi^{-} = 1/2\left\{[\chi(R)]^2 - \chi\left(R^2\right)\right\}$$

(ii) The photochemistry originates from specific ligand field states (i.e. the products come from different excited states). By using the MO diagram and the assignments you have made, explain the observed photochemistry.

(iii) Why is DMF substituted more easily than chlorine?

2.5: Problem Set 5

1. Chatt prepared the dinitrogen complexes, trans $-\mathrm{Mo(N_2)_2(PR_3)_4}$ in which the surprising result of two π-acid ligands coordinate trans to each other. Build the MO diagram for the complex. Draw the frontier d-orbital MOs and indicate the HOMO and LUMO orbitals.

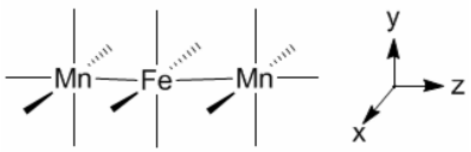
2. Shown below are two electronically different metal carbides. Use MO arguments to address the following:

   a. Draw the HOMO for each complex.

   b. Explain the vacant site trans to the carbide atom in the square pyramidal, Ru complex.

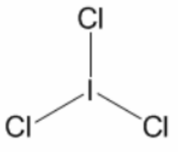
   c. How many pi electrons are donated from the anilides into the metal in the moly complex (assume that for each sp^2 hybirdized N-atom the tert-butly group point up, towards the apical carbide, and the aryl groups point down). Do the anilides and carbide compete for π symmetry orbitals on moly?

   d. Estimate the relative acidity of both carbide-carbon atoms. Which of these acids will protonate the carbide: $\mathrm{MeC_6H_5, HCPh_3, H_3CCOOH, H\,(OEt_2)\,B\,[3,5-C_6H_3(CF_3)_2]}$ (answer yes or no for each acid/carbide combination)?

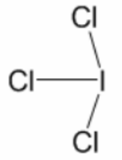


3. The synthesis of uranocene, $\left[\left(\eta^8-\mathrm{C_8H_8}\right)_2\mathrm{U}\right]$, is considered as the beginning of modern organoactinide chemistry. Organoactinides are distinguished by covalent interactions between the $5\mathrm{f}$ orbitals of the actinoids as well as the $6\,\mathrm{d}$ orbitals. Uranocene is paramagnetic, consisting of two planar $\mathrm{C_8H_8}^{2-}$ rings which are oriented in an eclipsed conformation, giving rise to its $\mathrm{D_{8\,h}}$ Symmetry.

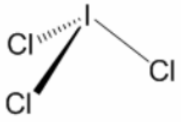
Create an MO diagram for $\mathrm{(COT)_2U}$. Be careful to consider both the d and f for U. Comment on the predicted stability of this compound. What is the oxidation state of U? How many unpaired electrons are expected? What is the electron count at U?



trigonal



bent-T



pyramidal

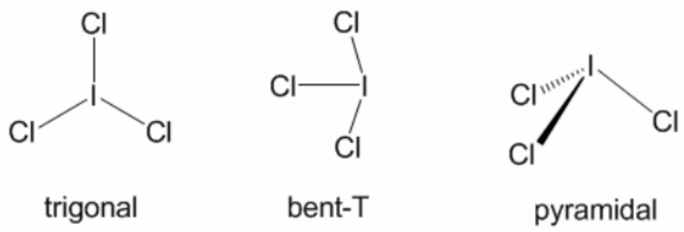
4. What is the barrier to rotation about the $\mathrm{M-N}$ bond in a d^0 linear imido complex? What about in $\mathrm{Cp_2Zr\,(NMe_2)\,Me}$?

5. The $\mathrm{D_{4\,h}}$ linear metal-metal bonded cluster, $\mathrm{Mn_2Fe(CO)_{14}}$, shown below, is produced upon photolysis of solutions containing $\mathrm{Mn_2(CO)_{10}}$ and $\mathrm{Fe(CO)_5}$.

   a. Construct the MO diagram (again, label the levels) of the cluster, considering the metal d-orbitals. Include in the MO diagram, the interaction arising from the $\mathrm{p_z}$ orbital of $\mathrm{Fe(CO)_4}$ with the $\mathrm{d_{z^2}}$ orbitals of the $\mathrm{Mn(CO)_5}$ fragments.

   b. Predict the lowest energy allowed transition of this cluster and give the spectroscopic notation for the transition.

6. The interhalogen compounds have the formula $\mathrm{X'X_3}$ $(\mathrm{e.g\cdot ICl_3})$. One atom surrounded by three others can presumably occur in three symmetrically different shapes: trigonal planar, pyramidal, or Tshaped. The structure of interhalogen molecules can be deduced immediately from Lewis dot structures and the VSEPR model.



Assume that you are teaching $5.11\mathrm{x}$ and a student challenges you to prove that VSEPR is indeed predicting the correct structure of $\mathrm{ICl_3}$. With access to a Raman and IR instrument you can verify the structure of the molecule.

a. Analyze all three molecular shapes to find the number and symmetries of their vibrations and the number and symmetries of their IR and Raman allowed vibrations.

b. How many IR bands and Raman peaks will be observed for each shape?

c. The Raman and infrared spectra of $\mathrm{ICl_3}$ each exhibit 6 active molecular vibrations. Which shape fits these IR and Raman data?

d. Determine the SALC's of the $\mathrm{I-Cl}$ stretching vibrations of the molecular shape that fits the spectroscopic data above (i.e. a basis set of only three $\mathrm{I-Cl}$ stretching vibrations is needed; not every molecular vibration in the molecule).

e. Sketch pictures of the symmetry coordinates and identify the irreducible representation to which the picture belongs.

The infrared spectrum of gaseous and the Raman spectrum of liquid $\mathrm{WF_4O}$ are set out below. Use them to decide the probable molecular geometry.

IR (in \left.\mathrm{cm}^{-1}\right)	Raman (in \mathrm{cm}^{-1})
1055 \mathrm{~m}	1057 s, pol
733 \mathrm{~m}	732 \mathrm{vs}, pol
698 \mathrm{vs}	
298 \mathrm{vw}	631 \mathrm{vw} \mathrm{br}
	328 br sh
	301
	298
248 \mathrm{w}	248 w, pol
236 \mathrm{~m}	234

(s = strong, m = medium, w = weak, v = very, br = broad, sh = should, pol = polarized)

CHAPTER OVERVIEW

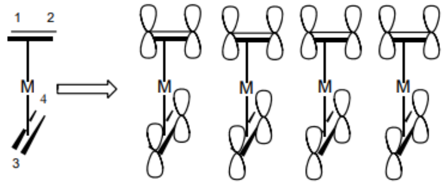
3: Exams

3.1: Exam 1

1. **(20 pts)** Below are vibrations and orbitals of molecules that transform according to irreducible representations of their given point groups. Note: no derivations are needed to answer this problem.

a. **(10 pts)** Five bending modes of XeF_4^{2-} are shown below. Assign the modes to their appropriate irreducible representations.

b. **(10 pts)** Olefins can bind to metal centers. Consider the simplets homoleptic complex, the bis(ethylene) complex. Ethylene binds to a metal through its pπ-orbitals. The four orbital symmetries appropriate for ligand binding to the metal are: A_1, B_2 and E. Below are shown the p-orbital contours for four orbitals. Color the p-orbitals to give the proper orbital symmetries. Label each of the completed diagrams with its irreducible representation



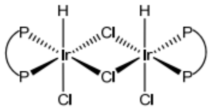
2. **(20 pts)** Show that the point groups C_{3h} and S_3 are equivalent. You may use a stereographic projection to answer this problem.

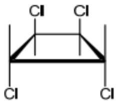
3. **(20 pts)** Short answers. Point values are assigned in parenthesis on each line.

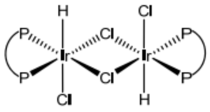
a. **(9 pts)** Identify the point group and list the generators for the letter S

b. **(5 pts)** To which irreducible representation does the f_{xz^2} orbital belong in the D_{2h} point group?

c. **(6 pts)** A molecule cannot be optically active if it has any S_n axes. Identify the optically active molecules below.







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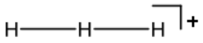
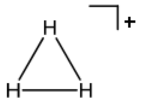
4. **(40 pts)** H_3^+ was discovered only 12 years ago by Professor Takeshi Oka of the University of Chicago. The discovery has been profound as this molecule has been observed now at the galactic core. As professor Oka discussed yesterday at MIT, the presence of this molecule in the universe provides an important mechanism for star formation. Construct an energy level diagram for the two molecules using the Hückel approximation to determine the energies. Draw a correlation diagram that relates the Hückel energy levels of the two fragments.

To shorten the time of this problem, consider using the D_{2h} point group for the linear isomer of H_3. Also, we provide one SALC for linear H_3^+ and two SALCs for cyclic H_3^+. You need only show work for the missing SALCs.



$1/\sqrt{2}$ [H2 – H3]



$1/\sqrt{2}$ [H2 – H3]
$1/\sqrt{6}$ [2H1 – H2 – H3]

3.2: Exam 2

1. **(30 pts)** A Rydberg transition promotes an electron to an orbital of a principal quantum number greater than that of any occupied orbital of the ground state. Consider the nd(n+1)s Rydberg excited state of a d^2 ion. Construct the correlation diagram for the excited state in a D_{4h} crystal field. For determining the ligand field states from the free ion states, you may use the equations given in the lecture notes and reproduced here (but it is not necessarily the only way to deduce the ligand field states):

$$\chi(\alpha) = 2l+1 \quad \text{for } \alpha = 0$$

$$\chi(\alpha) = \frac{\sin(l+1/2)\alpha}{\sin\frac{\alpha}{2}} \quad \text{for } \alpha \neq 0$$

2. **(30 pts)** Short answers.

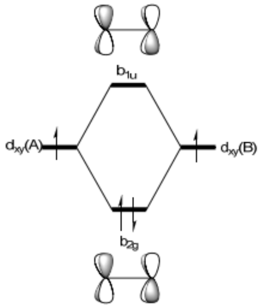
a. **(5 pts)** Which ligand will be stronger field, $HC{\equiv}C^-$ or OH^-? Justify your choice.

b. **(6 pts)** Is the ground state of $[CrCl_6]^{3-}$ subject to Jahn-Teller distortion? Explain why the $^4T_{2g}$ state (of $(t_{2g})^2\ (e_g)^1$ configuration) is subject to a Jahn-Teller distortion.

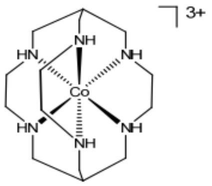
c. **(4 pts)** Under pressure, 10Dq of $[CrCl_6]^{3-}$ increases. Why?

d. **(5 pts)** In the lowest energy d-d excited state, $[Ni(CN)_4]^{2-}$ undergoes a $D_{4h} \rightarrow D_{2d}$ distortion. Explain.

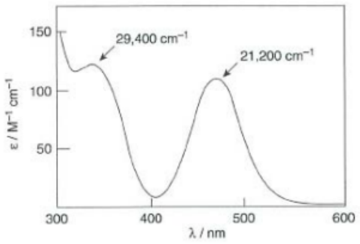
e. **(10 pts)** List the four states that arise from two electrons residing in two d_{xy} orbitals in a D_{4h} ligand field. The MO diagram with molecular orbital symmetries is given below.



3. **(40 pts)** The $Co(sep)_3^{3+}$ is called a sephulcrate, first synthesized by Alan Sargeson at the Australian National University.

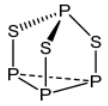


Two absorption bands arising from spin-allowed ligand field transitions are observed for this complex. Assign these transitions by using the $d^6(O_h)$ Tanabe-Sugano diagram. Predict the energies of the corresponding spin-forbidden triplet transitions.



3.3: Exam 3

1. **(29 pts)** The simplest stable phosphorous sulfide, tetraphosphourous trisulfide, P_4S_3 is shown below. The bands observed in the IR and Raman spectra of P_4S_3 in gas phase, melt and solution are listed.

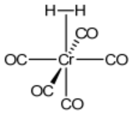


Infrared Data: **ν / cm^{-1}**	**Gas (550 °C)**	**Raman Data: Δ / cm^{-1}** **Melt (250 °C) CS$_2$ (25 °C)**	
		142	
184		187	
218	221	218	223
286	292	287	291
339	347	339	343
414	420	420	423
438	446	440	444

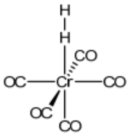
a. **(20 pts)** Determine the normal modes of vibration for P_4S_3 and how they transform.

b. **(9 pts)** Which are Raman and IR active?

2. **(41 pts)** A molecular orbital analysis of transition metal dihydrogen complexes provides critical insight into the bonding interactions between metals and hydrogen and established an elegant framework in which the reactivity between H_2 and transition metal complexes can be interpreted.



side-on



end-on

a. **(10 pts)** Construct the molecular orbital diagram of a side-on bonded $Cr(CO)_5(H_2)$ from group fragment orbitals.

b. **(6 pts)** Pictorially illustrate the σ and π interactions that stabilize the formation of the dihydrogen complex.

c. **(15 pts)** These interactions can effectively be used to rationalize several aspects of TM dihydrogen chemistry. In this regard, explain the following observations:

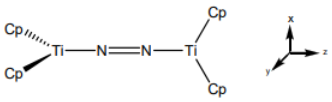
i. **(5 pts)** d^6 metals appear to form the most stable TM dihydrogen complexes

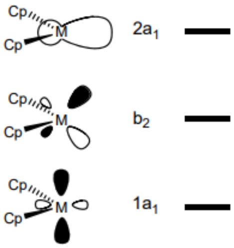
ii. **(5 pts)** many TM dihydrogen complexes synthesized to date have ancillary π-accepting ligands

iii. **(5 pts)** first row transition metals stabilize dihydrogen compounds while third row metals tend to promote dihydride compounds

d. **(10 pts)** Construct the MO diagram for an end-on bonded H_2 complex; and explain why (using the end- and side-on MO diagrams) end-on complexes are not favored energetically relative to side-on complexes.

3. **(30 pts)** The nitrogen chemistry of early transition metals was established with the preparation of the Ti complexes from the Bercaw group at Caltech during the mid-1970s. One of the compounds is shown below. Construct the qualitative molecular orbital diagram for the dinuclear titanium complex from the frontier orbitals of the bent Cp_2Ti fragment (in C_{2v} symmetry) and the appropriate frontier molecular orbitals of nitrogen. Label the MO with appropriate symmetry labels, identify the nature of the bond (i.e., σ, σ*, π, π*) and fill up the MO with the appropriate number of electrons.


Cp
Cp
Ti
N
N
Ti
Cp
Cp
x
y
z


Cp
Cp
M
2a$_1$
Cp
Cp
M
b$_2$
Cp
Cp
M
1a$_1$

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