Symmetry and Structure in Chemistry

POINT SYMMETRY

Unit 0: Motivation

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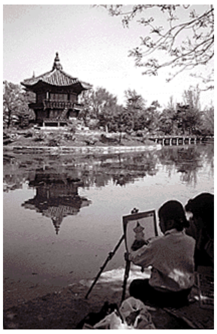
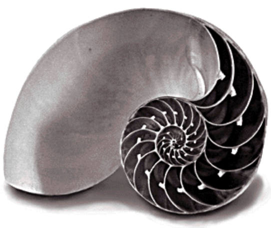
Symmetry



Plane of symmetry



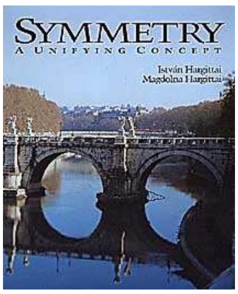
Rotational symmetry

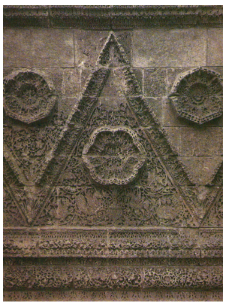
Bilateral symmetry

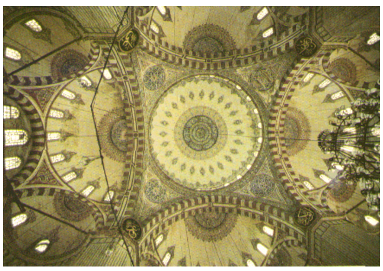
Translational symmetry

Animals produce symmetrical objects

Symmetry in the man-made creations







El 'sex appeal', cuestión de simetría | elmundo.es http://www.elmundo.es/elmundo/2008/08/19/ciencia/1219137219.html

elmundo.es

August 19, 2008

Portada > **Ciencia**

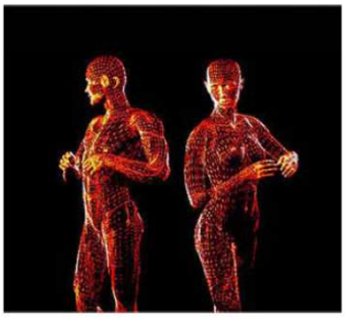
ESTUDIO PUBLICADO EN 'PNAS'

El 'sex appeal', cuestión de simetría

Actualizado miércoles 20/08/2008 19:30 (CET)

ROSA M. TRISTÁN

MADRID.- La simetría corporal es un valor añadido fundamental para tener 'sex appeal'. Si es un varón, esa simetría debe incluir un torso grande, buenos hombros, pechos pequeños, piernas fuertes y una altura aceptable. En el caso femenino triunfan las piernas largas, el pecho considerable, hombros pequeños y una proporción cintura-cadera determinada.



Cuerpo de un hombre y una mujer diseñados por ordenador. (Foto: PNAS)

Estas características **no son fortuitas ni se trata de modas.** Están directamente relacionadas con el potencial reproductor, la calidad de los genes, la capacidad competitiva y la salud, incluyendo la facultad para evitar a los parásitos con más facilidad.

Estas son las principales conclusiones de un exhaustivo análisis realizado por expertos británicos en psicología evolutiva de la Universidad de Brunel (en Reino Unido), publicadas esta semana en la revista Proceedings of National Academy of Science (PNAS).

Paul Dirac

«The dominating idea in this application of mathematics to physics is that the equations representing the laws of motion should be of a simple form. The whole success of the scheme is due to the fact that equations of simple form do seem to work....

We now see that we have to change the principle of simplicity into a principle of mathematical beauty … It often happens that the requirements of simplicity and of beauty are the same, but where they clash the latter must take precedence.»

Symmetry implies simplicity

Conservation laws and symmetries formulations:

- The conservation of energy = uniformity of time.
- The conservation of linear momentum = homogeneity of space.
- The conservation of angular momentum = isotropy of space.

Teorema de Noether

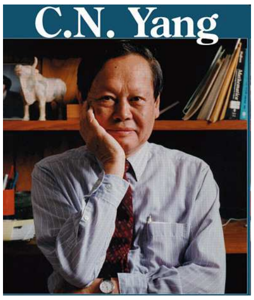
Any symmetry of a physical system is associated with a physical quantity that is conserved in this system

This theorem allows to derive the conserved physical quantity from the condition of invariance which defines the symmetry. It also works in the opposite direction.

Example: (a) the invariance of physical systems with respect to spatial translation (translational symmetry) implies the conservation of linear momentum. (b) If the momentum of a system is conserved, this system must be invariant under spatial translations.

The set of the numerical values corresponding to compatible observables (invariants) defines the quantum state of a system

The quantum state of a system is labeled by the symmetry of its Hamiltonian



Nobel de Física 1957

«If you look at the history of 20th century physics, you will find that the symmetry concept has emerged as a most fundamental theme, occupying center stage in today's theoretical physics. We cannot tell what the 21st century will bring to us but I feel safe to say that for the next ten or twenty years many theoretical physicists will continue to try variations on the fundamental theme of symmetry at the very foundation of our theoretical understanding of the structure of the physical universe.»

C. N. Yang, *Chinese J. Phys.* 32 (1994) 1437

The Nobel Prize in Physics 2008

"for the discovery of the mechanism of spontaneous broken symmetry in subatomic physics"

"for the discovery of the origin of the broken symmetry which predicts the existence of at least three families of quarks in nature"

Photo: University of Chicago

Yoichiro Nambu

1/2 of the prize

USA

Enrico Fermi Institute, University of Chicago
Chicago, IL, USA

Photo: KEK

Makoto Kobayashi

1/4 of the prize

Japan

High Energy Accelerator Research Organization (KEK)
Tsukuba, Japan

Photo: Kyoto University

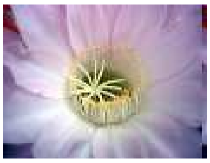
Toshihide Maskawa

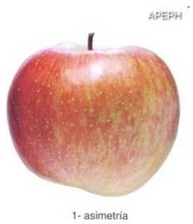
1/4 of the prize

Japan

Kyoto Sangyo University; Yukawa Institute for Theoretical Physics (YITP), Kyoto University
Kyoto, Japan

Exact and approximate symmetries





«What an imperfect word it would be if every symmetry was perfect.»

B.G. Wybourne

Francesco Iachello

Most of the symmetries of physics (and art) are not exact but are approximate ... Despite the fact that most of the dynamic symmetries are not exact, they provide us with the best tool we have for understanding complex structures.

The Physics comes in the process of breaking the symmetry

B.G. Wybourne
Ninth Intl. School of Condensed Matter Physics,
Bialowieza 1995

■ **1.3 Broken symmetry**

In practice very few symmetries are 'exact' and in most cases we are led to consider 'approximate' symmetries. A symmetry need not be exact to be useful. Indeed I would assert the following:

Proposition: *We should always strive to construct theories with the highest possible symmetry even if these are not exact symmetries of nature. The physics comes in the process of breaking the symmetry.*

Outline of the course:

Linear representations of groups.
Irreducible representations. Character tables.
Basis sets for a group representation: Normal modes.
Hybrid orbitals. Molecular orbitals.
Permutation group. Continuous Groups.
Products and powers of representations.
Selection rules. Electronic terms. Multipoles.
Dynamic groups...

Symmetry and Structure in Chemistry

POINT SYMMETRY

Unit 1: Linear Representations of a Group

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Contents

Group of transformations

The transformations that leave invariant a system (symmetries) form a group.

A group is a set, G, together with a composition law "•" fulfilling:

- ***Closure:*** $\forall\, a, b \in G,\; a \bullet b \in G$
- ***Associative:*** $\forall\, a, b, c \in G,\; (a \bullet b) \bullet c = a \bullet (b \bullet c)$
- ***Identity:*** $\forall\, a \in G,\; \exists\, e \in G \;/\; e \bullet a = a \bullet e = a$
- ***Inverse:*** $\forall\, a \in G,\; \exists\, b \in G \;/\; a \bullet b = b \bullet a = e$
  we say $b = a^{-1}$

An Abelian or commutative group is a group (G, •) additionally fulfilling:

- ***Commutative:*** $\forall\, a, b \in G,\; a \bullet b = b \bullet a$

Group Table

The group structure can be grasped in the group or Cayley table.

Example.

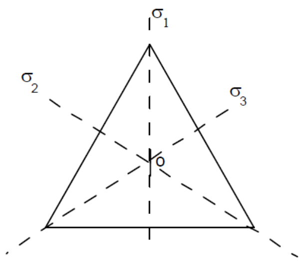
	E	A	B
E	E•E	E•A	E•B
A	A•E	A•A	A•B
B	B•E	B•A	B•B

→

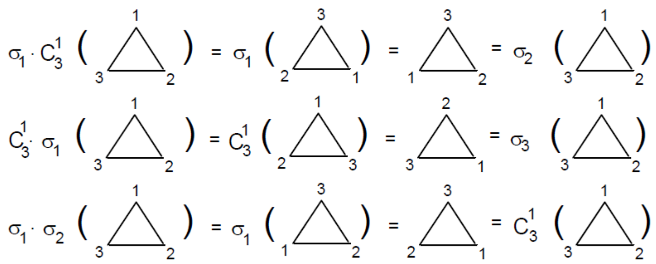
	E	A	B
E	E	A	B
A	A	B	E
B	B	E	A

Caution! Left first and right then, the product may be not commutative

C_{3v} group table



	E	C_3^1	C_3^2	σ_1	σ_2	σ_3
E	E	C_3^1	C_3^2	σ_1	σ_2	σ_3
C_3^1	C_3^1	C_3^2	E	σ_3	σ_1	σ_2
C_3^2	C_3^2	E	C_3^1	σ_2	σ_3	σ_1
σ_1	σ_1	σ_2	σ_3	E	C_3^1	C_3^2
σ_2	σ_2	σ_3	σ_1	C_3^2	E	C_3^1
σ_3	σ_3	σ_1	σ_2	C_3^1	C_3^2	E



Subgroups

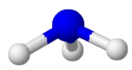
***Subgroup**: A subset $H \subset G$ is called a subgroup of (G, •) if (H, •) is a group.*

*H is a **proper** subgroup of a group G if $H \neq G$.*
*H is a **trivial** subgroup of a group G if H = {E}*
G is sometimes called an overgroup (or supergroup) of H

	E	C_3^1	C_3^2	σ_1	σ_2	σ_3
E	E	C_3^1	C_3^2	σ_1	σ_2	σ_3
C_3^1	C_3^1	C_3^2	E	σ_3	σ_1	σ_2
C_3^2	C_3^2	E	C_3^1	σ_2	σ_3	σ_1
σ_1	σ_1	σ_2	σ_3	E	C_3^1	C_3^2
σ_2	σ_2	σ_3	σ_1	C_3^2	E	C_3^1
σ_3	σ_3	σ_1	σ_2	C_3^1	C_3^2	E

C_{3v} proper subgroups:

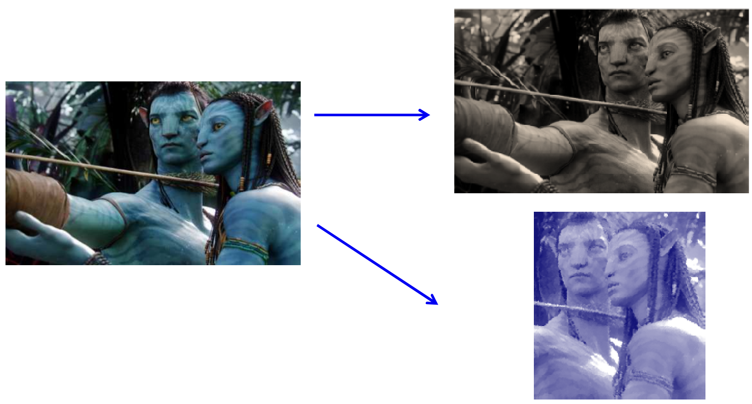
{E}, {E, C_3^1, C_3^2}, {E, σ_1, σ_2, σ_3}



Homomorphism (for pedestrian)

***Homomorphism** is like a movie:*

you cannot see all but you can grasp what is going on…



Group isomorphism. Homomorphism

Homomorphism: is a map h: G→H between two groups (G,) and (H, •) preserving the multiplication law, i.e., fulfilling: h(u*v) = h(u) • h(v)*

Example: $\{E, C_4^2, \sigma_x, \sigma_y\}$ *and* $\{E, \sigma_x\}$ *are homomorphous*

The mapping: $E, C_4^2 \leftrightarrow E \;;\; \sigma_x, \sigma_y \leftrightarrow \sigma_x$ *preserves the multiplication law:*

$$C_4^2 \cdot \sigma_x = \sigma_y \;,\; E \cdot \sigma_x = \sigma_x$$
$$C_4^2 \cdot \sigma_y = \sigma_x \;,\; E \cdot \sigma_x = \sigma_x$$

Isomorphism: is an isomorphic or bijective homomorphism

Two groups with the same Cayley table are isomorphic

Conjugate elements and equivalence classes

Two elements a and b of G are called conjugate if $\exists\, g \in G$: $g\, a\, g^{-1} = b$

Conjugacy "~ " is an equivalence relation, i.e.

- *Reflexivity: a ~ a*
- *Symmetry: if a ~ b, then b ~ a*

  proof: $a \sim b \longrightarrow g\, a\, g^{-1} = b \;;\; \longrightarrow g^{-1} g\, a\, g^{-1} g = a = g^{-1} b\, g = c\, b\, c^{-1} \longrightarrow b \sim a$
- *Transitivity: if a ~ b and b ~ c then a ~ c*

Conjugacy makes a partition of G into equivalence classes.

- *Every element of class is a member of this and only this class.*
- *Identity forms a class by himself* $A \sim E \leftrightarrow A = T^{-1} \cdot E \cdot T = T^{-1} \cdot T = E \rightarrow A = E$
- *All classes of Abelian groups contains only an element*

  proof: $A \sim B \leftrightarrow A = T^{-1} \cdot B \cdot T = T^{-1} \cdot T \cdot B = E \cdot B = B \rightarrow A = B$

C_{3v} classes

C_{3v} contains three equivalence classes: E, $2C_3$, 2σ

	E	C_3^1	C_3^2	σ_1	σ_2	σ_3
E	E	C_3^1	C_3^2	σ_1	σ_2	σ_3
C_3^1	C_3^1	C_3^2	E	σ_3	σ_1	σ_2
C_3^2	C_3^2	E	C_3^1	σ_2	σ_3	σ_1
σ_1	σ_1	σ_2	σ_3	E	C_3^1	C_3^2
σ_2	σ_2	σ_3	σ_1	C_3^2	E	C_3^1
σ_3	σ_3	σ_1	σ_2	C_3^1	C_3^2	E

$$E^{-1} \cdot C_3^1 \cdot E = C_3^1 \qquad E^{-1} \cdot \sigma_1 \cdot E = \sigma_1$$

$$C_3^{1\,-1} \cdot C_3^1 \cdot C_3^1 = C_3^1 \qquad C_3^{1\,-1} \cdot \sigma_1 \cdot C_3^1 = \sigma_3$$

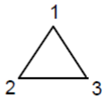
$$C_3^{2\,-1} \cdot C_3^1 \cdot C_3^2 = C_3^1 \qquad C_3^{2\,-1} \cdot \sigma_1 \cdot C_3^2 = \sigma_2$$

$$\sigma_1^{-1} \cdot C_3^1 \cdot \sigma_1 = C_3^2 \qquad \sigma_1^{-1} \cdot \sigma_1 \cdot \sigma_1 = \sigma_1$$

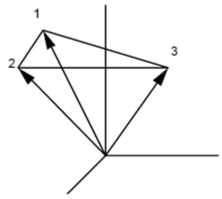
$$\sigma_2^{-1} \cdot C_3^1 \cdot \sigma_2 = C_3^2 \qquad \sigma_2^{-1} \cdot \sigma_1 \cdot \sigma_2 = \sigma_3$$

$$\sigma_3^{-1} \cdot C_3^1 \cdot \sigma_3 = C_3^2 \qquad \sigma_2^{-1} \cdot \sigma_1 \cdot \sigma_3 = \sigma_1$$

Linear representation of a group



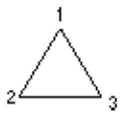
correspondence $\begin{pmatrix} 1 \\ 2 \\ 3 \end{pmatrix}$



correspondences:

$$E = \begin{bmatrix} 1&0&0 \\ 0&1&0 \\ 0&0&1 \end{bmatrix} \quad C_3^1 = \begin{bmatrix} 0&1&0 \\ 0&0&1 \\ 1&0&0 \end{bmatrix} \quad C_3^2 = \begin{bmatrix} 0&0&1 \\ 1&0&0 \\ 0&1&0 \end{bmatrix} \quad \sigma_1 = \begin{bmatrix} 1&0&0 \\ 0&0&1 \\ 0&1&0 \end{bmatrix} \quad \sigma_3 = \begin{bmatrix} 0&1&0 \\ 1&0&0 \\ 0&0&1 \end{bmatrix} \quad \sigma_2 = \begin{bmatrix} 0&0&1 \\ 0&1&0 \\ 1&0&0 \end{bmatrix}$$

e.g. C_3^1



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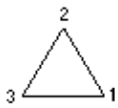
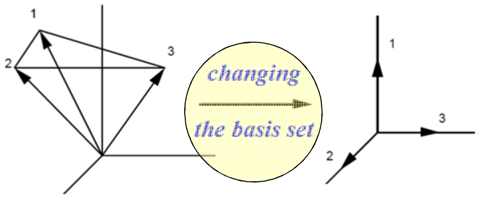


$$\equiv \begin{bmatrix} 0&1&0 \\ 0&0&1 \\ 1&0&0 \end{bmatrix} \begin{bmatrix} 1 \\ 2 \\ 3 \end{bmatrix} = \begin{bmatrix} 2 \\ 3 \\ 1 \end{bmatrix}$$

Note that if 1, 2, 3 label the vectors instead of the vertices of the triangle, the same matrices that transform the vertices transform the vectors

Linear representations



$$E = \left[\begin{array}{c|cc} 1 & 0 & 0 \\ \hline 0 & 1 & 0 \\ 0 & 0 & 1 \end{array}\right] \qquad C_3^1 = \left[\begin{array}{c|cc} 1 & 0 & 0 \\ \hline 0 & \cos 120 & \text{sen } 120 \\ 0 & -\text{sen } 120 & \cos 120 \end{array}\right]$$

$$C_3^2 = \left[\begin{array}{c|cc} 1 & 0 & 0 \\ \hline 0 & \cos 240 & \text{sen } 240 \\ 0 & -\text{sen } 240 & \cos 240 \end{array}\right] \qquad \sigma_1 = \left[\begin{array}{c|cc} 1 & 0 & 0 \\ \hline 0 & -1 & 0 \\ 0 & 0 & 1 \end{array}\right] \qquad \text{etc.}$$

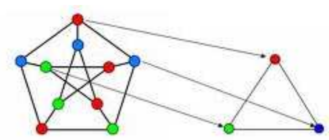
A change in basis of the vector space leads the matrices representing the symmetry operations to acquire a block form.

But ... what is a group representation?

What is to represent a group?

→ ***To represent a group is to establish a homomorphism between a group G and a group of operators T(G). These operators T(G) acquire matrix form when we represent them in a n-dimensional linear space V.***

Warning! *The set of matrices T not necessarily form a group. (different elements of G may have the same matrix representation T).*



Equivalent representations of a group

$$V\text{ (basis 2)} \xrightarrow{M^{-1}} V\text{ (basis 1)} \xrightarrow{G} V\text{ (basis 1)} \xrightarrow{M} V\text{ (basis 2)}$$

$$V\text{ (basis 2)} \xrightarrow{MGM^{-1}} V\text{ (basis 2)}$$

M is the the matrix of the change-of-basis
G represents an automorphism
$G' = M\,G\,M^{-1}$ is the same automorphism
represented in the new basis
G and G' are equivalent

Reducible and irreducible representations

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad C_3^1 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos 120 & \text{sen } 120 \\ 0 & -\text{sen } 120 & \cos 120 \end{bmatrix} \qquad \text{etc.}$$

The (3 x 3) matrix representation is equivalent to the set of two smaller (1 x 1) and (2 x 2) matrix representations

In general:

$$\begin{pmatrix} T^{(1)}(A) & & & 0 \\ & T^{(2)}(A) & & \\ & & T^{(3)}(A) & \\ 0 & & & \ddots \end{pmatrix}$$

$$T(A) = a_1 D^1(A) \oplus a_2 D^2(A) \oplus \ldots = \sum_\mu a_\mu D^\mu(A)$$

$$V(A) = V^1(A) \oplus V^2(A) \oplus \ldots = \sum_\mu V^\mu(A)$$

Unitary representations

Orthogonal basis sets

$$B_1 \quad \{|i\rangle\} \qquad \langle i|j\rangle = \delta_{ij} \qquad 1 = \sum_{i=1}^{N} |i\rangle\langle i|$$

$$B_2 \quad \{|\alpha\rangle\} \qquad \langle \alpha|\beta\rangle = \delta_{\alpha\beta} \qquad 1 = \sum_{\alpha=1}^{N} |\alpha\rangle\langle \alpha|$$

Changing the basis set

$$|\alpha\rangle = 1|\alpha\rangle = \sum_i |i\rangle\langle i|\alpha\rangle = \sum_i |i\rangle U_{i\alpha} = \sum_i |i\rangle (\mathbf{U})_{i\alpha}$$

$$|i\rangle = 1|i\rangle = \sum_\alpha |\alpha\rangle\langle \alpha|i\rangle = \sum_\alpha |\alpha\rangle U^*_{i\alpha} = \sum_\alpha |\alpha\rangle (\mathbf{U}^\dagger)_{\alpha i}$$

The basis sets transformation U is unitary

$$\delta_{ij} = \langle i|j\rangle = \sum_\alpha \langle i|\alpha\rangle\langle \alpha|j\rangle = \sum_\alpha (\mathbf{U})_{i\alpha} (\mathbf{U}^\dagger)_{\alpha j} = (\mathbf{U}\mathbf{U}^\dagger)_{ij}$$

*We will chose orthogonal basis sets. We will always chose **unitary representations***

Reducible and Irreducible Representations

- If for a given representation $\{\mathcal{D}(g_i) : i = 1, \dots, h\}$, an equivalent representation $\{\mathcal{D}'(g_i) : i = 1, \dots, h\}$ can be found that is block diagonal

$$\mathcal{D}'(g_i) = \begin{pmatrix} \mathcal{D}'_1(g_i) & 0 \\ 0 & \mathcal{D}'_2(g_i) \end{pmatrix} \qquad \forall g_i \in \mathcal{G}$$

  then $\{\mathcal{D}(g_i) : i = 1, \dots, h\}$ is called reducible, otherwise irreducible.

- It is crucial that the same block diagonal form is obtained for all representation matrices $\mathcal{D}(g_i)$ simultaneously.

- Block-diagonal matrices do not mix, i.e., if $\mathcal{D}'(g_1)$ and $\mathcal{D}'(g_2)$ are block diagonal, then $\mathcal{D}'(g_3) = \mathcal{D}'(g_1)\mathcal{D}'(g_2)$ is likewise block diagonal.
  $\Rightarrow$ Decomposition of RRs into IRs allows one to decompose the problem into the smallest subproblems possible.

Decomposition of a reducible representation

A representation $\Gamma^{(f)}$ can be reduced or decomposed into a sum of representations if there exist a non-singular matrix A that turns every $\Gamma^{(f)}$ matrix in an equivalent block matrix form, i.e.,

$$\forall \hat{R} \in \mathcal{G} \qquad \underline{\underline{A}}\,\underline{\underline{D}}^{(f)}(\hat{R})\,\underline{\underline{A}}^{-1} = \begin{pmatrix} \underline{\underline{D}}^{(a)}(\hat{R}) & \underline{\underline{0}} & \cdots & \underline{\underline{0}} \\ \underline{\underline{0}} & \underline{\underline{D}}^{(b)}(\hat{R}) & \cdots & \underline{\underline{0}} \\ \vdots & \vdots & \ddots & \vdots \\ \underline{\underline{0}} & \underline{\underline{0}} & \cdots & \underline{\underline{D}}^{(z)}(\hat{R}) \end{pmatrix}$$

This equivalence transformation reduces $\Gamma^{(f)}$ into a direct sum of representations $\Gamma^{(a)}, \Gamma^{(b)} \ldots \Gamma^{(z)}$:

$$\Gamma^{(f)} = \Gamma^{(a)} \oplus \Gamma^{(b)} \oplus \ldots \oplus \Gamma^{(z)}$$

The representations that cannot by simplified this way are referred to as irreducible representations (irreps)

Character of a representation

How can we characterize equivalent representations?

Hint: the trace of a matrix is invariant under equivalence transformations

→ ***The character of two equivalent representations is the same***

(The character $\chi^{\mu}(R)$ is trace of the representation μ of the symmetry element R)

Proof:

Equivalent transformation: $T'(A) = S^{-1} \cdot T(A) \cdot S$ ***Character:*** $\chi'(A) = \sum_i T'_{ii}(A)$

$$T'_{ii}(A) = \sum_{kl} S^{-1}_{ik} \cdot T_{kl}(A) \cdot S_{li}$$

$$\chi'(A) = \sum_i \sum_{kl} S^{-1}_{ik} \cdot T_{kl}(A) \cdot S_{li} = \sum_{kl} T_{kl}(A) \sum_i S_{li} \cdot S^{-1}_{ik} =$$

$$= \sum_{kl} T_{kl}(A) \cdot \delta_{kl} = \sum_k T_{kk}(A) = \chi(A)$$

Corollary: The conjugate elements (those in the same class) have the same character.

Character Tables

The decomposition of a group into non-equivalent irreps and into equivalence classes is unique.

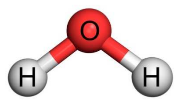
Character table of a group: is a table containing all characters of non-equivalent irreps of a group, where the irreps (Γ^i) label the rows and the classes (C_j) the columns.

$\mathcal{G}$	C_1	$\cdots$	C_i	$\cdots$
$\Gamma^{(1)}$	$\chi_1^{(1)}$	$\cdots$	$\chi_i^{(1)}$	$\cdots$
$\Gamma^{(2)}$	$\chi_1^{(2)}$	$\cdots$	$\chi_i^{(2)}$	$\cdots$
$\vdots$	$\vdots$	$\ddots$	$\vdots$	$\ddots$
$\Gamma^{(f)}$	$\chi_1^{(f)}$	$\cdots$	$\chi_i^{(f)}$	$\cdots$
$\vdots$	$\vdots$	$\ddots$	$\vdots$	$\ddots$

C_{2v} Character Table

Point group

Symmetry operations



C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

Mülliken symbols

Characters
+1 symmetric behavior
-1 antisymmetric

Each row is an irreducible representation

C_{3v} Character Table

Classes of operations

x, y, z
Symmetry of translations (p orbitals)
R_x, R_y, R_z: rotations

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

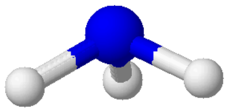
d_{xy}, d_{xz}, d_{yz}, as xy, xz, yz

$d_{x^2-y^2}$ behaves as $x^2 - y^2$

d_{z^2} behaves as $2z^2 - (x^2 + y^2)$

p_x, p_y, p_z behave as x, y, z

s behaves as $x^2 + y^2 + z^2$



The Great Orthogonality Theorem

Let $\Gamma^{(f)}$ and $\Gamma^{(g)}$ (R) any two irreps of a group G of h elements, then:

$$\sum_{\hat{R}} D_{ij}^{(f)}(\hat{R})\, D_{kl}^{(g)}(\hat{R}^{-1}) = \frac{h}{d_f}\,\delta_{fg}\,\delta_{il}\,\delta_{jk}$$

where the sum is extended to all group elements and d_f is the dimension of $\Gamma^{(f)}$.

Using unitary representation: $D_{kl}(\hat{R}^{-1}) = D_{lk}^{*}(\hat{R})$

Corollary: The Little Orthogonality Theorem (row orthogonality)

$$\sum_{\hat{R}\in\mathcal{G}} \chi^{(f)}(\hat{R}) \left[\chi^{(g)}(\hat{R})\right]^{*} \equiv \sum_{i} \eta_i\, \chi_i^{(f)}\, \chi_i^{(g)*} = h\delta_{fg}$$

where η_i is the dimension of i-th class.

The Great Orthogonality Theorem (cont.)

Column orthogonality in the character table: $\sum_f \chi_i^{(f)} \left[\chi_j^{(f)}\right]^* = \frac{h}{\eta_i}\delta_{ij}$

Square in a row of the character table: $\sum_{\hat{R}} \left|\chi(\hat{R})\right|^2 = \sum_i \eta_i \left|\chi_i\right|^2 = h.$

etc. (see e.g. Bishop 7.7)

This allows an automatic building of the character tables →

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_1	1	1	1
Γ_2	1	1	−1
Γ_3	2	−1	0

Another relevant corollary: Decomposition of a reducible representation as a sum of irreps:

$$\Gamma = \sum_f a_f \Gamma^{(f)} \longrightarrow a_f = \frac{1}{h}\sum_{\hat{R}\in\mathcal{G}} \chi(\hat{R})\,\chi^{(f)*}(\hat{R}) = \frac{1}{h}\sum_i^{\text{classes}} \eta_i\,\chi_i\,\chi_i^{(f)*}$$

Mulliken notation

- *One-dimensional irreducible representations are called A or B.*
- *The difference between A and B is that the character for a rotation Cn is always 1 for A and -1 for B.*
- *The subscripts 1, 2, 3 etc. are arbitrary labels.*
- *Subscripts g and u stands for gerade and ungerade, meaning symmetric or antisymmetric with respect to inversion.*
- *Superscripts ’ and ” denotes symmetry or antisymmetry with respect to reflection through a horizontal mirror plane.*
- *Two-dimensional irreducible representations are called E.*
- *Three-dimensional irreducible representations are called T (F).*

In some groups there are couples of one-dimensional irreps complex conjugate of each other . Sometimes they are represented together as a two-dimensional irrep.

C_3	$\hat{E}$	$\hat{C}_3^1$	$\hat{C}_3^2$	$\epsilon = e^{2\pi i/3}$	
A	1	1	1	z, R_z	x^2+y^2, z^2
E	$\left\{\begin{matrix}1 \\ 1\end{matrix}\right.$	$\begin{matrix}\epsilon \\ \epsilon^*\end{matrix}$	$\left.\begin{matrix}\epsilon^* \\ \epsilon\end{matrix}\right\}$	$(x,y)(R_x,R_y)$	$(x^2-y^2, xy)(yz, xz)$

C_3	$\hat{E}$	$\hat{C}_3^1$	$\hat{C}_3^2$	$\theta = 2\cos(2\pi/3)$	
A	1	1	1	z, R_z	x^2+y^2, z^2
E	2	θ	θ	$(x,y)(R_x,R_y)$	$(x^2-y^2, xy)(yz, xz)$

The character table of $C_{\infty v}$ and $D_{\infty h}$ employ the angular momentum notation:

$\lvert M_L \rvert$	0	1	2	3	...
irrep	Σ	Π	Δ	Φ	...

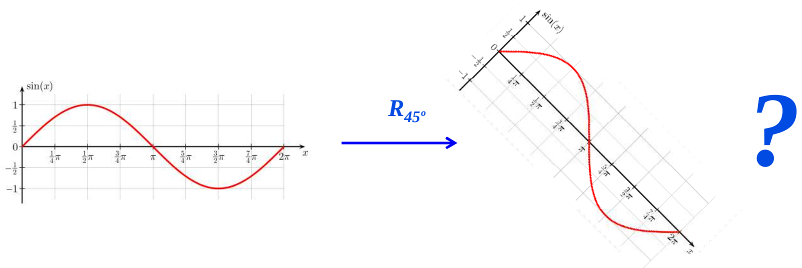
Example: The complete C_{4v} character table

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$			
A_1	1	1	1	1	1	z	x^2+y^2, z^2	z^2
A_2	1	1	1	-1	-1	R_z		
B_1	1	-1	1	1	-1		x^2-y^2	$z(x^2-y^2)$
B_2	1	-1	1	-1	1		xy	xyz
E	2	0	-2	0	0	$(x,y),(R_x,R_y)$	(xz, yz)	$(xz^2, yz^2),[x(x^2-3y^2), y(3x^2-y^2)]$

These are basis functions for the irreducible representations. They have the same symmetry properties as the atomic orbitals with the same names.

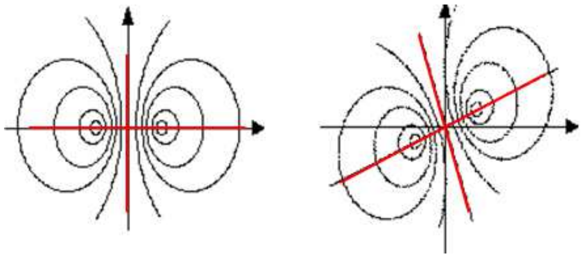
The functions space as a basis set for irreps

How can we do a 45 degrees rotation on the sine function?



The functions space as a basis set for irreps

Rotating a function:

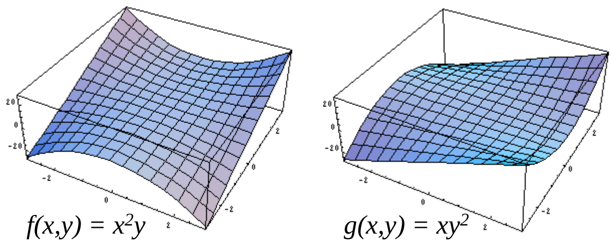


We define rotated function to the function which looks like the original when the original one is referred to the coordinates axes that have been backward rotated:

$$O_R\, f(x) = f(R^{-1}\, x)$$

Rotating the functions vs. rotating its argument

$$\mathbf{O}_R f(x) = f(R^{-1}x)$$



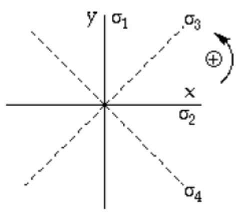
$f(x,y) = x^2y$ $\quad$ $g(x,y) = xy^2$

$f(x,y) = x^2y$

$O_{\pi/2} f(x,y) = f(R_{-\pi/2}(x,y)) = f(-y,x) = (-y)^2(x) = y^2x$

Some examples of functions as basis for irreps

$C_{4v} = \{E, 2C_4(z), C_2(z), 2\sigma_v, 2\sigma_d\}$ acting on $f(x,y) = x^2y$



$$\hat{E}\begin{bmatrix}x\\y\end{bmatrix}=\begin{bmatrix}x\\y\end{bmatrix}=\begin{bmatrix}1&0\\0&1\end{bmatrix}\begin{bmatrix}x\\y\end{bmatrix}$$

$$\hat{C}_4^1\begin{bmatrix}x\\y\end{bmatrix}=\begin{bmatrix}y\\-x\end{bmatrix}=\begin{bmatrix}0&1\\-1&0\end{bmatrix}\begin{bmatrix}x\\y\end{bmatrix}$$

$$\hat{C}_4^3\begin{bmatrix}x\\y\end{bmatrix}=\begin{bmatrix}-y\\x\end{bmatrix}=\begin{bmatrix}0&-1\\1&0\end{bmatrix}\begin{bmatrix}x\\y\end{bmatrix}$$

$$\hat{C}_2\begin{bmatrix}x\\y\end{bmatrix}=\begin{bmatrix}-x\\-y\end{bmatrix}=\begin{bmatrix}-1&0\\0&-1\end{bmatrix}\begin{bmatrix}x\\y\end{bmatrix}$$

$$\hat{\sigma}_1\begin{bmatrix}x\\y\end{bmatrix}=\begin{bmatrix}-x\\y\end{bmatrix}=\begin{bmatrix}-1&0\\0&1\end{bmatrix}\begin{bmatrix}x\\y\end{bmatrix}$$

$$\hat{\sigma}_2\begin{bmatrix}x\\y\end{bmatrix}=\begin{bmatrix}x\\-y\end{bmatrix}=\begin{bmatrix}1&0\\0&-1\end{bmatrix}\begin{bmatrix}x\\y\end{bmatrix}$$

$$\hat{\sigma}_3\begin{bmatrix}x\\y\end{bmatrix}=\begin{bmatrix}y\\x\end{bmatrix}=\begin{bmatrix}0&1\\1&0\end{bmatrix}\begin{bmatrix}x\\y\end{bmatrix}$$

$$\hat{\sigma}_4\begin{bmatrix}x\\y\end{bmatrix}=\begin{bmatrix}-y\\-x\end{bmatrix}=\begin{bmatrix}0&-1\\-1&0\end{bmatrix}\begin{bmatrix}x\\y\end{bmatrix}$$

$$\mathbf{O}_{\hat{E}}\, f\left(\begin{bmatrix}x\\y\end{bmatrix}\right)=f\left(\hat{E}\begin{bmatrix}x\\y\end{bmatrix}\right)=f\left(\begin{bmatrix}x\\y\end{bmatrix}\right)$$

$$\mathbf{O}_{\hat{C}_4^1}\, f\left(\begin{bmatrix}x\\y\end{bmatrix}\right)=f\left(\hat{C}_4^3\begin{bmatrix}x\\y\end{bmatrix}\right)=f\left(\begin{bmatrix}-y\\x\end{bmatrix}\right)=y^2x\equiv g$$

$$\mathbf{O}_{\hat{C}_4^3}\, f\left(\begin{bmatrix}x\\y\end{bmatrix}\right)=f\left(\hat{C}_4^1\begin{bmatrix}x\\y\end{bmatrix}\right)=f\left(\begin{bmatrix}y\\-x\end{bmatrix}\right)=-y^2x\equiv -g$$

$$\mathbf{O}_{\hat{C}_2}\, f\left(\begin{bmatrix}x\\y\end{bmatrix}\right)=f\left(\hat{C}_2\begin{bmatrix}x\\y\end{bmatrix}\right)=f\left(\begin{bmatrix}-x\\-y\end{bmatrix}\right)=-x^2y\equiv -f$$

$$\mathbf{O}_{\hat{\sigma}_1}\, f\left(\begin{bmatrix}x\\y\end{bmatrix}\right)=f\left(\hat{\sigma}_1\begin{bmatrix}x\\y\end{bmatrix}\right)=f\left(\begin{bmatrix}-x\\y\end{bmatrix}\right)=x^2y\equiv f$$

$$\mathbf{O}_{\hat{\sigma}_2}\, f\left(\begin{bmatrix}x\\y\end{bmatrix}\right)=f\left(\hat{\sigma}_2\begin{bmatrix}x\\y\end{bmatrix}\right)=f\left(\begin{bmatrix}x\\-y\end{bmatrix}\right)=-x^2y\equiv -f$$

$$\mathbf{O}_{\hat{\sigma}_3}\, f\left(\begin{bmatrix}x\\y\end{bmatrix}\right)=f\left(\hat{\sigma}_3\begin{bmatrix}x\\y\end{bmatrix}\right)=f\left(\begin{bmatrix}y\\x\end{bmatrix}\right)=y^2x\equiv g$$

$$\mathbf{O}_{\hat{\sigma}_4}\, f\left(\begin{bmatrix}x\\y\end{bmatrix}\right)=f\left(\hat{\sigma}_4\begin{bmatrix}x\\y\end{bmatrix}\right)=f\left(\begin{bmatrix}-y\\-x\end{bmatrix}\right)=-y^2x\equiv -g$$

C_{4v} acting on $g(x,y) = y^2x$

$$\mathbf{O}_{\hat{E}}\, g = g;\ \mathbf{O}_{\hat{C}_4^1}\, g = -f;\ \mathbf{O}_{\hat{C}_4^3}\, g = f;\ \mathbf{O}_{\hat{C}_2}\, g = -g;$$
$$\mathbf{O}_{\hat{\sigma}_1}\, g = -g;\ \mathbf{O}_{\hat{\sigma}_2}\, g = g;\ \mathbf{O}_{\hat{\sigma}_3}\, g = f;\ \mathbf{O}_{\hat{\sigma}_4}\, g = -f$$

$$\mathbf{O}_{\hat{E}}\left(\begin{bmatrix} f \\ g \end{bmatrix}\right) = \begin{bmatrix} f \\ g \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}\begin{bmatrix} f \\ g \end{bmatrix} \qquad \mathbf{O}_{\hat{\sigma}_1}\left(\begin{bmatrix} f \\ g \end{bmatrix}\right) = \begin{bmatrix} f \\ -g \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}\begin{bmatrix} f \\ g \end{bmatrix}$$

$$\mathbf{O}_{\hat{C}_4^1}\left(\begin{bmatrix} f \\ g \end{bmatrix}\right) = \begin{bmatrix} g \\ -f \end{bmatrix} = \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}\begin{bmatrix} f \\ g \end{bmatrix} \qquad \mathbf{O}_{\hat{\sigma}_2}\left(\begin{bmatrix} f \\ g \end{bmatrix}\right) = \begin{bmatrix} -f \\ g \end{bmatrix} = \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}\begin{bmatrix} f \\ g \end{bmatrix}$$

$$\mathbf{O}_{\hat{C}_4^3}\left(\begin{bmatrix} f \\ g \end{bmatrix}\right) = \begin{bmatrix} -g \\ f \end{bmatrix} = \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}\begin{bmatrix} f \\ g \end{bmatrix} \qquad \mathbf{O}_{\hat{\sigma}_3}\left(\begin{bmatrix} f \\ g \end{bmatrix}\right) = \begin{bmatrix} g \\ f \end{bmatrix} = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}\begin{bmatrix} f \\ g \end{bmatrix}$$

$$\mathbf{O}_{\hat{C}_2}\left(\begin{bmatrix} f \\ g \end{bmatrix}\right) = \begin{bmatrix} -f \\ -g \end{bmatrix} = \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}\begin{bmatrix} f \\ g \end{bmatrix} \qquad \mathbf{O}_{\hat{\sigma}_4}\left(\begin{bmatrix} f \\ g \end{bmatrix}\right) = \begin{bmatrix} -g \\ -f \end{bmatrix} = \begin{bmatrix} 0 & -1 \\ -1 & 0 \end{bmatrix}\begin{bmatrix} f \\ g \end{bmatrix}$$

$$\chi(E) = \mathbf{2},\ \chi(C_4^1) = \chi(C_4^3) = \mathbf{0},\ \chi(C_2) = \mathbf{-2},\ \chi(\sigma_1) = \chi(\sigma_2) = \chi(\sigma_3) = \chi(\sigma_4) = \mathbf{0}$$

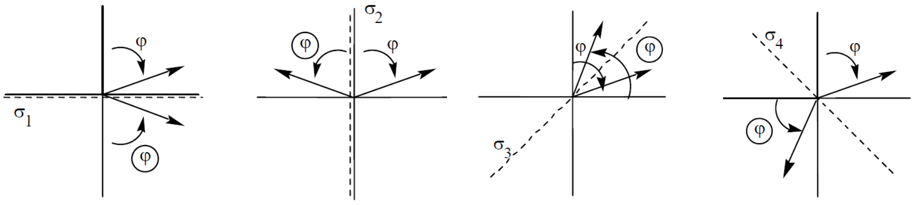
The p atomic orbitals as a basis set for C_{4v}

$$\begin{cases} p_x = N_{xy}(r) \sin\theta \cos\varphi \\ p_y = N_{xy}(r) \sin\theta \sin\varphi \\ p_z = N_z(r) \cos\theta \end{cases}$$

The coordinates (r, θ) are invariant under C_{4v}

The p_z by itself forms a basis set for a fully symmetric one-dimensional irrep of C_{4v}

C_{4v} acting on the variable φ:



$\sigma_1 \varphi = \pi - \varphi$ $\quad \sigma_2 \varphi = -\varphi$ $\quad \sigma_3 \varphi = \pi/2 - \varphi$ $\quad \sigma_4 \varphi = 3\pi/2 - \varphi$

The p atomic orbitals as a basis set for C_{4v}

$$\hat{E}\varphi = \varphi;\ \hat{C}_4^1\varphi = \frac{\pi}{2}+\varphi;\ \hat{C}_4^3\varphi = \frac{3\pi}{2}+\varphi;\ \hat{C}_2\varphi = \pi+\varphi;$$

$$\hat{\sigma}_1\varphi = \pi - \varphi;\ \hat{\sigma}_2\varphi = -\varphi;\ \hat{\sigma}_3\varphi = \frac{\pi}{2} - \varphi;\ \hat{\sigma}_4\varphi = \frac{3\pi}{2} - \varphi.$$

$$O_{\hat{E}}\sin\varphi = \sin\varphi;$$

$$O_{\hat{C}_4^1}\sin\varphi = \sin\left[\hat{C}_4^3\varphi\right] = \sin\left[\frac{3\pi}{2}+\varphi\right] = -\cos\varphi;$$

$$O_{\hat{C}_4^3}\sin\varphi = \sin\left[\hat{C}_4^1\varphi\right] = \sin\left[\frac{\pi}{2}+\varphi\right] = \cos\varphi;$$

$$O_{\hat{C}_2}\sin\varphi = \sin\left[\hat{C}_2\varphi\right] = \sin[\pi+\varphi] = -\sin\varphi;$$

$$O_{\hat{\sigma}_1}\sin\varphi = \sin[\hat{\sigma}_1\varphi] = \sin[\pi-\varphi] = \sin\varphi;$$

$$O_{\hat{\sigma}_2}\sin\varphi = \sin[\hat{\sigma}_2\varphi] = \sin[-\varphi] = -\sin\varphi;$$

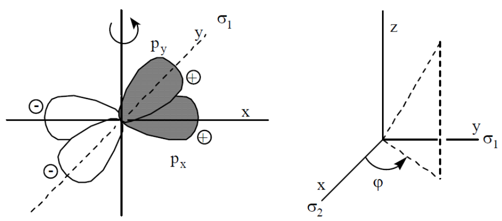
$$O_{\hat{\sigma}_3}\sin\varphi = \sin[\hat{\sigma}_3\varphi] = \sin\left[\frac{\pi}{2}-\varphi\right] = \cos\varphi;$$

$$O_{\hat{\sigma}_4}\sin\varphi = \sin[\hat{\sigma}_4\varphi] = \sin\left[\frac{3\pi}{2}-\varphi\right] = -\cos\varphi.$$

$$O_{\hat{E}}\begin{bmatrix}p_x\\p_y\end{bmatrix}=\begin{bmatrix}p_x\\p_y\end{bmatrix};\quad O_{\hat{C}_4^1}\begin{bmatrix}p_x\\p_y\end{bmatrix}=\begin{bmatrix}p_y\\-p_x\end{bmatrix};\quad O_{\hat{C}_4^3}\begin{bmatrix}p_x\\p_y\end{bmatrix}=\begin{bmatrix}-p_y\\p_x\end{bmatrix};\quad O_{\hat{C}_2}\begin{bmatrix}p_x\\p_y\end{bmatrix}=\begin{bmatrix}-p_x\\-p_y\end{bmatrix};$$

$$O_{\hat{\sigma}_1}\begin{bmatrix}p_x\\p_y\end{bmatrix}=\begin{bmatrix}-p_x\\p_y\end{bmatrix};\quad O_{\hat{\sigma}_2}\begin{bmatrix}p_x\\p_y\end{bmatrix}=\begin{bmatrix}p_x\\-p_y\end{bmatrix};\quad O_{\hat{\sigma}_3}\begin{bmatrix}p_x\\p_y\end{bmatrix}=\begin{bmatrix}p_y\\p_x\end{bmatrix};\quad O_{\hat{\sigma}_4}\begin{bmatrix}p_x\\p_y\end{bmatrix}=\begin{bmatrix}-p_y\\-p_x\end{bmatrix}.$$

The p atomic orbitals as a basis set for C_{4v}

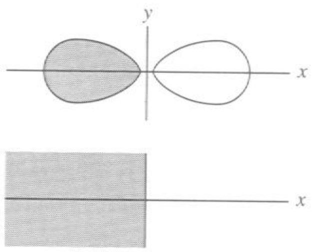


$$O_{\hat{E}}\begin{bmatrix}p_x\\p_y\end{bmatrix}=\begin{bmatrix}p_x\\p_y\end{bmatrix};\quad O_{\hat{C}_4^1}\begin{bmatrix}p_x\\p_y\end{bmatrix}=\begin{bmatrix}p_y\\-p_x\end{bmatrix};\quad O_{\hat{C}_4^3}\begin{bmatrix}p_x\\p_y\end{bmatrix}=\begin{bmatrix}-p_y\\p_x\end{bmatrix};\quad O_{\hat{C}_2}\begin{bmatrix}p_x\\p_y\end{bmatrix}=\begin{bmatrix}-p_x\\-p_y\end{bmatrix};$$

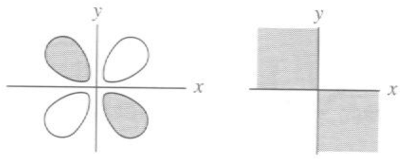
$$O_{\hat{\sigma}_1}\begin{bmatrix}p_x\\p_y\end{bmatrix}=\begin{bmatrix}-p_x\\p_y\end{bmatrix};\quad O_{\hat{\sigma}_2}\begin{bmatrix}p_x\\p_y\end{bmatrix}=\begin{bmatrix}p_x\\-p_y\end{bmatrix};\quad O_{\hat{\sigma}_3}\begin{bmatrix}p_x\\p_y\end{bmatrix}=\begin{bmatrix}p_y\\p_x\end{bmatrix};\quad O_{\hat{\sigma}_4}\begin{bmatrix}p_x\\p_y\end{bmatrix}=\begin{bmatrix}-p_y\\-p_x\end{bmatrix}.$$

{x,y} and {p_x,p_y} have same transformation properties

Symmetry of Atomic Orbitals



p_x orbitals have the same symmetry as x (positive in half the quadrants, negative in the other half).



d_{xy} orbitals have the same symmetry as the function xy (sign of the function in the four quadrants).

Angular part of atomic orbitals in Cartesian coordinates

$$p_z = N_1^c \frac{z}{r} = Y_1^0$$

$$p_x = N_1^c \frac{x}{r} = \frac{1}{\sqrt{2}} \left(Y_1^1 - Y_1^{-1}\right)$$

$$p_y = N_1^c \frac{y}{r} = i \frac{1}{\sqrt{2}} \left(Y_1^1 + Y_1^{-1}\right)$$

$$N_1^c = \left(\frac{3}{4\pi}\right)^{1/2}$$

$$d_{z^2} = N_2^c \frac{3z^2 - r^2}{2r^2\sqrt{3}} = Y_2^0$$

$$d_{xz} = N_2^c \frac{xz}{r^2} = -\frac{1}{\sqrt{2}} \left(Y_2^1 - Y_2^{-1}\right)$$

$$d_{yz} = N_2^c \frac{yz}{r^2} = \frac{i}{\sqrt{2}} \left(Y_2^1 + Y_2^{-1}\right)$$

$$d_{xy} = N_2^c \frac{xy}{r^2} = -\frac{i}{\sqrt{2}} \left(Y_2^2 - Y_2^{-2}\right)$$

$$d_{x^2-y^2} = N_2^c \frac{x^2 - y^2}{2r^2} = \frac{1}{\sqrt{2}} \left(Y_2^2 + Y_2^{-2}\right)$$

$$N_2^c = \left(\frac{15}{4\pi}\right)^{1/2}$$

Axial vectors as basis for irreps

An axial vector is a quantity that transforms like a vector under a proper rotation, but gains an additional sign flip under an improper rotation such as a reflection.

Axial vectors are represented as a cross product of two polar vectors:

$$\vec{L} = \vec{r} \wedge \vec{p} \qquad \vec{\omega} = \vec{r} \wedge \vec{v}/r^2 \qquad \vec{B} = \vec{\nabla} \wedge \vec{A}$$

The components of an axial vector $\vec{R} = \vec{P} \wedge \vec{Q}$ *are:*

$$R_z = P_x Q_y - P_y Q_x$$
$$R_x = P_y Q_z - P_z Q_y$$
$$R_y = P_z Q_x - P_x Q_z$$

Axial vectors as basis for irreps

C_{3v} ={E,2C_3(z), 3σ_v} acting on R_z=$P_x Q_y$-$P_y Q_x$,

We assume that P and Q are polar vectors, i.e., transform like r=(x,y,z)

$$E(R_z) = R_z$$

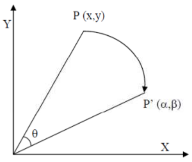
$$\sigma_{yz}(R_z) = \sigma_{yz}P_x\sigma_{yz}Q_y - \sigma_{yz}P_y\sigma_{yz}Q_x = -P_xQ_y - P_y(-Q_x) = -Rz$$

$$C_3^1(R_z) = (P_x\cos\theta + P_y\sin\theta)(-Q_x\sin\theta + Q_y\cos\theta) - (-P_x\sin\theta + P_y\cos\theta)(Q_x\cos\theta + Q_y\sin\theta) = P_xQ_y - P_yQ_x = R_z$$

The obtained characters are: $\chi^\mu(E) = 1$, $\chi^\mu(C_3) = 1$, $\chi^\mu(\sigma_v) = -1$, corresponding to the irrep A_2.

Operators as basis for irreps

An example: rotation of the 2D kinetic energy operator: $\mathcal{H} = -\frac{1}{2}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)$



$$(x\,y) = \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix}\begin{pmatrix} \alpha \\ \beta \end{pmatrix} \longrightarrow \begin{cases} \frac{\partial x}{\partial \alpha} = \cos\theta & \frac{\partial x}{\partial \beta} = -\sin\theta \\ \frac{\partial y}{\partial \alpha} = \sin\theta & \frac{\partial y}{\partial \beta} = \cos\theta \end{cases}$$

The Hamiltonian is invariant if $\mathcal{H}(\alpha,\beta)=\mathcal{H}(x,y)$

Let's consider a rotation θ *[from* (α,β) *to (x,y)]* ⟵ $\mathbf{O}_R\, f(x) = f(R^{-1}x)$

$$\frac{\partial}{\partial \alpha} = \frac{\partial x}{\partial \alpha}\frac{\partial}{\partial x} + \frac{\partial y}{\partial \alpha}\frac{\partial}{\partial y} = \cos\theta\frac{\partial}{\partial x} + \sin\theta\frac{\partial}{\partial y};$$

$$\frac{\partial^2}{\partial \alpha^2} = \frac{\partial}{\partial \alpha}\frac{\partial}{\partial \alpha} = \frac{\partial x}{\partial \alpha}\frac{\partial(\cos\theta\frac{\partial}{\partial x} + \sin\theta\frac{\partial}{\partial y})}{\partial x} + \frac{\partial y}{\partial \alpha}\frac{\partial(\cos\theta\frac{\partial}{\partial x} + \sin\theta\frac{\partial}{\partial y})}{\partial y}$$

$$\frac{\partial^2}{\partial \alpha^2} = \cos^2\theta\frac{\partial^2}{\partial x^2} + 2\cos\theta\sin\theta\frac{\partial^2}{\partial x\partial y} + \sin^2\theta\frac{\partial^2}{\partial y^2};$$

$$\frac{\partial^2}{\partial \beta^2} = \sin^2\theta\frac{\partial^2}{\partial x^2} - 2\cos\theta\sin\theta\frac{\partial^2}{\partial x\partial y} + \cos^2\theta\frac{\partial^2}{\partial y^2}$$

$$\mathcal{O}_{R_z}(\theta)\,[\mathcal{H}(x,y)] = \mathcal{H}(x,y)$$

↑

$$\frac{\partial^2}{\partial \alpha^2} + \frac{\partial^2}{\partial \beta^2} = (\cos^2\theta + \sin^2\theta)(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}) = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}; \longrightarrow \mathcal{H}(\alpha,\beta) = \mathcal{H}(x,y)$$

<u>*Alternatively*</u>

$$\mathcal{O}_R\mathcal{H}\Psi = E\mathcal{O}_R\Psi$$

$$\mathcal{O}_R\mathcal{H}\mathcal{O}_R^{-1}\mathcal{O}_R\Psi = E\mathcal{O}_R\Psi$$

$$\mathcal{H}'\Phi = E\Phi \longrightarrow \begin{matrix} \mathcal{H}' = \mathcal{O}_R\mathcal{H}\mathcal{O}_R^{-1} \\ \Phi = \mathcal{O}_R\Psi \end{matrix}$$

if $[\mathcal{H},\mathcal{O}_R] = 0 \longrightarrow \mathcal{H}\mathcal{O}_R = \mathcal{O}_R\mathcal{H}$

$\longrightarrow \mathcal{O}_R\mathcal{H}\mathcal{O}_R^{-1} = \mathcal{H}$

The Hamiltonian is invariant in case it commute with the symmetry transformation

Example:

if $[\mathcal{H},\mathcal{O}_{R_z}(\theta)] = 0$ *where* $\mathcal{O}_{R_z}(\theta) = e^{-i\theta\hat{L}_z}$ *then,* L_z *is a constant of motion*

Invariant vector spaces: some remarks

In terms of vector and linear spaces, reducing a representation as a sum of irreps is equivalent to determine the subspaces of the vector space spanning the reducible representation which are invariant under the group transformations.

Invariant vector subspace means that the action of the group on the subspace is closed, i.e., the action of every symmetry element of the group upon any vector of this subspace yields another vector in it.

The representation of a group on a vector space V is irreducible if V does not contain any (non-trivial) invariant space under the group transformations. Otherwise, the representation is reducible.

Symmetry and Structure in Chemistry

POINT SYMMETRY

Unit 2: Normal modes as basis sets for irreps.

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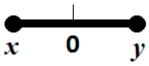
Normal Modes: one-dimensional diatomic molecule



$r = y - x$ $\quad r_{eq}=0$

$m_x=m_y=1 \quad k=1$

$$V = \frac{1}{2}r^2 = \frac{1}{2}(y-x)^2 = \frac{1}{2}\begin{pmatrix} x & y \end{pmatrix}\begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix}\begin{pmatrix} x \\ y \end{pmatrix}$$

Orthogonal change of coordinates

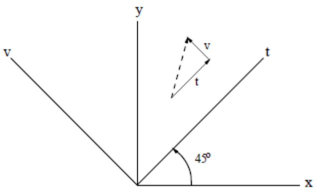
$$\begin{bmatrix} t \\ v \end{bmatrix} = \begin{bmatrix} o_{xx} & o_{xy} \\ o_{yx} & o_{yy} \end{bmatrix}\begin{bmatrix} x \\ y \end{bmatrix}$$

Normal modes: Orthogonal coordinates diagonalizing the V matrix: $\mathcal{O} V \mathcal{O}^t = \Lambda$

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

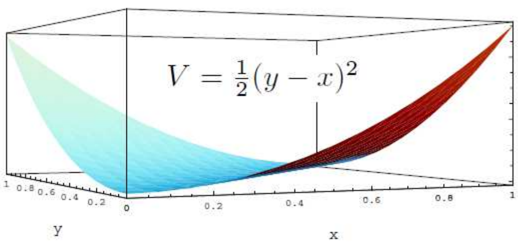
$$\rightarrow \begin{bmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{bmatrix} \quad \begin{bmatrix} -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{bmatrix} \rightarrow \quad \begin{bmatrix} t \\ v \end{bmatrix} = \begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{bmatrix}\begin{bmatrix} x \\ y \end{bmatrix}$$

$$\lambda = 0 \qquad \lambda = 2$$



$$t = \frac{1}{\sqrt{2}}x + \frac{1}{\sqrt{2}}y$$
$$v = -\frac{1}{\sqrt{2}}x + \frac{1}{\sqrt{2}}y$$

$$\Lambda = \mathcal{O}\, V\, \mathcal{O}^t = \begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{bmatrix}\begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix}\begin{bmatrix} \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \end{bmatrix} = \begin{bmatrix} 0 & 0 \\ 0 & 2 \end{bmatrix}$$



$$E = E_t + E_v$$
$$2E_t = (\dot{t})^2 + 0\, t^2$$
$$2E_v = (\dot{v})^2 + 2\, v^2$$

The normal modes associated to a zero force constant that do not change the position of the center of mass are referred to as rotations. Those associated to a zero force constant that change the position of the center of mass are referred to as translations. All the rest of normal modes are associated to non-zero force constants and are called vibrations.

Normal Modes and symmetry

In terms of normal modes: $V = \frac{1}{2}\sum_i k'_{ii}\alpha_i^2$

<u>Theorem</u>: Two normal modes associated to different force constants can not belong to the same irrep.

$$\mathbf{O}_R V(\alpha_i) = V(\alpha_i) = V(R^{-1}\alpha_i)$$

The potential energy is a scalar → invariant under symmetry transformations

$$2V = \sum_i k'_i\alpha_i^2 = \sum_{ijk} k'_i D_{ji} D_{ki} \alpha_j \alpha_k$$

Equation valid for all α_i. In particular, it is valid for $\alpha_i = 0$ when $i \neq 0$

$$k'_0\,\alpha_0^2 = \sum_i k'_i D_{0i}^2 \alpha_0^2$$ *D is a unitary matrix:* $\sum_i D_{0i}^2 = 1$

$$\rightarrow \quad \sum_i \left(\frac{k'_i}{k'_0} - 1\right) D_{0i}^2 = 0 \rightarrow \begin{cases} k'_i = k'_0 & \forall\, i \\ D_{0i}^2 = 0 & \forall\, i \neq 0 \end{cases}$$

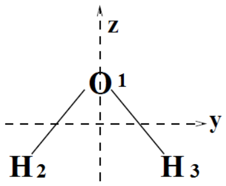
$\begin{cases} k'_i = k'_0 & \forall\, i \\ D_{0i}^2 = 0 & \forall\, i \neq 0 \end{cases}$ ⟶ Against the hypothesis $i \neq 0$
⟶ α_i and α_0 do not mix ⟶ belong to basis of different representations

If $k_1 = k_0$, then $\{\alpha_1,\alpha_0\}$ can be mixed by a symmetry transformation, i.e., {a1,a0} belong to the same basis of a multidimensional group representation (*intrinsic degeneration*)

It must be point out that two normal modes associated to the same force constant could not be mixed by any of the symmetry transformations of the system (*accidental degeneracy*). However, it is almost impossible finding out an *exact* accidental degeneracy.

If we ignore the possible occurrence of accidental degeneration, we can assume that the group representations of the normal modes are irreducible. Why?

Symmetry transformations upon Cartesian coordinates



$$C_2\begin{pmatrix}x1\\y1\\z1\\x2\\y2\\z2\\x3\\y3\\z3\end{pmatrix}=\left(\begin{array}{ccc|ccc|ccc}-1&0&0&0&0&0&0&0&0\\0&-1&0&0&0&0&0&0&0\\0&0&1&0&0&0&0&0&0\\\hline 0&0&0&0&0&0&-1&0&0\\0&0&0&0&0&0&0&-1&0\\0&0&0&0&0&0&0&0&1\\\hline 0&0&0&-1&0&0&0&0&0\\0&0&0&0&-1&0&0&0&0\\0&0&0&0&0&1&0&0&0\end{array}\right)\begin{pmatrix}x1\\y1\\z1\\x2\\y2\\z2\\x3\\y3\\z3\end{pmatrix}$$

$$\chi(C_2)=-1$$

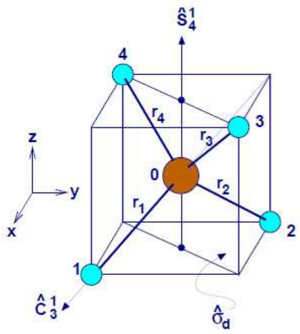
$$C_2\begin{pmatrix}O_1\\H_2\\H_3\end{pmatrix}=\begin{pmatrix}1&0&0\\0&0&1\\0&1&0\end{pmatrix}\begin{pmatrix}O_1\\H_2\\H_3\end{pmatrix}$$

$$C_2\begin{pmatrix}x\\y\\z\end{pmatrix}=\begin{pmatrix}-1&0&0\\0&-1&0\\0&0&1\end{pmatrix}\begin{pmatrix}x\\y\\z\end{pmatrix}$$

$$\chi(C_2)=(1+0+0)(-1-1+1)=-1$$

Normal Modes: el methane CH_4 case

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	$h=24$
A_1	1	1	1	1	1	$x^2+y^2+z^2$
A_2	1	1	1	-1	-1	
E	2	-1	2	0	0	$(3z^2-r^2, x^2-y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)
T_2	3	0	-1	-1	1	(x,y,z), (yz, xz, xy)
χ^{xyz}	3	0	-1	-1	1	
$N_{\hat{R}}$	5	2	1	1	3	
$\chi^{(3N)}$	15	0	-1	-1	3	

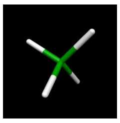


CH_4	A_1	A_2	E	T_1	T_2	
Γ^{3N}	1	0	1	1	3	
Trasl.	0	0	0	0	1	
Rot.	0	0	0	1	0	
Vib.	1	0	1	0	2	Active modes
IR active	no	no	no	no	YES	2
Raman active	YES	no	YES	no	YES	4

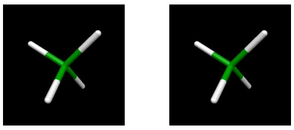
Normal Modes

Symmetry	ν(cm^{-1})
1 A_1	2917.0
2 E	1533.6
3 T_2	3019.5
4 T_2	1306.2

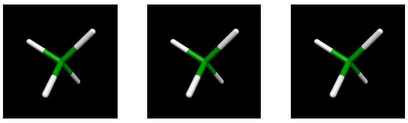
Methane Normal Modes



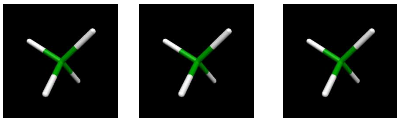
A_1



E



T_1



T_2

Symmetry and Structure in Chemistry

POINT SYMMETRY

Unit 3: Direct product of representations.

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Direct product of representations

Let f_α *belonging to the irrep "i" and* g_β *to the irrep "j".*

$$\mathbf{R}\, f_\alpha = \sum_{\mu}^{n} D^{i}_{\mu\alpha}(\mathbf{R})\, f_\mu \qquad \mathbf{R}\, g_\beta = \sum_{\nu}^{m} D^{j}_{\nu\beta}(\mathbf{R})\, g_\nu$$

Then, we build up the Cartesian products: $f_\mu g_\nu$

$$\mathbf{R}(f_\alpha\, g_\beta) = \mathbf{R}(f_\alpha)\mathbf{R}(g_\beta) = \sum_{\mu}^{n}\sum_{\nu}^{m} D^{i}_{\mu\alpha}(\mathbf{R})\, D^{j}_{\nu\beta}(\mathbf{R})\, f_\mu\, g_\nu$$

We unify indexes by defining: $h_\sigma = f_\mu g_\nu$, $h_\rho = f_\alpha g_\beta$

$$\longrightarrow \quad D^{i\otimes j}_{\sigma\rho}(\mathbf{R}) = D^{i}_{\mu\alpha}(\mathbf{R})\, D^{j}_{\nu\beta}(\mathbf{R})$$

$$\longrightarrow \quad \chi^{i\otimes j}(\mathbf{R}) = \sum_{\sigma} D^{i\otimes j}_{\sigma\sigma}(\mathbf{R}) = \sum_{\mu}\sum_{\nu} D^{i}_{\mu\mu}(\mathbf{R})\, D^{j}_{\nu\nu}(\mathbf{R}) = \chi^{i}(\mathbf{R})\, \chi^{j}(\mathbf{R})$$

Direct product of representations

Then, from two representations Γ^i *and* Γ^j *of a group G with dimensions* d_f *and* d_g*, respectively, we have defined the so-called direct or Cartesian product of them,* $\Gamma^{i\otimes j} = \Gamma^i \otimes \Gamma^j$*, which is a* $(d_i \times d_j)$ *dimensional representation with matrix elements:*

$$\forall\, R \in G \quad [D^{i\otimes j}(R)]_{(\mu\nu),(\alpha\beta)} = D^{i}_{\mu\alpha}(R) D^{j}_{\nu\beta}(R) \qquad \mu,\alpha = 1 \ldots d_i \;\; \nu,\beta = 1 \ldots d_j$$

In this equation (ik) labels a single index ranging from one up to $d_f \times d_g$*, as also (jl) does.*

The product yields a new, a priori reducible representation with characters:

$$\chi^{i\otimes j}(R) = \chi^{i}(R)\chi^{j}(R)$$

Example:

C_{4v}	$\hat{E}$	$2\hat{C}_4$	$\hat{C}_2$	$2\hat{\sigma}_v$	$2\hat{\sigma}_d$	
B_2	1	−1	1	−1	1	
E	2	0	−2	0	0	
$B_2 \otimes B_2$	1	1	1	1	1	$= A_1$
$E \otimes E$	4	0	4	0	0	$= A_1 \oplus A_2 \oplus B_1 \oplus B_2$

Teorem: The decomposition of the product of two irreps contains the representation totally symmetric (A1) only if both are identical (except for conjugation, in case of complex irreps)

Proof: Just consider the theorem of the orthogonality of characters

$$a_1 = \frac{1}{g}\sum_c n_c [\chi^{\nu}(c)\, \chi^{\mu}(c)^*](1) = \delta_{\mu\nu}$$

Eigenvectors of an irreducible representation

A vector ψ_i^f *belongs or is transformed according to the i-th basis of the irrep* Γ^f *if* $\forall\, R \in G$:

$$\hat{R}\psi_i^f = \sum_{j=1}^{d_f} \psi_j^f D_{ji}^f(\hat{R})$$

The set of vectors $\{\psi_1^f, \psi_2^f, \dots \psi_{d_f}^f\}$ *form a basis.*

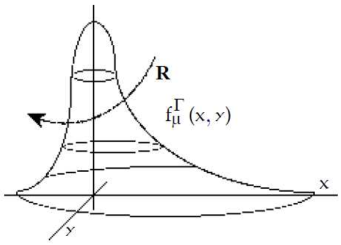
Teorem: If ψ_i^f, ψ_j^g *belong to bases of different irreps, they are orthogonal*

$$\langle \psi_i^f | \psi_j^g \rangle = \delta_{fg} C$$

Prior to prove this theorem, we are must clarify what does "a symmetry transformation acting upon an integral" means (an integral is a just a real or complex number...).

Vanishing Integrals

Consider the action of a rotation on the integral $\mathbf{I} = \int f_\mu^\Gamma (x,y)\, dx\, dy$



An integral (which is a number) must be invariant under any symmetry transformation.

Rotate an integral must mean calculating the integral once the function is rotated in the opposite direction.

$$\mathbf{O}_R\, f(x) = f(R^{-1} x)$$

Teorema: If f_μ^Γ is not a basis for the fully symmetric representation, then I=0

Prof: $\mathbf{R\,I = I} \longrightarrow \frac{1}{g}\sum_{\mathbf{R}} \mathbf{R\,I = I}$

$$\mathbf{I} = \frac{1}{g}\sum_{\mathbf{R}} \mathbf{R\,I} = \frac{1}{g}\sum_{\mathbf{R}}\int \mathbf{O_R}\, f_\mu^\Gamma(x)\,dx = \frac{1}{g}\sum_{\mathbf{R}}\int\sum_{\nu} D_{\nu\mu}^\Gamma(\mathbf{R})\, f_\nu^\Gamma(x)\,dx$$

$$= \sum_{\nu}\Big(\frac{1}{g}\sum_{\mathbf{R}} D_{\nu\mu}^\Gamma(\mathbf{R})\Big)\int f_\nu^\Gamma(x)\,dx = \sum_{\nu}\delta_{\Gamma A_1}\delta_{\mu\nu}\delta_{\mu 1}\int f_\mu^\Gamma(x)\,dx$$

$$\longrightarrow \mathbf{I} = \mathbf{I}\;\delta_{\Gamma A_1}\,\delta_{\mu 1}$$

Vanishing Integrals (cont.)

Teorem: if ψ_i^f, ψ_j^g belong to bases of different irreps, they are orthogonal

$$\langle \psi_i^f | \psi_j^g \rangle = \delta_{fg} C$$

Proof: Just consider that if the irreps are different, the decomposition of their product does not contain the fully symmetric irrep and hence the integral must be zero.

Spectroscopic selection rules

$$\int \psi_i(r)^* \vec{r}\, \psi_f(r)dr$$

Selection rules of diatomic molecules in microwaves

Absorption $< Y_{JM} \mid \vec{\mu} \mid Y_{J'M'} >$

$$D_{J,\varepsilon(J)} \otimes D_{1u} \otimes D_{J',\varepsilon(J')}$$

$$D_J \otimes D_{J'} = D_{J+J'} \oplus D_{J+J'-1} \oplus D_{J+J'-2} \oplus \dots \oplus D_{|J-J'|}$$

$$g \otimes g = u \otimes u = g \;;\; g \otimes u = u \otimes g = u$$

→ $\Delta J = \pm 1$

Raman $< Y_{JM} \mid \alpha \mid Y_{J'M'} >$

$$\left(D_{J,\varepsilon(J)} \otimes D_{J',\varepsilon(J')}\right) \otimes \left(D_{0g} \oplus D_{2g}\right)$$

→ $\Delta J = 0 \pm 2$

Vibrational (IR) spectra

BF_3 is a planar (D_{3h}) or a pyramidal (C_{3v}) molecule?

cm^{-1}	IR	Raman
482,0	*Strong*	*Medium*
719,5	*Strong*	-
888,0	-	*Strong*

A'_1 (888 cm^{-1}, *stretching*)
A''_2 (719 cm^{-1}, *stretching+bending*)
E' (482 cm^{-1}, *bending*)

		Dipole moment	Polarizability
pyramidal (C_{3v})	$\Gamma_v = 2A_1 \oplus 2E$	$A_1 \oplus E$	$A_1 \oplus E$
planar (D_{3h})	$\Gamma_v = A'_1 \oplus A''_2 \oplus 2E'$	$A''_2 \oplus E'$	$A'_1 \oplus E' \oplus E''$

PLANAR

Symmetry and Structure in Chemistry

POINT SYMMETRY

Unit 4: Atomic and molecular orbitals.

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Projection and shift operators

Action of the symmetry operation R on the μ-th function of the irrep Γ

$$\mathbf{R} f_\mu^\Gamma = \sum_\nu \mathbf{D}_{\nu\mu}^\Gamma(\mathbf{R}) f_\nu^\Gamma$$

Some manipulation ⟶

$$\mathbf{D}_{\sigma\mu}^\Gamma(\mathbf{R})^* \,\mathbf{R}\, f_\mu^\Gamma = \sum_\nu \mathbf{D}_{\sigma\mu}^\Gamma(\mathbf{R})^* \mathbf{D}_{\nu\mu}^\Gamma(\mathbf{R}) f_\nu^\Gamma$$

$$\longrightarrow \frac{n_\Gamma}{g}\sum_{\mathbf{R}} \mathbf{D}_{\sigma\mu}^\Gamma(\mathbf{R})^* \,\mathbf{R}\, f_\mu^\Gamma = \sum_\nu \frac{n_\Gamma}{g}\sum_{\mathbf{R}} \mathbf{D}_{\sigma\mu}^\Gamma(\mathbf{R})^* \mathbf{D}_{\nu\mu}^\Gamma(\mathbf{R}) f_\nu^\Gamma = \sum_\nu f_\nu^\Gamma \delta_{\nu\sigma} = f_\sigma^\Gamma$$

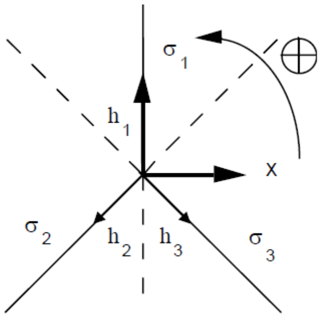
Then, we define:

$$\mathbf{P}_{\sigma\mu}^\Gamma = \frac{n_\Gamma}{g}\sum_{\mathbf{R}} \mathbf{D}_{\sigma\mu}^\Gamma(\mathbf{R})^* \,\mathbf{R} \longrightarrow \mathbf{P}_{\sigma\mu}^\Gamma f_\nu^\Gamma = f_\sigma^\Gamma \delta_{\mu\nu}$$

$$\mathbf{P}_{\mu\mu}^\Gamma = \frac{n_\Gamma}{g}\sum_{\mathbf{R}} \mathbf{D}_{\mu\mu}^\Gamma(\mathbf{R})^* \,\mathbf{R} \longrightarrow \mathbf{P}_{\mu\mu}^\Gamma f_\nu^\Gamma = f_\mu^\Gamma \delta_{\mu\nu}$$

$$\mathbf{P}^\Gamma = \sum_\mu \mathbf{P}_{\mu\mu}^\Gamma = \frac{n_\Gamma}{g}\sum_{\mathbf{R}} \chi^\Gamma(\mathbf{R})^* \,\mathbf{R} \longrightarrow \mathbf{P}^\Gamma f_\mu^\Gamma = f_\mu^\Gamma$$

Híbrid Orbitals(sp^2)



C_{3v}	E	$2C_3$	$3\sigma_v$	
A_1	1	1	1	z
A_2	1	1	-1	
E	2	-1	0	(x,y)
h	3	0	1	$A_1 \oplus E$

$$E = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad C_3^1 = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \quad C_3^2 = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$$

E →

$$\sigma_1 = \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} \quad \sigma_2 = \begin{bmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \quad \sigma_3 = \begin{bmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$$

$$P_{11}^{A_1} = \frac{1}{6}(E + C_3^1 + C_3^2 + \sigma_1 + \sigma_2 + \sigma_3)$$

$$P_{11}^{E} = \frac{2}{6}(E - \frac{1}{2}C_3^1 - \frac{1}{2}C_3^2 - \sigma_1 + \frac{1}{2}\sigma_2 + \frac{1}{2}\sigma_3) \quad P_{12}^{E} = \frac{2}{6}(\frac{\sqrt{3}}{2}C_3^1 - \frac{\sqrt{3}}{2}C_3^2 + \frac{\sqrt{3}}{2}\sigma_2 - \frac{\sqrt{3}}{2}\sigma_3)$$

$$P_{21}^{E} = \frac{2}{6}(-\frac{\sqrt{3}}{2}C_3^1 + \frac{\sqrt{3}}{2}C_3^2 + \frac{\sqrt{3}}{2}\sigma_2 - \frac{\sqrt{3}}{2}\sigma_3) \quad P_{22}^{E} = \frac{2}{6}(E - \frac{1}{2}C_3^1 - \frac{1}{2}C_3^2 + \sigma_1 - \frac{1}{2}\sigma_2 - \frac{1}{2}\sigma_3)$$

$$P_{11}^{A_1} h_1 = \frac{1}{3}(h_1 + h_2 + h_3) \quad P_{11}^{E} h_1 = 0 \quad P_{12}^{E} h_1 = 0$$

$$P_{21}^{E} h_1 = \frac{\sqrt{3}}{3}(h_3 - h_2) \quad P_{22}^{E} h_1 = \frac{1}{3}(2h_1 - h_2 - h_3)$$

$$\begin{bmatrix} s \\ p_y \\ p_x \end{bmatrix} = \begin{bmatrix} 1/\sqrt{3} & 1/\sqrt{3} & 1/\sqrt{3} \\ 2/\sqrt{6} & -1/\sqrt{6} & -1/\sqrt{6} \\ 0 & -1/\sqrt{2} & 1/\sqrt{2} \end{bmatrix} \begin{bmatrix} h_1 \\ h_2 \\ h_3 \end{bmatrix} \qquad \begin{bmatrix} h_1 \\ h_2 \\ h_3 \end{bmatrix} = \begin{bmatrix} 1/\sqrt{3} & 2/\sqrt{6} & 0 \\ 1/\sqrt{3} & -1/\sqrt{6} & -1/\sqrt{2} \\ 1/\sqrt{3} & -1/\sqrt{6} & 1/\sqrt{2} \end{bmatrix} \begin{bmatrix} s \\ p_y \\ p_x \end{bmatrix}$$

Using Projectors (only characters are now needed):

$$P^{A_1} = \frac{1}{6}(E + C_3^1 + C_3^2 + \sigma_1 + \sigma_2 + \sigma_3) \qquad s = \frac{1}{\sqrt{3}}(h_1 + h_2 + h_3)$$

$$P^{E} = \frac{2}{6}(2E - C_3^1 - C_3^2)$$

Non-orthogonality problem:

$$P^{E} h_1 = \frac{1}{3}(2h_1 - h_2 - h_3)$$

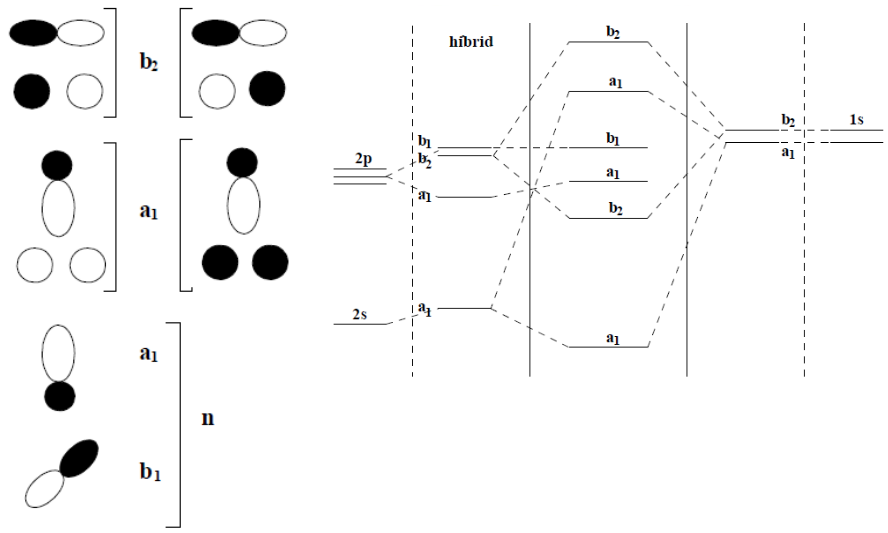
$$P^{E} h_2 = \frac{1}{3}(2h_2 - h_3 - h_1)$$

orthogonalitzation: →

$$\frac{1}{\sqrt{6}}(2h_1 - h_2 - h_3)$$

$$\frac{1}{\sqrt{2}}(h_2 - h_3)$$

Molecular Orbitals: the water molecule case



Molecular Orbitals: the benzene case

$$\begin{vmatrix} x & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x \end{vmatrix} = 0$$

Polynomial equation of degree 6 → x = ±1, ±1, ±2.
Then, we should find the associated eigenvectors

The set of 6 AOs 2pz form a basis for a reducible representation of the D6h group and also of its subgroups (D6, C6h, C6)

D_6	E	$2C_6$	$2C_3$	C_2	$3C'_2$	$3C''_2$
Γ	6	0	0	0	-2	0

$$\Gamma = A_2 \oplus B_2 \oplus E_1 \oplus E_2$$

We can calculate the D6 symmetry adapted basis set by means of projectors:

$$P^{A_2} = E + C_6^1 + C_6^5 + C_3^1 + C_3^2 + C_2 - \\ - C'_2(1) - C'_2(2) - C'_2(3) - C''_2(1) - C''_2(2) - C''_2(3)$$

$$P^{B_2} = E - C_6^1 - C_6^5 + C_3^1 + C_3^2 - C_2 - \\ - C'_2(1) - C'_2(2) - C'_2(3) + C''_2(1) + C''_2(2) + C''_2(3)$$

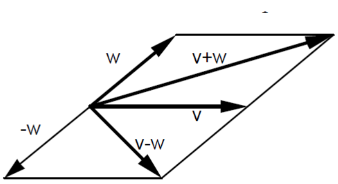
etc.

$$P^{A_2}\phi_1 = 2\,(\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6) = \varphi_1$$
$$P^{B_2}\phi_1 = 2\,(\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6) = \varphi_2$$
$$P^{E_1}\phi_1 = 2\,\phi_1 + \phi_2 - \phi_3 - 2\,\phi_4 - \phi_5 + \phi_6 = \varphi_3$$
$$P^{E_1}\phi_2 = \phi_1 + 2\,\phi_2 + \phi_3 - \phi_4 - 2\,\phi_5 - \phi_6 = \varphi_4$$
$$P^{E_2}\phi_1 = 2\,\phi_1 - \phi_2 - \phi_3 + 2\,\phi_4 - \phi_5 - \phi_6 = \varphi_5$$
$$P^{E_2}\phi_2 = -\phi_1 + 2\,\phi_2 - \phi_3 - \phi_4 + 2\,\phi_5 - \phi_6 = \varphi_6$$

Problem: the projections upon multidimensional irreps are not automatically calculated orthogonal

$$\langle \varphi_3 | \varphi_4 \rangle \neq 0 \qquad \langle \varphi_5 | \varphi_6 \rangle \neq 0$$

Symmetric Orthogonalitzation



$$\Psi_1(A_2) = \frac{1}{\sqrt{6}} (\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)$$

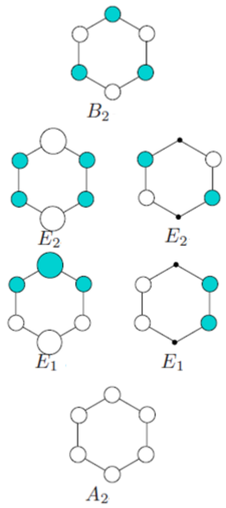
$$\Psi_2(E_1) = \frac{1}{2\sqrt{3}} (\phi_1 - \phi_2 - 2\phi_3 - \phi_4 + \phi_5 + 2\phi_6)$$

$$\Psi_3(E_1) = \frac{1}{2} (\phi_1 + \phi_2 - \phi_4 - \phi_5)$$

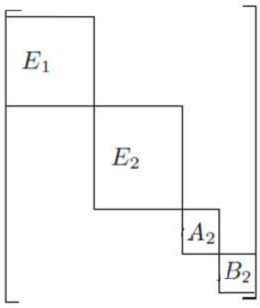
$$\Psi_4(E_2) = \frac{1}{2\sqrt{3}} (\phi_1 + \phi_2 - 2\phi_3 + \phi_4 + \phi_5 - 2\phi_6)$$

$$\Psi_5(E_2) = \frac{1}{2} (\phi_1 - \phi_2 + \phi_4 - \phi_5)$$

$$\Psi_6(B_2) = \frac{1}{\sqrt{6}} (\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6)$$



H =



The C6 group is Abelian

C_6 (6)	E	C_6	C_3	C_2	C_3^2	C_6^5
A	1	1	1	1	1	1
B	1	–1	1	–1	1	–1
E_1	1	ε	$-\varepsilon^*$	–1	$-\varepsilon$	ε^*
	1	ε^*	$-\varepsilon$	–1	$-\varepsilon^*$	ε
E_2	1	$-\varepsilon^*$	$-\varepsilon$	1	$-\varepsilon^*$	$-\varepsilon$
	1	$-\varepsilon$	$-\varepsilon^*$	1	$-\varepsilon$	$-\varepsilon^*$

$$\Psi_1(A) = \frac{1}{\sqrt{6}} (\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6)$$

$$\Psi_2(E_1) = \frac{1}{\sqrt{6}} (\phi_1 + \varepsilon\phi_2 - \varepsilon^*\phi_3 - \phi_4 - \varepsilon\phi_5 + \varepsilon^*\phi_6)$$

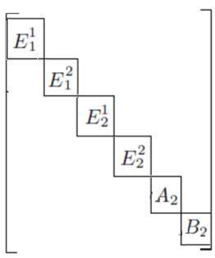
$$\Psi_3(E_1) = \frac{1}{\sqrt{6}} (\phi_1 + \varepsilon^*\phi_2 - \varepsilon\phi_3 - \phi_4 - \varepsilon^*\phi_5 + \varepsilon\phi_6)$$

$$\Psi_4(E_2) = \frac{1}{\sqrt{6}} (\phi_1 - \varepsilon^*\phi_2 - \varepsilon\phi_3 + \phi_4 - \varepsilon^*\phi_5 + \varepsilon\phi_6)$$

$$\Psi_5(E_2) = \frac{1}{\sqrt{6}} (\phi_1 - \varepsilon\phi_2 - \varepsilon^*\phi_3 + \phi_4 - \varepsilon\phi_5 + \varepsilon^*\phi_6)$$

$$\Psi_6(B) = \frac{1}{\sqrt{6}} (\phi_1 - \phi_2 + \phi_3 - \phi_4 + \phi_5 - \phi_6)$$

H =



Symmetry and Structure in Chemistry

POINT SYMMETRY

Unit 5: The symmetric or permutation group.

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Symmetric group of permutations

$$\begin{pmatrix} 1234 \\ 4132 \end{pmatrix} x_1 x_2 x_3 x_4 = x_4 x_1 x_3 x_2 \qquad \begin{pmatrix} 1234 \\ 4132 \end{pmatrix} = (142)(3) = (142)$$

Example 1: $(142)\, x_1 x_2 x_3 x_4 = x_4 x_1 x_3 x_2$

Example 2: $A = x_1^2 x_2 x_3 + 2 x_2^2 x_3^4 \qquad (12) A = x_2^2 x_1 x_3 + 2 x_1^2 x_3^4$

Item 1. Disjoint cycles commute

$$(123)(45) = \begin{pmatrix} 12345 \\ 23154 \end{pmatrix} = \begin{pmatrix} 45123 \\ 54231 \end{pmatrix} = (45)(123)$$

Item 2. Cyclic permutation, e.g. (123)=(231)=(312)

$$(123) = \begin{pmatrix} 123 \\ 231 \end{pmatrix} = \begin{pmatrix} 231 \\ 312 \end{pmatrix} = (231)$$

Item 3. decomposition of a cycle as product of transpositions (ab)

$$\left.\begin{array}{l}(123)\ x_1x_2x_3 = x_2x_3x_1 \\ (12)(23)\ x_1x_2x_3 = (12)x_1x_3x_2 = x_2x_3x_1\end{array}\right\}\ (123) = (12)\,(23)$$

Caution to the ordering!

$$(23)(12)\ x_1x_2x_3 = (23)x_2x_1x_3 = x_3x_1x_2 = (132)x_1x_2x_3$$

$$(23)(12) = (32)(21) = (321) = (132)$$

Item 4. The product of two cycles in reverse order yields the neutral element

$$(12)(21)x_1x_2x_3 = (12)x_2x_1x_3 = x_1x_2x_3 = e\ x_1x_2x_3$$

$$(123)(321) = (12)(23)(32)(21) = (12)e(21) = (12)(21) = e$$

Item5. Products of two cycles with repeated elements

$$(12)(324) = (12)(243) = (1243)$$

***Definition**. A permutation is even (odd) if the number of transpositions it contains is even (odd)*

e is even (zero transpositions)

$(123)(67) = (12)(23)(67)$ és odd (3 transpositions)

$(246) = (24)(46)$ és even (2 transpositions)

Conjugation relation and equivalence classes

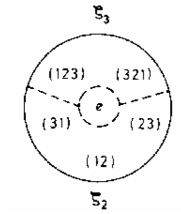
$q \sim p \Leftrightarrow q = t^{-1}p\,t$

reflexivity : $a \sim a\ (a = eae^{-1} = eae = ea = a)$

symmetry : $a \sim b \Leftrightarrow b \sim a\ \ (a = t^{-1}bt \Leftrightarrow tat^{-1} = tt^{-1}btt^{-1} = b)$

transitivity : $a \sim b, b \sim c \Rightarrow a \sim c\ (a = t^{-1}bt = t^{-1}s^{-1}cst = (st)^{-1}cst = r^{-1}cr)$

Example: S_3 (3 classes):



- $\xi_1 = \{ e \}$ identity
- $\xi_2 = \{ (12), (23), (31) \}$ 2-cycles
- $\xi_3 = \{ (123), (321) \}$ 3-cycles

Permutations with the same cyclic structure belong to the same class

Number of elements in a class $(\nu) \equiv (1^{\nu_1}\ 2^{\nu_2} \ldots n^{\nu_n})$ $\quad \dfrac{n!}{\prod_i i^{\nu_i} \nu_i!}$

$$e = (1)(2)(3) : \frac{3!}{1^3 3! \cdot 2^0 0! \cdot 3^0 0!} = 1$$

$$(12) : \frac{3!}{1^1 1! \cdot 2^1 1! \cdot 3^0 0!} = 3$$

$$(123) : \frac{3!}{1^0 0! \cdot 2^0 0! \cdot 3^1 1!} = 2$$

Partitions and classes $(\nu) \equiv (1^{\nu_1}\ 2^{\nu_2} \ldots n^{\nu_n}) \longrightarrow n = \nu_1 + 2\nu_2 + \ldots n\,\nu_n$

$$\nu_1 + \nu_2 + \ldots \nu_n = \lambda_1$$
$$\nu_2 + \ldots \nu_n = \lambda_2$$
$$\ldots$$
$$\nu_n = \lambda_n$$

$\longrightarrow$ $\lambda_1 + \lambda_2 + \ldots \lambda_n = n$, $\quad \lambda_1 \geq \lambda_2 \geq \ldots \lambda_n \geq 0$

Label of class (ν) o [λ]: $\quad (1^{\nu_1}\ 2^{\nu_2} \ldots n^{\nu_n}) \quad [\lambda_1\ \ \lambda_2 \ldots\ \ \lambda_n]$

Example S_4

partitions of 4: ***4 = 4 = 3+1 = 2+2 = 2+1+1 = 1+1+1+1***

classes of 4: ***(1^4) $(2\ 1^2)$ (2^2) $(3\ 1)$ e***

classes of 4: ***$[4]$ $[3\ 1]$ $[2^2]$ $[2\ 1^2]$ $[1^4]$***

Example S_4 ***partitions of 4: 4, 3+1, 2+2, 2+1+1, 1+1+1+1***

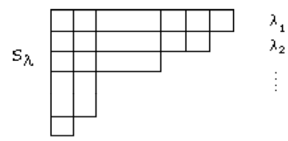
[4].- e: (1) (2) (3) (4)	1	(1^4)	$\frac{4!}{4!} = 1$
[3 1].- Cicles de 2 : (12); (13); (14); (23); (24); (34)	6	$(2\,1^2)$	$\frac{4!}{2!\,2\ \ 1!} = 6$
[2^2].- (12) (34); (13) (24); (14) (23)	3	(2^2)	$\frac{4!}{2!\,2^2} = 3$
[2 1^2].- (123); (132); (124); (142); (134); (143); (234); (243)	8	(3 1)	$\frac{4!}{1!\,3\ \ 1!} = 8$
[1^4].- (1234); (1243); (1324); (1342); (1423); (1432)	6	(4)	$\frac{4!}{4\ \ 1!} = 6$

Partition	Cycles structure	Cardinal class	Example
[4]	(1^4)	1	e
[1^4]	(4^1)	6	(1432)
[2^2]	(2^2)	3	(14)(32)
[2 1^2]	$(1^1\,3^1)$	8	(132)
[3 1]	$(1^2\,2^1)$	6	(12)

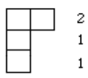
Classes and Young Tableaux

$\lambda_1 + \lambda_2 + \ldots.\ \lambda_n = n$

$\lambda_1 \geq \lambda_2 \geq \ldots.\ \lambda_n \geq 0$

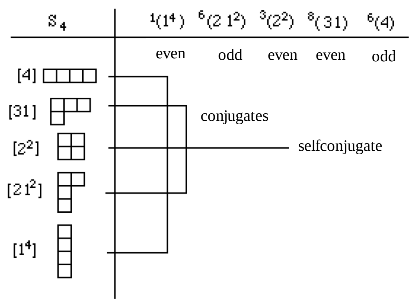


Ex. Partition [2 1^2]



Example S_4

IR	Young Tableaux	Dimension
[4]	1 2 3 4	1
[3 1]	1 2 3 / 4 ; 1 3 4 / 2 ; 1 2 4 / 3	3
[2^2]	1 2 / 3 4 ; 1 3 / 2 4	2
[2 1^2]	1 2 / 3 / 4 ; 1 4 / 2 / 3 ; 1 3 / 2 / 4	3
[1^4]	1 / 2 / 3 / 4	1

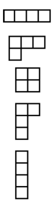


Caracter Tables

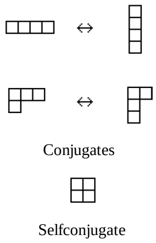
We build them by using the orthogonality theorem, as with the point symmetry groups

S_2	${}^1(1^2)$	${}^1(2)$
[2]	1	1
$[1^2]$	1	-1

S_3	${}^1(1^3)$	${}^3(2\ 1)$	${}^2(3)$
[3]	1	1	1
[21]	2	0	-1
$[1^3]$	1	-1	1



S_4	${}^1(1^4)$	${}^6(2\ 1^2)$	${}^3(2^2)$	${}^8(3\ 1)$	${}^6(4)$
	1	1	1	1	1
	3	1	-1	0	-1
	2	0	2	-1	0
	3	-1	-1	0	1
	1	-1	1	1	-1



Please note:

$$\chi^{[1^n]}(P) = (-1)^p$$

$$\chi^{\tilde{\mu}}(P) = (-1)^p \chi^{\mu}(P)$$

Theorem *The decomposition of the tensorial product of two irreps of the symmetric group contains the fully antisymmetric irrep $[1^n]$ if and only if the irreps in the product are dual of each other. In this case, the multiplicity is 1, i.e., the $[1^n]$ irrep appears only once.*

Remainder:

$$\chi^{\mu\otimes\nu}(P) = \chi^{\mu}(P)\ \chi^{\nu}(P)$$

$$\chi^{[1^n]}(P) = (-1)^p$$

$$\chi^{\tilde{\mu}}(P) = (-1)^p \chi^{\mu}(P)$$

Proof:

$$a_{[1^n]} = \frac{1}{n!}\sum_P \chi^{\mu\otimes\nu}(P)\,\chi^{[1^n]}(P)$$

$$= \frac{1}{n!}\sum_P \chi^{\mu}(P)\ \chi^{\nu}(P)\ (-1)^p$$

$$= \frac{1}{n!}\sum_P \chi^{\mu}(P)\ \chi^{\tilde{\nu}}(P) = \delta_{\mu\tilde{\nu}}$$

Obtaining spin-adapted functions (using shift operators)

S_3	$^1(1^3)$	$^3(2\,1)$	$^2(3)$
[3]	1	1	1
[21]	2	0	-1
$[1^3]$	1	-1	1

S_3	(12)	(23)
[3]	1	1
[21]	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$
$[1^3]$	-1	-1

Spin functions:

$$\Theta_1 = |\tfrac{1}{2},\tfrac{1}{2},1> \; = \; 2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha$$
$$\Theta_2 = |\tfrac{1}{2},\tfrac{1}{2},2> \; = \; \alpha\beta\alpha - \beta\alpha\alpha$$

Orbital functions: (ijk represents $\phi_i(1)\phi_j(2)\phi_k(3)$):

$$\chi_1 = ijk + jik - \tfrac{1}{2} ikj - \tfrac{1}{2} kji - \tfrac{1}{2} jki - \tfrac{1}{2} kij$$
$$\chi_2 = ikj - kji + jki - kij$$

$$\xi_2 = ijk - jik + \tfrac{1}{2} ikj + \tfrac{1}{2} kji - \tfrac{1}{2} jki - \tfrac{1}{2} kij$$
$$\xi_1 = ikj - kji - jki + kij$$

Total wave functions: $(\Psi = \sum \chi_k \Theta_k)$:

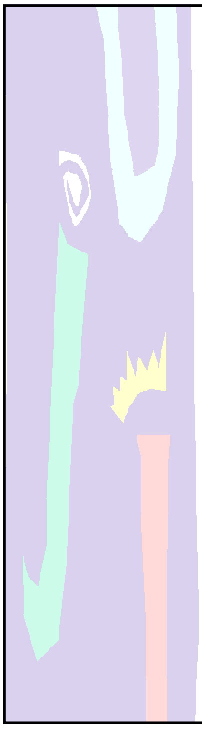
$$\Psi_{\frac{1}{2}\frac{1}{2}1}(1,2,3) = (\chi_1\Theta_1 + \chi_2\Theta_2)$$
$$\Psi_{\frac{1}{2}\frac{1}{2}2}(1,2,3) = (\xi_1\Theta_1 + \xi_2\Theta_2)$$

$$(123) = (12)(23) = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$$

$$(132) = (123)^{-1} = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}^t = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$$

$$(13) = (12)(132) = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$$

S_4	(12)	(23)	(34)
[4]	1	1	1
[31]	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{3} & \frac{\sqrt{8}}{3} & 0 \\ \frac{\sqrt{8}}{3} & \frac{1}{3} & 0 \\ 0 & 0 & 1 \end{pmatrix}$
$[2^2]$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$
$[21^2]$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -\frac{1}{3} & \frac{\sqrt{8}}{3} \\ 0 & \frac{\sqrt{8}}{3} & \frac{1}{3} \end{pmatrix}$
$[1^4]$	-1	-1	-1



Symmetry and Structure in Chemistry

POINT SYMMETRY

Unit 6: Symmetrized powers of group representations

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Powers of irreps

An example:

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	z^2, x^2+y^2
A_2	1	1	-1	R_z	
E	2	-1	0	(x,y)	(x^2-y^2, xy) (xz, yz)
$E\otimes E$	4	1	0		(xx,xy,yx,yy)

$E\otimes E = A_1 \oplus A_2 \oplus E$

S_2	$^1(1^2)$	$^1(2)$
[2]	1	1
[1^2]	1	-1
$E\otimes E$	4	2

(xx,xy,yx,yy)

$E\otimes E = 3\,[2] \oplus [1^2]$

$P^{\pm} = \frac{1}{2}(E \pm P_{12})$

symmetric

$x^2 + y^2 \rightarrow A_1$

$x^2 - y^2$, $xy + yx \rightarrow E$

antisymmetric

$R_z = xy - yx \rightarrow A_2$

$E\otimes E = A_1 \oplus [A_2] \oplus E$

The basis set of the second power of an irreducible representation can always be decomposed as a direct sum of two subspaces stable (invariant) under the S2 permutation symmetry (symmetric and antisymmetric). Each of these subspaces can in turn be decomposed into subspaces stable under the point symmetry group.

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
$A_1 \oplus E$	3	0	1

$E \overset{+}{\otimes} E = A_1 \oplus E$

$E \overset{-}{\otimes} E = A_2$

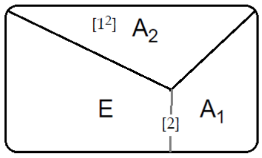
$$\chi_{\mu^2}^{[2]}(R) = \frac{1}{2}\left[\chi_\mu^2(R) + \chi_\mu\left(R^2\right)\right]$$

$$\chi_{\mu^2}^{[1^2]}(R) = \frac{1}{2}\left[\chi_\mu^2(R) - \chi_\mu\left(R^2\right)\right]$$

$$x_E^{\pm}(E) = \frac{1}{2}[x_E^2(E) \pm x_E(E^2)] = \frac{1}{2}(4 \pm 2) = \begin{matrix} 3 \\ 1 \end{matrix}$$

$$x_E^{\pm}(C_3) = \frac{1}{2}[x_E^2(C_3) \pm x_E(C_3^2)] = \frac{1}{2}(1 \pm (-1)) = \begin{matrix} 0 \\ 1 \end{matrix}$$

$$x_E^{\pm}(\sigma_v) = \frac{1}{2}[x_E^2(\sigma_v) \pm x_E(\sigma_3^2)] = \frac{1}{2}(0 \pm 2) = \begin{matrix} 1 \\ -1 \end{matrix}$$



In general:

$$\chi_{\mu^n}^{[\lambda]}(R) = \frac{\ell_{[\lambda]}}{n!} \sum_{C \in S_n} \chi^{[\lambda]}(C)\, m_C \prod_{i=1}^{n} \chi^{\nu_i}(R^i)$$

n	the power
[λ]	irrep of S_n
$\ell_{[\lambda]}$	dimension of [λ]
C	class of S_n
m_c	number of elements of class C
$\chi^{[\lambda]}(C)$	character of the irrep [λ]of Sn
$\chi(R)$	character of the irrep μ of the point group
ν_i	number of i-elements cycles of C

J. Planelles and C. Zicovich-Wilson, Int. J. Quant. Chem. 47(1993) 319.

Boyle Tables *(Int.J.Quantum Chem. 6 (1972) 725-746):*

TABLE II. The symmetrized cubes of the irreducible representations of non-centrosymmetric point groups.

C_3	$E^3 = \{2A + E \mid \mathscr{A}_1\} + \{E \mid \mathscr{E}\}$
C_{3h}	$E'^3 = \{2A' + E' \mid \mathscr{A}_1\} + \{E' \mid \mathscr{E}\}$
	$E''^3 = \{2A'' + E'' \mid \mathscr{A}_1\} + \{E'' \mid \mathscr{E}_1\}$
C_{3v}, D_3	$E^3 = \{A_1 + A_2 + E \mid \mathscr{A}_1\} + \{E \mid \mathscr{E}\}$
D_{3h}	$E'^3 = \{A_1' + A_2' + E' \mid \mathscr{A}_1\} + \{E' \mid \mathscr{E}\}$
	$E''^3 = \{A_1'' + A_2'' + E'' \mid \mathscr{A}_1\} + \{E'' \mid \mathscr{E}\}$
$C_4, D_{2d}, S_4, C_{4v}, D_4$	$E^3 = 2\{E \mid \mathscr{A}_1\} + \{E \mid \mathscr{E}\}$
D_{4d}, S_8	$E_1^3 = \{E_1 + E_3 \mid \mathscr{A}_1\} + \{E_1 \mid \mathscr{E}\}$
	$E_2^3 = 2\{E_2 \mid \mathscr{A}_1\} + \{E_2 \mid \mathscr{E}\}$
	$E_3^3 = \{E_1 + E_3 \mid \mathscr{A}_1\} + \{E_3 \mid \mathscr{E}\}$
⋮	⋮ ⋮ ⋮ ⋮
$C_{\infty v}, D_\infty$	$E_n^3 = \{E_n + E_{3n} \mid \mathscr{A}_1\} + \{E_n \mid \mathscr{E}\} \quad (E_1 \equiv \Pi, E_2 \equiv \Delta, \cdots)$
T	$E^3 = \{2A + E \mid \mathscr{A}_1\} + \{E \mid \mathscr{E}\}$
	$T^3 = \{A + 3T \mid \mathscr{A}_1\} + \{A \mid \mathscr{A}_2\} + \{E + 2T \mid \mathscr{E}\}$
T_d O,	$E^3 = \{A_1 + A_2 + E \mid \mathscr{A}_1\} + \{E \mid \mathscr{E}\}$
	$T_1^3 = \{A_2 + 2T_1 + T_2 \mid \mathscr{A}_1\} + \{A_1 \mid \mathscr{A}_2\} + \{E + T_1 + T_2 \mid \mathscr{E}\}$
	$T_2^3 = \{A_1 + T_1 + 2T_2 \mid \mathscr{A}_1\} + \{A_1 \mid \mathscr{A}_2\} + \{E + T_1 + T_2 \mid \mathscr{E}\}$
K	$D_1^3 = \{D_1 + D_3 \mid \mathscr{A}_1\} + \{D_0 \mid \mathscr{A}_2\} + \{D_1 + D_2 \mid \mathscr{E}\}$
	$D_2^3 = \{D_0 + D_2 + D_3 + D_4 + D_6 \mid \mathscr{A}_1\} + \{D_1 + D_3 \mid \mathscr{A}_2\} + \{D_1 + 2D_2 + D_3 + D_4 + D_5 \mid \mathscr{E}\}$
	....

$\mathscr{P}_3$	$\chi^3(\mathbf{R})$	$2\chi(\mathbf{R}^3)$	$3\chi(\mathbf{R})\chi(\mathbf{R}^2)$
$\mathscr{A}_1$	1	1	1
$\mathscr{A}_2$	1	1	−1
$\mathscr{E}$	2	−1	0

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
$E^{\otimes 3}$	8	-1	0
$A_1 \oplus A_2 \oplus E$	4	1	0
$E \mid \mathscr{E}$	4	-2	0

Boyle Tables *(cont): Terms of electronic atomic configurations*

TABLE II. The symmetrized cubes of the irreducible representations of K

$$D_1^3 = \{D_1 + D_3 \mid \mathscr{A}_1\} + \{D_0 \mid \mathscr{A}_2\} + \{D_1 + D_2 \mid \mathscr{E}\}$$
$$D_2^3 = \{D_0 + D_2 + D_3 + D_4 + D_6 \mid \mathscr{A}_1\} + \{D_1 + D_3 \mid \mathscr{A}_2\} + \{D_1 + 2D_2 + D_3 + D_4 + D_5 \mid \mathscr{E}\}$$

....

$$D_{1/2}^3 = \{D_{3/2} \mid \mathscr{A}_1\} + \{D_{1/2} \mid \mathscr{E}\}$$
$$D_{3/2}^3 = \{D_{3/2} + D_{5/2} + D_{9/2} \mid \mathscr{A}_1\} + \{D_{3/2} \mid \mathscr{A}_2\} + \{D_{1/2} + D_{3/2} + D_{5/2} + D_{7/2} \mid \mathscr{E}\}$$
$$D_{5/2}^3 = \{D_{3/2} + D_{5/2} + D_{7/2} + D_{9/2} + D_{11/2} + D_{15/2} \mid \mathscr{A}_1\} + \{D_{3/2} + D_{5/2} + D_{9/2} \mid \mathscr{A}_2\} + \{D_{1/2} + D_{3/2} + 2D_{5/2} + 2D_{7/2} + D_{9/2} + D_{11/2} + D_{13/2} \mid \mathscr{E}\}$$

. . . .

Terms of p^3 configuration

$$D_1^3 = \{D_1 + D_3 \mid \mathscr{A}_1\} + \{D_0 \mid \mathscr{A}_2\} + \{D_1 + D_2 \mid \mathscr{E}\}$$
$$D_{1/2}^3 = \{D_{3/2} \mid \mathscr{A}_1\} + \{D_{1/2} \mid \mathscr{E}\}$$

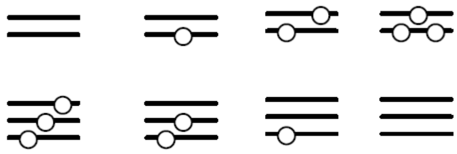
$^2P,\ ^2D,\ ^4S$

Terms of d^3 configuration

$$D_2^3 = \{D_0 + D_2 + D_3 + D_4 + D_6 \mid \mathscr{A}_1\} + \{D_1 + D_3 \mid \mathscr{A}_2\} + \{D_1 + 2D_2 + D_3 + D_4 + D_5 \mid \mathscr{E}\}$$
$$D_{1/2}^3 = \{D_{3/2} \mid \mathscr{A}_1\} + \{D_{1/2} \mid \mathscr{E}\}$$

$^4P,\ ^4F,\ ^2P,\ ^2D(2),\ ^2F,\ ^2G,\ ^2H$

Boyle Tables (cont): Terms of electronic molecular configurations



t_2^3 < $t_2^2 e$ < $t_2 e^2$ < e^3

configuration t_2^3:

$$t_2^3 = \{A_1 + T_1 + 2T_2 \mid [3]\} \oplus \{A_2 \mid [1^3]\} \oplus \{E + T_1 + T_2 \mid [21]\}$$

$$D^3_{1/2} = \{D_{3/2} \mid [3]\} \oplus \{D_{1/2} \mid [21]\}$$

$$\boxed{{}^4A_2 + {}^2E + {}^2T_1 + {}^2T_2}$$

configuration $t_2^2 e$:

subconfiguration t_2^2:

$$t_2^2 = A_1 + E + [T_1] + T_2$$

$$D^2_{1/2} = D_1 \oplus [D_0]$$

$$\longrightarrow {}^3T_1 + {}^1T_2 + {}^1E + {}^1A_1$$

subconfiguration e: ${}^2E$

Terms in the configuration $t_2^2 e$:

$$({}^3T_1 + {}^1T_2 + {}^1E + {}^1A_1) \otimes {}^2E =$$

$$= {}^4T_1 + {}^4T_2 + {}^2T_1(2) + {}^2T_2(2) + {}^2A_1 + {}^2A_2 + {}^2E(2)$$

configuration $t_2 e^2$

$$^4T_1 + {}^2T_1(2) + {}^2T_2(2)$$

configuration e^3 :

$$e^3 = \{A_1 + A_2 + E|\ [3]\} \oplus \{E|\ [21]\}$$

$$D^3_{1/2} = \{D_{3/2}|\ [3]\} \oplus \{D_{1/2}|\ [21]\}$$

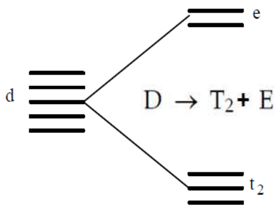
^2E

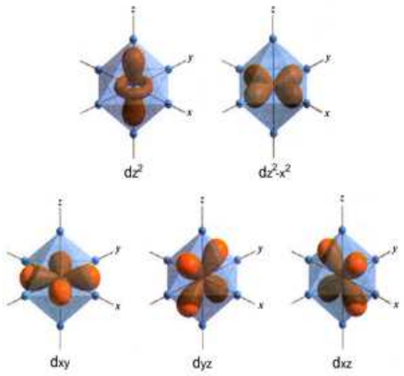
Correlation diagrams (Tanabe-Sugano) *d^2 configuration*

$D_2 \otimes D_2 = D_4 \oplus [D_3] \oplus D_2 \oplus [D_1] \oplus D_0$

$D_{1/2} \otimes D_{1/2} = D_1 \oplus [D_0]$.

$^3F < {}^1D < {}^3P < {}^1G < {}^1S$





$F \rightarrow T_1 < T_2 < A_2$

$D \rightarrow T_2 < E$

$G \rightarrow T_1 < T_2 < E < A_1$

$P \rightarrow T_1$

$S \rightarrow A_1$

d^2 configuration

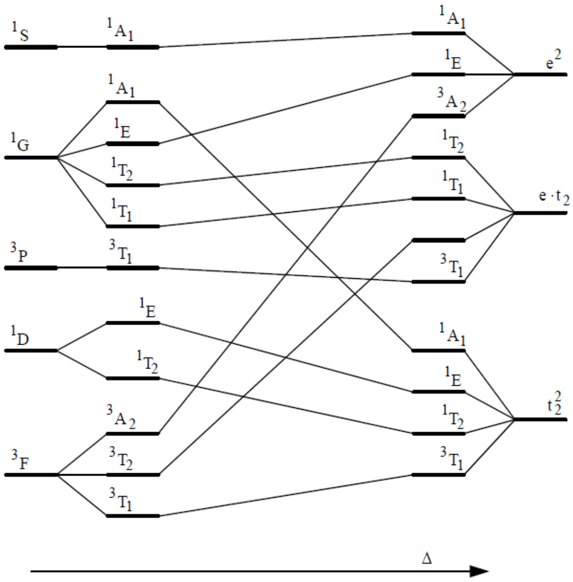
$F \rightarrow T_1 < T_2 < A_2$

$D \rightarrow T_2 < E$

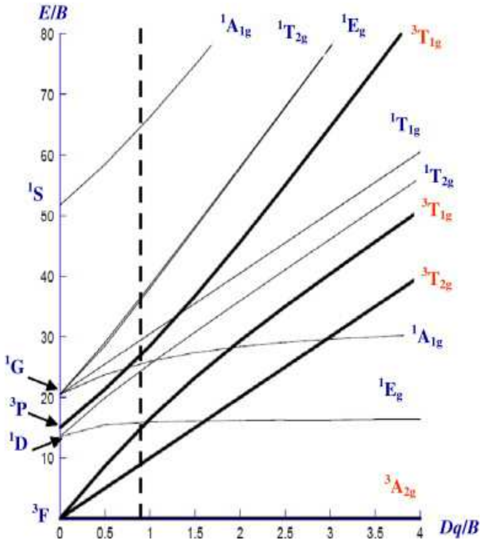
$G \rightarrow T_1 < T_2 < E < A_1$

$P \rightarrow T_1$

$S \rightarrow A_1$



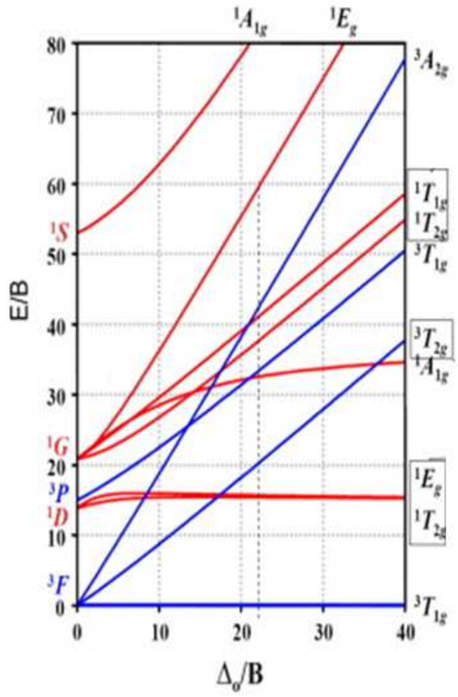
Tanabe–Sugano diagram for the Ni(II) $3d^8$ in octahedral CF.
vertical dashed line indicates the CF strength for MgO:Ni^{2+}.



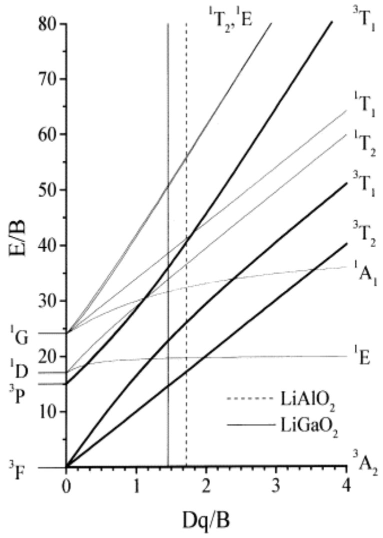
N. Mironova-Ulmanea,M.G. Brikb, I. Sildos
Journal of Luminescence 135 (2013) 74–78

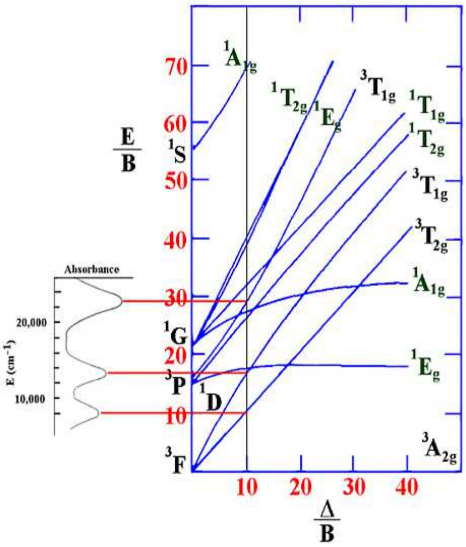
V^{3+} (d^2 configuration) ion in α-$ZnAl_2S_4$ host crystal.

S. Anghela, G. Boulonb,L. Kulyuka, K. Sushkevichc
Physica B: Condensed Matter 406 (2011) 4600–4603

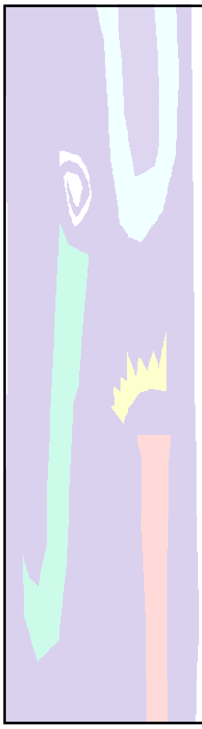


V^{3+} in $LiAlO_2$ and $LiGaO_2$ are indicated by vertical lines
S. Kück and P. Jander, Optical Materials, 13 (1999) 299–310





Octahedral Ni(II) complex (d^8) by Robert J. Lancashire,
http://wwwchem.uwimona.edu.jm/courses/Tanabe-Sugano/TShelp.html



Symmetry and Structure in Chemistry

POINT SYMMETRY

Unit 7: Continuous symmetry: Lie groups

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The group of rotations around an axis: C_∞ o SO(2)

C_∞	E	$C_z^\phi,\ \phi \in (0, 2\pi)$

This group has infinite number of elements, $\phi \in (0, 2\pi)$. It is a commutative group, i.e. has an infinite number of classes. Then, its character table cannot be derived from the orthogonality theorems, used for finite groups.

infinitesimal rotation $C_z^{\delta\phi}$ on $f(\theta)$:

$$C_z^{\delta\phi} f(\theta) = f(\theta - \delta\phi) = f(\theta) - \delta\phi \frac{df(\theta)}{d\theta} = (1 - \delta\phi \frac{d}{d\theta}) f(\theta)$$

Remember: $\hat{L}_z = -i\hbar \frac{d}{d\theta}$

$$\boxed{C_z^{\delta\phi} = (1 - i\frac{\delta\phi}{\hbar}\hat{L}_z)}$$

Finite rotation : $C_z^{\phi} = \lim_{N\to\infty} (C_z^{\delta\phi})^N$ ***with*** $\delta\phi = \lim_{N\to\infty} \frac{\phi}{N}$

Remember: $e = \lim_{N\to\infty} (1 + \frac{1}{N})^N$

$$C_z^{\phi} = \lim_{N\to\infty} (C_z^{\delta\phi})^N = \lim_{N\to\infty} \left[\left(1 + \frac{1}{\frac{iN\hbar}{\phi \hat{L}_z}} \right)^{\frac{iN\hbar}{\phi \hat{L}_z}} \right]^{\frac{\phi \hat{L}_z}{i\hbar}} = e^{-i\phi \hat{L}_z/\hbar}$$

The eigenfunctions of $\hat{L}_z$ are eigenfunctions of C_z^{ϕ}

$$C_z^{\phi} e^{iM\theta} = e^{-i\phi \hat{L}_z/\hbar} f(\theta) = \left[1 - \frac{i\phi}{\hbar} \hat{L}_z + \frac{1}{2} (\frac{i\phi}{\hbar} \hat{L}_z)^2 + \ldots \right] e^{iM\theta}$$

$$= \left[1 - i\phi M + \frac{1}{2} (-i\phi M)^2 + \ldots \right] e^{iM\theta}$$

→The eigenfunctions of Lz are bases for the irreps of the SO(2) group.

The line group SO(2) or C∞: $C_z^{\phi} e^{iM\theta} = e^{-iM\phi} e^{iM\theta}$

C_∞	(també $SO(2)$)	E	C_z^{ϕ}	Bases
0	Σ	1	1	$1,\ z,\ R_z$
±1	Π {	1 1	$e^{-i\phi}$ $e^{i\phi}$	$e^{i\theta}$ $e^{-i\theta}$ } (x,y)
±2	Δ {	1 1	$e^{-2i\phi}$ $e^{2i\phi}$	$e^{2i\theta}$ $e^{-2i\theta}$
...	...	...	...	...

The symmetry group of the sphere K or SO(3)
(special orthogonal 3D group)

Since $L_z = \vec{L} \cdot \vec{k}$ the rotation operator around the z axis (defined by the vector k) is: $C_z^{\phi} = e^{-i\frac{\phi}{\hbar}\vec{L}\cdot\vec{k}}$

The symmetry group of the sphere K or SO(3)
(special orthogonal 3D group)

Finite rotation around an axis defined by the vector u: $C_u^{\phi} = e^{-i\frac{\phi}{\hbar}\vec{L}\cdot\vec{u}}$

The sphere group K includes all rotations around all sphere symmetry axes.

K is not a commutative group. Rotations of the same angle around different axes belong to the same class.

Since rotations cannot change the length of the angular momentum (since L±=Lx ±i Ly and |LM> is an eigenfunciton of Lz).

Then, the complete set of functions {|LM>, M=-L,...,L} are basis for the irreps of K

K	(també $SO(3)$)	E	∞C_u^{ϕ}
S	D_0	1	1
P	D_1	3	$1+2\cos\phi$
D	D_2	5	$1+2\cos\phi+2\cos 2\phi$
F	D_3	7	$1+2\cos\phi+2\cos 2\phi+2\cos 3\phi$
...	...	...	...

Decomposition of the direct product of representations

The same than that of angular momentum

$$D^{l_1} \otimes D^{l_2} = D^{l_1+l_2} \oplus D^{l_1+l_2-1} \oplus \ldots \oplus D^{|l_1-l_2|}$$

Symmetric and antisymmetric part

$$\begin{cases} D^{[+]}_{l\otimes l} = D^{2l} \oplus D^{2l-2} \oplus D^{2l-4} \oplus \ldots \\ D^{[-]}_{l\otimes l} = D^{2l-1} \oplus D^{2l-3} \oplus D^{2l-5} \oplus \ldots \end{cases}$$

$$D^{l} \otimes D^{l} = D^{2l} \oplus [D^{2l-1}] \oplus D^{2l-2} \oplus [D^{2l-3}] \oplus D^{2l-4} \oplus \ldots$$

Group of the CO molecule: $C_{\infty v}$

In a similar way to:

$$C_{3V} = \sigma_V \otimes C_3$$

C_{3v}	C_3	E	$2C_3$	$3\sigma_v$
A	A_1	1	1	1
	A_2	1	1	-1
E	$E\{^+_-$	2	$2\cos 2\pi/3$	0

We have:

$$\mathcal{C}_{\infty v} = \sigma_v \otimes \mathcal{C}_{\infty}$$

$C_{\infty v}$	E	C_z^{ϕ}	$\infty\sigma_v$	Bases
Σ^+	1	1	1	z
Σ^-	1	1	-1	R_z
Π	2	$2\cos\phi$	0	(x,y)
Δ	2	$2\cos 2\phi$	0	
$\ldots$	$\ldots$	$\ldots$	$\ldots$	$\ldots$

Decomposition of the direct product of representations

$\mathcal{C}_{\infty v}$	E	C_z^{ϕ}	$\infty\sigma_v$
$\Pi \otimes \Pi$	4	$4\cos^2\phi$	0

$$1+\cos 2\phi = 2\cos^2\phi \longrightarrow 4\cos^2\phi = 2+2\cos 2\phi$$

$$\longrightarrow \Pi\otimes\Pi = \Sigma^+ \oplus \Sigma^- \oplus \Delta$$

Alternatively:

	1	-1
1	2	0
-1	0	-2

Symmetry and Structure in Chemistry

POINT SYMMETRY

Unit 7b: The translation group

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Grup de translacions

Translation operator: $\hat{T}_n f(x) = f(x + na)$

Linear momentum as generator of translations $\hat{T}_n = e^{ian\hat{p}}$

Proof:

$$e^{i\,a\,n\,\hat{p}} f(x) = \sum_j^{\infty} \frac{(a\,n)^j}{j!} \frac{d^j f(x)}{dx^j} = f(x + a\,n)$$

Since $n \in Z$ the translation group has infinite number of elements.

It is an abelian group $\hat{T}_n \hat{T}_m = \hat{T}_m \hat{T}_n = e^{ia(n+m)\hat{p}}$

Then, it has an infinite numbers of one-dimensional irreps

The eigenfunctions of the linear momentum are also eigenfunctions of the translation operator. Then, we may employ the eigenfunctions exp(ikx) of the linear momentum to calculate the character table.

$$\hat{T}_n\, e^{i\,k\,x} = \sum_q^{\infty} \frac{(i\,a\,n)^q}{q!} \hat{p}^q\, e^{i\,k\,x} = \sum_q^{\infty} \frac{(i\,a\,n\,k)^q}{q!} e^{i\,k\,x} = e^{i\,a\,n\,k}\, e^{i\,k\,x}$$

	E	$\hat{T}_n,\ n \in Z$	basis
k	1	$e^{i\,k\,n\,a}$	$e^{i\,k\,x}$

The eigenvalue k is not bounded. However, the eigenfunctions associated with $k' = k + 2\pi m/a$, $m \in Z$ are equivalent (have the same characters).

The fully symmetric A_1 irrep corresponds to k = 0. Therefore, it is convenient to definek $\in (-\pi/a, \pi/a)$ This region is called the ***First Brillouin zone***

The Bloch functions $\Psi_{\mathbf{k}}(\mathbf{r}) = e^{i\,\mathbf{k}\,\mathbf{r}}\, u(\mathbf{r})$, on $u(\mathbf{r} + \mathbf{a}) = u(\mathbf{r})$
are also bases of the irreps of this group.

Symmetry and Structure in Chemistry

POINT SYMMETRY

Unit 8: Spin functions and double groups

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Spin functions and double groups

Let's consider C_2:

C_2	E	C_2	
A	1	1	z
B	1	-1	x,y

Since the eigenfunctions of L_z are bases of the irreps of C_∞ they must also be bases of the irreps of C_2

$$E\ e^{im\theta} = e^{im\theta}$$

$$C_2\ e^{im\theta} = e^{im(\theta-\pi)} = e^{-im\pi}\ e^{im\theta} \qquad m = 0 \pm 1 \pm 2 \dots$$

The eigenfunctions with even "m" are basis for the irrep A, those of odd "m" are basis of the irrep B.

Consider the action of C_2 on the function $f(\theta)$ = Exp(-i θ/2)

$$E\, e^{-i\theta/2} = e^{-i\theta/2}$$

$$C_2\, e^{-i\theta/2} = e^{-i(\theta-\pi)/2} = i\, e^{i\theta/2}$$

C_2	E	C_2	
A	1	1	z
B	1	-1	x,y

C_2	E	C_2	
Γ	1	i	$e^{-i\theta/2}$

The one-dimensional Γ representation is obviously not reducible, but it is neither A nor B!

The paradox comes from the fact that when acting on these functions $C_2^2 \neq E$

We define $Q = C_2^2 \neq E$ *and complete the group by carrying out all the products:*

$$C_2^* = \{E, C_2, Q = C_2^2, Q \otimes C_2 = C_2^3\}$$

The resulting group is abelian and it is isomorphic to C_4

The abelian group obtained, isomorphic to C_4, is referred to as double group of C_2 (C_2)*

C_2^*	E	C_2	Q	$Q \otimes C_2$
Γ_1	1	1	1	1
Γ_2	1	-1	1	-1
Γ_3	1	i	-1	-i
Γ_4	1	-i	-1	i

Consider the action of this group on the functions z, x, $e^{-i\theta/2}$ and $e^{i\theta/2}$.

It is immediate to check that they are basis of the irreps Γ_1, Γ_2, Γ_3 and Γ_4, respectively.

Furthermore, if we remove Q and Q⊗C_2 (and therefore we remove Γ_3 and Γ_4), the functions z and x, basis of Γ_1 and Γ_2, become basis of A and B of the group C_2, as we already knew.

Why are we interested in building up double groups? Because like the functions $e^{\pm i\theta/2}$, the spin functions flip the sign if we rotate them an angle 2π.

$$e^{-i2\pi \hat{S}_z/\hbar}|\alpha\rangle = e^{-i2\pi(\hbar/2)/\hbar}|\alpha\rangle = -|\alpha\rangle$$

Summarizing: $R(\theta+2\pi)=R(\theta)$

If $f(\theta) \neq f(\theta+2\pi)$ but $f(q) \neq f(\theta+2\pi m)$

we say that $f(\theta)$ is *m-evaluated*.

The multi-evaluated functions cannot be used as basis to represent a group because $O_R\, f(\theta) \neq f(R^{-1}\theta)$.

The multi-evaluated representations cannot be ignored because they are important in Physics! (e.g. the spin functions)

The strategy followed to build C_2** shows that we always can construct a group G* with all representations single-evaluated starting from a group G having multi-evaluated representations.*

Every irrep of G (single- or multi-evaluated) is single-evaluated in G.*

*The orthogonality theorems are applicable to double groups G**

Symmetry and Structure in Chemistry

POINT SYMMETRY

Unit 9: Dynamic and degeneration groups

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System

Symmetry Group

Linear transformation of the states which commutes with the Hamiltonian: [H,G]=0

Dynamic Group

Group that contains the whole energy spectrum as a basis of a single irrep:

The ladder operators reach every eigenstate

e.g. The Heisenberg group for the harmonic oscillator and the SO(4,2) for the hydrogen atom

Degeneracy Group

The degenerate states belong to the same irrep.

The ladder operators reach every eigenstate within the degeneration

Dynamic Group ⊃ Degeneracy Group ⊃ Symmetry Group

Dynamic groups: An example

The Heisenberg group and the harmonic oscillator

Heisenberg algebra

Elements: {1, p, q}

Commutations:
$$\begin{cases}[p,1]=0\\ [q,1]=0\\ [p,q]=-i\end{cases}$$

Alternatively:
$$b^+=\frac{1}{\sqrt{2}}\left(q-\frac{d}{dq}\right)=\frac{1}{\sqrt{2}}(q-ip)$$
$$b=\frac{1}{\sqrt{2}}\left(q+\frac{d}{dq}\right)=\frac{1}{\sqrt{2}}(q+ip)$$
$$[b^+,1]=0 \qquad [b,1]=0 \qquad [b,b^+]=1$$

HO Hamiltonian: $\mathcal{H} = \frac{1}{2}\left(p^2 + q^2\right)$

$$\left.\begin{array}{l}[\mathcal{H}, b] = -b \\ [\mathcal{H}, b^+] = b^+\end{array}\right\} \quad \begin{array}{l}[\mathcal{H}, \frac{b+b^+}{\sqrt{2}}] = [\mathcal{H}, q] = \frac{1}{\sqrt{2}}\left(-b+b^+\right) = -i\,p \\ [\mathcal{H}, \frac{b-b^+}{i\,\sqrt{2}}] = [\mathcal{H}, p] = \frac{1}{i\,\sqrt{2}}\left(-b-b^+\right) = i\,q\end{array}$$

Group element:

$$G(\alpha, \beta, \gamma) = \exp[i\ \left(\alpha, \beta b^+ + \gamma b\right) \longrightarrow \boxed{[\mathcal{H}, G] \neq 0}$$

The Heisenberg group as a dynamic group:

$$\begin{cases} |v\rangle = \frac{1}{\sqrt{v!}}(b^+)^v|0\rangle \\ |0\rangle = \frac{1}{\sqrt{v!}}b^v|v\rangle \end{cases}$$

The SO(4,2) as dynamic group for the Hydrogen atom
B.G. Wybourne, Classical groups for physicists, cap 21.

Degeneracy groups: An example

The SO(4) or R(4) group and the Hydrogen atom

The SO(4) Group

3D rotation (x,y,z) $A_1 = z\partial_y - y\partial_z$ $\quad A_2 = x\partial_z - z\partial_x$ $\quad A_3 = y\partial_x - x\partial_y$

4D rotation (x,y,z,t) $B_1 = x\partial_t - t\partial_x$ $\quad B_2 = y\partial_t - t\partial_y$ $\quad B_3 = z\partial_t - t\partial_z$

Commutations

$$[A_i, B_i] = 0 \qquad [A_1, B_2] = B_3 \qquad [A_1, B_3] = -B_2$$

$$[A_i, A_{i+1}] = A_{i+2} \qquad [A_2, B_1] = -B_3 \qquad [A_2, B_3] = B_1$$

$$[B_i, B_{i+1}] = A_{i+2} \qquad [A_3, B_1] = B_2 \qquad [A_3, B_2] = -B_1$$

Define: $J_i = \frac{1}{2}(A_i + B_i) \qquad K_i = \frac{1}{2}(A_i - B_i)$

$[J_i, J_{i+1}] = J_{i+2} \longrightarrow$ ***Angular momentum algebra*** $\mathcal{B}_1$

$[K_i, K_{i+1}] = K_{i+2} \longrightarrow$ ***Angular momentum algebra*** $\mathcal{B}'_1$

$[J_i, K_j] = 0$

$\mathcal{D}_2 = \mathcal{B}_1 \oplus \mathcal{B}'_1$

{J_i} and {K_j} span two disjoint subalgebras ($[J_i, K_j]=0$)

We define ***(analogy with angular momentum algebra)***

$$H_1 = \frac{i}{\sqrt{2}} J_3 \qquad H_2 = \frac{i}{\sqrt{2}} K_3$$

$$E_{\pm\alpha} = \frac{i}{2}(J_1 \pm i\, J_2) \qquad E_{\pm\beta} = \frac{i}{2}(K_1 \pm i\, K_2)$$

The associated Casimir operators (L^2 analog.)

$$F_1 = H_1^2 + E_\alpha E_{-\alpha} + E_{-\alpha} E_\alpha$$

$$F_2 = H_2^2 + E_\beta E_{-\beta} + E_{-\beta} E_\beta$$

Casimir operators acting upon functions:

$$F_1 |j_1 m_1\rangle = \frac{1}{2} j_1 (j_1 + 1) |j_1 m_1\rangle$$

$$F_2 |j_2 m_2\rangle = \frac{1}{2} j_2 (j_2 + 1) |j_2 m_2\rangle$$

Define symmetric anti-symmetric part: $\begin{cases} C = F_1 + F_2 \\ F_1 - F_2 = 0 \longrightarrow j_1 = j_2 \end{cases}$

$$C |j_1 m_1\rangle |j_2 m_2\rangle = \frac{1}{2}[j_1(j_1+1) + j_2(j_2+1)] |j_1 m_1\rangle |j_2 m_2\rangle$$

$$j(j+1) = j^2 + j = \frac{1}{4}[(2j+1)^2 - 1] = \frac{1}{4}[n^2 - 1]$$

$n = 1, 2, 3, \ldots$ ***Degeneracy:*** n^2

Lowering symmetry: SO(4) $\Longrightarrow$ SO(3)

$$j_1 \otimes j_2 = (j_1 + j_2) \oplus (j_1 + j_2 - 1) \oplus \cdots \oplus |j_1 + j_2|$$

$$n = 1 \qquad j_1 = j_2 = 0 \qquad D_{00} \to D_0 \qquad (1s)$$

$$n = 2 \qquad j_1 = j_2 = \frac{1}{2} \qquad D_{\frac{1}{2}\frac{1}{2}} \to D_1 \oplus D_0 \qquad (2s\,+\,2p)$$

$$n = 3 \qquad j_1 = j_2 = 1 \qquad D_{11} \to D_2 \oplus D_1 \oplus D_0 \qquad (3s\,+\,3p\,+\,3d)$$

Is SO(4) the degeneration group of the Hydrogen atom?

Hydrogen Hamiltonian: $\mathcal{H} = \dfrac{p^2}{2m} - \dfrac{Z}{r}$

Invariants: $L = r \times p \qquad [\mathcal{H}, L] = 0$

$$R = \frac{1}{2}(L \times p - p \times L) + Z\frac{\mathbf{r}}{r} \qquad [\mathcal{H}, R] = 0$$

We define:

$$A_1 = -iL_x \qquad A_2 = -iL_y \qquad A_3 = -iL_z$$

$$B_1 = \frac{i}{\sqrt{-2E}}R_x \qquad B_2 = \frac{i}{\sqrt{-2E}}R_y \qquad B_3 = \frac{i}{\sqrt{-2E}}R_z$$

In front of the subspace $\{|n, \ell, m\rangle, \ell = 0, 1, \ldots (n-1), m = -\ell, \ldots 0, \ldots \ell\}$
A_i, B_i behaves like in SO(4) (same commutation rules)

Casimir operators :

$$C = F_1 + F_2 = \ldots = -\frac{1}{4}(A_1^2 + A_2^2 + A_3^2 + B_1^2 + B_2^2 + B_3^2) = \ldots = \frac{1}{4}(L^2 - \frac{R^2}{2E})$$

We have: $R^2 = 2\mathcal{H}\, L^2 + 2\mathcal{H} + Z^2$

$$\longrightarrow \quad C = -\frac{Z^2}{8\mathcal{H}} - \frac{1}{4}$$

Eigenvalues de C :

$$\frac{1}{4}(n^2 - 1) = -\frac{Z^2}{8E} - \frac{1}{4} \to \frac{1}{4}n^2 = -\frac{Z^2}{8E} \to E = -\frac{Z^2}{2n^2}$$

degeneration: n^2

Coordinate representation

Spherical coordinates are naturally adapted to SO(3)
SO(4) is more easily exhibited in parabolic coordinates:

$$x = \sqrt{\xi\eta}\cos\varphi, \quad y = \sqrt{\xi\eta}\sin\varphi, \quad z = \frac{1}{2}(\xi - \eta)$$

Schrodinger equation in parabolic coordinates:

$$-\frac{\hbar^2}{2M}\left\{\frac{4}{\xi+\eta}\left[\frac{\partial}{\partial\xi}\left(\xi\frac{\partial}{\partial\xi}\right) + \frac{\partial}{\partial\eta}\left(\eta\frac{\partial}{\partial\eta}\right)\right] + \frac{1}{\xi\eta}\frac{\partial^2}{\partial\varphi^2}\right\}\psi - \frac{2e^2}{\xi+\eta}\psi = E\psi$$

From above, the basic algebra operators: $A_j = -iL_j \quad B_j = \frac{i}{\sqrt{-2E}}R_j$

From them we defined: $J_i = \frac{1}{2}(A_i + B_i) \quad K_i = \frac{1}{2}(A_i - B_i)$

And the creators and annihilators:

$$J_\pm = \frac{i}{2}(J_1 \pm i\, J_2) \qquad K_\pm = \frac{i}{2}(K_1 \pm i\, K_2)$$

L and R can be expressed s a function of x, y, z coordinates.
So, can be expressed as a function of parabolic coordinates

$$J_+ = \hbar e^{i\phi}\left(\sqrt{u}\frac{\partial}{\partial u} + \frac{i}{2\sqrt{u}}\frac{\partial}{\partial\phi} + \frac{\sqrt{u}}{2}\right) \times \left(\sqrt{v}\frac{\partial}{\partial v} + \frac{i}{2\sqrt{v}}\frac{\partial}{\partial\phi} - \frac{\sqrt{v}}{2}\right),$$

$$J_- = \hbar e^{-i\phi}\left(\sqrt{u}\frac{\partial}{\partial u} - \frac{i}{2\sqrt{u}}\frac{\partial}{\partial\phi} - \frac{\sqrt{u}}{2}\right) \times \left(\sqrt{v}\frac{\partial}{\partial v} - \frac{i}{2\sqrt{v}}\frac{\partial}{\partial\phi} + \frac{\sqrt{v}}{2}\right),$$

$$K_+ = -\hbar e^{i\phi}\left(\sqrt{u}\frac{\partial}{\partial u} + \frac{i}{2\sqrt{u}}\frac{\partial}{\partial\phi} - \frac{\sqrt{u}}{2}\right) \times \left(\sqrt{v}\frac{\partial}{\partial v} + \frac{i}{2\sqrt{v}}\frac{\partial}{\partial\phi} + \frac{\sqrt{v}}{2}\right),$$

$$K_- = -\hbar e^{-i\phi}\left(\sqrt{u}\frac{\partial}{\partial u} - \frac{i}{2\sqrt{u}}\frac{\partial}{\partial\phi} + \frac{\sqrt{u}}{2}\right) \times \left(\sqrt{v}\frac{\partial}{\partial v} - \frac{i}{2\sqrt{v}}\frac{\partial}{\partial\phi} - \frac{\sqrt{v}}{2}\right),$$

Torres et al, Rev. Mex. Fis. 54 (2008) 454

They act upon the states: $|j\ m_1\ m_2\rangle$

In particular: $J_+|j,j,j\rangle = 0, \qquad K_+|j,j,j\rangle = 0$

$$\longrightarrow \quad \psi_{j,j,j} = N e^{-(u+v)/2}(uv)^j e^{i2j\phi}$$

etc.

Symmetry and Structure in Chemistry

POINT SYMMETRY

Unit 10: Tensors as basis set of group representations

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Irreducible tensor operators

The character of a physical magnitude and its associated quantum mechanical operator is defined by its rotational properties

Generators of the rotational group: {J_z, $J_\pm$}

Every rotation $R_{\mathbf{u}}(\phi) = \exp[-i\phi(\mathbf{J}\cdot\mathbf{u})/\hbar]$

If an operator commutes with {J_z, $J_\pm$} is an invariant under rotations

Scalar and scalar operator:

A quantity is called scalar if it is invariant under all rotations.

It is basis of the irreducible D_0 representation of the rotation group.

Examples: mass, length, energy … and every scalar product of two polar vectors

Vector (polar vector) and vector operator

A vector V and a vector operator V have magnitude and direction.

They have components and behave as the vector position r and like r form a basis of the irrep. D_1.

We may use Cartesian (V_x,V_y,V_z) or spherical (V_1,V_0,V_{-1}) coordinates.

Spherical coordinates are invariants under rotations generated by the associated generator: $[J_z,V_0]=[J_+,V_{+1}]=[J_-,V_{-1}]=0$

$$V_1 = -\frac{V_x + i\,V_y}{\sqrt{2}}, \quad V_0 = V_z, \quad V_{-1} = \frac{V_x - i\,V_y}{\sqrt{2}}$$

We may consider the full sphere group. Then, we have two possible representations: $D_J \rightarrow D_{Jg}$ and D_{Ju}

Scalars are invariants, then they are basis of D_{0g}

Polar vector change its sign with inversion, , then they are basis of D_{1u}

Axial vector and Axial vector operator:

An axial vector is invariant under inversion.

Examples: Magnetic field, angular momentum, etc.

We may see them as a cross product of two polar vectors: L = r x p

They for basis for the irrep. D_{1g}.

Actually, they are second order zero trace anti-symmetric tensors

Peudoscalar and pseudoscalar operator:

A pseudoscalar change its sign under inversion and it is invariant under rotations.

It is then basis of the irreducible D_{0u}.

We may see them as a scalar product of a polar times an axial vector.

Example: magnetic flux : Φ = B · S

Spherical tensor with 2ω+1 components operator

It forms a base for the irrep. D_ω

Then, its component transforms into a linear combination of themselves:

$$\mathcal{R} T_\mu^{(\omega)} \mathcal{R}^{-1} = \sum_\nu T_\nu^{(\omega)} D(R)_{\nu\mu}^{[\omega]}$$

As with vectors, we may use Cartesian, T_{xy}, or spherical, T_m, coordinates.

Rotations transforms T_{xy} as they transforms the polynomial xy:

$$\mathcal{R} T_{xy} \mathcal{R}^{-1} = \sum_{i,j} T_{ij}\, D(R)_{x,i}\, D(R)_{y,j} \equiv \sum_\alpha T_\alpha\, D(R)_{\beta,\alpha}$$

Second order Cartesian tensors can be built as direct product of two polar vectors, then they form a basis for the reducible representation:

$$D_{1u} \otimes D_{1u} = D_{0g} \oplus D_{1g} \oplus D_{2g}$$

Then, we may consider the Cartesian tensor as a sum of three spherical tensors

Decomposition of a cartesian tensor into sum of spherical tensors

$$D_{1u} \otimes D_{1u} = D_{0g} \oplus D_{1g} \oplus D_{2g}$$

D_{0g}→The trace $Tr(T) = T_{xx} + T_{yy} + T_{zz}$ ***is this invariant.***

D_{1g}→ We should extract a traceless anti-symmetric tensor

$$A_x = \frac{1}{2}(T_{yz} - T_{zy}) \;\; A_y = \frac{1}{2}(T_{zx} - T_{xz}) \;\; A_z = \frac{1}{2}(T_{xy} - T_{yx})$$

D_{2g}→ We form a traceless symmetric second order tensor

$$S_{ij} = \frac{1}{2}(T_{ij} + T_{ji}) - \frac{1}{3}Tr(T)$$

Alternatively we may choose the most common basis for D_{2g}

$$\{S_{xy}, S_{yz}, S_{zx}, S_{xx} - S_{yy}, 2S_{zz} - S_{xx} - S_{yy}\}$$

Example

$$\mathbb{T} = \begin{pmatrix} x_1x_2 & x_1y_2 & x_1z_2 \\ y_1x_2 & y_1y_2 & y_1z_2 \\ z_1x_2 & z_1y_2 & z_1z_2 \end{pmatrix}$$

$$= \frac{1}{3}Tr(\mathbb{T})\mathbb{I} + \frac{1}{2}\begin{pmatrix} 0 & x_1y_2 - y_1x_2 & x_1z_2 - z_1x_2 \\ y_1x_2 - x_1y_2 & 0 & y_1z_2 - z_1y_2 \\ z_1x_2 - x_1z_2 & z_1y_2 - y_1z_2 & 0 \end{pmatrix}$$

$$+\frac{1}{2}\begin{pmatrix} x_1x_2 + x_2x_1 - \frac{2}{3}Tr(\mathbb{T}) & x_1y_2 + y_1x_2 & x_1z_2 + z_1x_2 \\ y_1x_2 + x_1y_2 & y_1y_2 + y_2y_1 - \frac{2}{3}Tr(\mathbb{T}) & y_1z_2 + z_1y_2 \\ z_1x_2 + x_1z_2 & z_1y_2 + y_1z_2 & z_1z_2 + z_2z_1 - \frac{2}{3}Tr(\mathbb{T}) \end{pmatrix}$$

$$= \frac{1}{3}Tr(\mathbb{T})\mathbb{I} + \begin{pmatrix} 0 & a & b \\ -a & 0 & c \\ -b & -c & 0 \end{pmatrix} + \begin{pmatrix} D_1 & A & B \\ A & D_2 & C \\ B & C & D_3 \end{pmatrix}$$

$$\mathbb{T}^{(0)} = Tr(\mathbb{T}) \quad \mathbb{T}^{(1)} = \{a,\ b,\ c\}$$

$$\mathbb{T}^{(2)} = \{A,\ B,\ C,\ D_1,\ D_2\}$$

$$D_1 + D_2 + D_3 = 0$$

Building a secon order tensor as a product of polar vectors in spherical coordinates

$$T_0 = \sum_\mu (-1)^\mu V_\mu U_\mu^* = \sum_\mu (-1)^\mu V_\mu U_{-\mu}$$

$$T^{[1]}_{\pm 1} = V_{\pm 1}U_0 - V_0 U_{\pm 1}$$
$$T^{[1]}_{0} = V_1 U_{-1} - V_{-1} U_1$$

$$T^{[2]}_{\pm 2} = V_{\pm 1}U_{\pm 1}$$
$$T^{[2]}_{\pm 1} = V_{\pm 1}U_0 + V_0 U_{\pm 1}$$
$$T^{[2]}_{0} = 2V_0 U_0 + V_1 U_{-1} + V_{-1} U_1$$

Example 1

$Y_{00} = \frac{1}{\sqrt{4\pi}}$	$Y_{20} = \frac{1}{\sqrt{4\pi}}\left[\frac{3}{2}\cos^2\theta - \frac{1}{2}\right]$
$Y_{10} = (\frac{3}{4\pi})^{1/2}\cos\theta$	$Y_{2\pm1} = \mp(\frac{15}{8\pi})^{1/2}\sin\theta\,\cos\theta\, e^{\pm i\phi}$
$Y_{1\pm1} = \mp(\frac{3}{8\pi})^{1/2}\sin\theta\, e^{\pm i\phi}$	$Y_{2\pm2} = (\frac{15}{32\pi})^{1/2}\sin^2\theta\, e^{\pm 2i\phi}$

$$D_{1u} \otimes D_{1u} = D_{0g} \oplus D_{1g} \oplus D_{2g}$$

$$T_0 = \sum_\mu (-1)^\mu V_\mu U_\mu^*$$

$$T_0 = (-1)^0 Y_{10}Y_{10}^* + (-1)^{\pm 1}(Y_{11}Y_{1-1}^* + Y_{1-1}Y_{11}^*)$$
$$= \frac{3}{4\pi}\cos^2\theta + 2\frac{3}{8\pi}\sin^2\theta = \frac{3}{4\pi} \qquad \boxed{D_{0g}}$$

$$\{Y_{10}\ Y_{1\pm1}\}\ D_{1u}$$

$$T^{[1]}_{\pm 1} = V_{\pm 1}U_0 - V_0 U_{\pm 1}$$
$$T^{[1]}_{0} = V_1 U_{-1} - V_{-1} U_1$$

$$\mathbf{U}\wedge\mathbf{V} = \begin{bmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ U_0 & U_+ & U_- \\ V_0 & V_+ & V_- \end{bmatrix} = \qquad \boxed{D_{1g}}$$
$$= \mathbf{i}(U_+V_- - U_-V_+) + \mathbf{j}(U_0V_- - U_-V_0) + \mathbf{k}(U_0V_+ - U_+V_0)$$

$$Y_{00} = \frac{1}{\sqrt{4\pi}} \qquad Y_{20} = \frac{1}{\sqrt{4\pi}}\left[\frac{3}{2}\cos^2\theta - \frac{1}{2}\right]$$

$$Y_{10} = (\frac{3}{4\pi})^{1/2}\cos\theta \qquad Y_{2\pm1} = \mp(\frac{15}{8\pi})^{1/2}\sin\theta\,\cos\theta\,e^{\pm i\phi}$$

$$Y_{1\pm1} = \mp(\frac{3}{8\pi})^{1/2}\sin\theta\,e^{\pm i\phi} \qquad Y_{2\pm2} = (\frac{15}{32\pi})^{1/2}\sin^2\theta\,e^{\pm 2i\phi}$$

$$Y_{1\pm1}^2 = \frac{3}{8\pi}\sin^2\theta e^{\pm 2i\phi}$$

$$T_{\pm2}^{[2]} = V_{\pm1}U_{\pm1} \qquad Y_{1\pm1}Y_{10} = \mp\frac{3}{4\pi\sqrt{2}}\sin\theta\cos\theta e^{\pm i\phi}$$

$$T_{\pm1}^{[2]} = V_{\pm1}U_0 + V_0U_{\pm1}$$

$$T_0^{[2]} = 2V_0U_0 + V_1U_{-1} + V_{-1}U_1 \qquad 2Y_{10}^2 + 2Y_{11}Y_{1-1} = 2\frac{3}{4\pi}\cos^2\theta - 2\frac{3}{8\pi}\sin^2\theta$$

$$= \frac{6}{4\pi}(\frac{3}{2}\cos^2\theta - \frac{1}{2})$$

D_{2g}

Example 2 $D_{1u}\otimes D_{1u} = D_{0g}\oplus D_{1g}\oplus D_{2g}$

Cartesian $\{x, y, z\}$ ***Spherical*** $\{-\frac{x+iy}{\sqrt{2}}, \frac{x-iy}{\sqrt{2}}, z\}$

$$\hat{L}_x = -i(y\partial_z - z\partial_y) \qquad \hat{L}_x x = 0 \qquad \hat{L}_x y = (-i)(-z) = i\,z$$

$$\hat{L}_y = -i(z\partial_x - x\partial_z) \qquad \hat{L}_y y = 0 \qquad \hat{L}_y x = -i\,z$$

$$\hat{L}_z = -i(x\partial_y - y\partial_x) \qquad \hat{L}_\pm|\ell\,m\rangle = \sqrt{(\ell+1)+m(m\pm1)}|\ell\,m\pm1\rangle$$

$$\hat{L}_+(-\frac{x+iy}{\sqrt{2}}) = 0$$

$$\hat{L}_+x = (\hat{L}_x + i\hat{L}_y)x = i(-i)z = z$$

$$\hat{L}_-x = (\hat{L}_x - i\hat{L}_y)x = -z$$

$$\hat{L}_-(-\frac{x+iy}{\sqrt{2}}) = \sqrt{2}\,z$$

$$\hat{L}_+y = (\hat{L}_x + i\hat{L}_y)y = i\,z$$

$$\hat{L}_+(\frac{x-iy}{\sqrt{2}}) = \sqrt{2}\,z$$

$$\hat{L}_-y = (\hat{L}_x - i\hat{L}_y)y = i\,z$$

$$\hat{L}_-(\frac{x-iy}{\sqrt{2}}) = 0$$

$$T_0 = \sum_\mu (-1)^\mu V_\mu U_\mu^*$$

$$\{-\frac{x+iy}{\sqrt{2}}, \frac{x-iy}{\sqrt{2}}, z\}$$

$$T_0^{(0)} = z^2 + (-1)(-\frac{1}{2})[(x+i\,y)^2 + (x+i\,y)^2]$$
$$= z^2 + x^2 + y^2 = r^2$$

$$T_{\pm 2}^{[2]} = V_{\pm 1} U_{\pm 1}$$
$$T_{\pm 1}^{[2]} = V_{\pm 1} U_0 + V_0 U_{\pm 1}$$
$$T_0^{[2]} = 2 V_0 U_0 + V_1 U_{-1} + V_{-1} U_1$$

$$T_{\pm 2}^{(2)} = \frac{(x \pm i\,y)^2}{2} = \frac{1}{2} r^2 e^{\pm 2 i \phi}$$
$$T_{\pm 1}^{(2)} = 2 \frac{(x \pm i\,y)^2}{\sqrt{2}} z = \sqrt{2}\, r\, z\, e^{\pm i \phi}$$
$$T_0^{(2)} = z^2 + \frac{1}{2}(x+i\,y)(x-i\,y) \cdot 2 = r^2$$

$$T_{\pm 1}^{[1]} = V_{\pm 1} U_0 - V_0 U_{\pm 1}$$
$$T_0^{[1]} = V_1 U_{-1} - V_{-1} U_1$$

$$\mathbf{r}(1) \times \mathbf{r}(2) = \begin{bmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \\ r_0(1) & r_+(1) & r_-(1) \\ r_0(2) & r_+(2) & r_-(2) \end{bmatrix}$$
$$= \mathbf{i}[r_+(1) r_-(2) - r_-(1) r_+(2)]$$
$$+ \mathbf{j}[r_0(1) r_-(2) - r_-(1) r_0(2)]$$
$$+ \mathbf{k}[r_0(1) r_+(2) - r_+(1) r_0(2)]$$

Addendum

The transformation property $\mathcal{R} T_\mu^{(\omega)} \mathcal{R}^{-1} = \sum_\nu T_\nu^{(\omega)} D(R)_{\nu\mu}^{[\omega]}$

is equivalent to the fulfillment of the commutations:

$$[\hat{J}_z, T_\mu^{(\omega)}] = \mu\, T_\mu^{(\omega)}$$

$$[\hat{J}_\pm, T_\mu^{(\omega)}] = \sqrt{\omega(\omega+1) - \mu(\mu \pm 1)}\; T_{\mu \pm 1}^{(\omega)}$$

Immediate to be checked if the tensor is the set of the 2j+1 spherical harmonics associated to J

General proof related to the fact that : {J_z, $J_\pm$} are the generators of any possible rotation. (details e.g. Joshi chapter 6)

***Addendum 2* Wigner-Eckart Theorem**

$$\langle \alpha\, j\, m | T_q^{(k)} | \alpha'\, j'\, m' \rangle = (-1)^{j-m} \begin{pmatrix} j & k & j' \\ -m & q & m' \end{pmatrix} \langle \alpha\, j || \mathbf{T}^{(k)} || \alpha'\, j' \rangle$$

where $$\begin{pmatrix} j & k & j' \\ -m & q & m' \end{pmatrix} = \frac{(-1)^{j-k-m'}}{\sqrt{2j+1}} \langle j, -m | \langle k, q | \cdot | j'(j,k), -m \rangle$$

Corollary $$\frac{\langle \alpha\, j\, m | T_q^{(k)} | \alpha'\, j'\, m' \rangle}{\langle \alpha\, j\, m | U_q^{(k)} | \alpha'\, j'\, m' \rangle} = \frac{\langle \alpha\, j || \mathbf{T}^{(k)} || \alpha'\, j' \rangle}{\langle \alpha\, j || \mathbf{U}^{(k)} || \alpha'\, j' \rangle} = C$$

$$\longrightarrow \quad \langle \alpha\, j\, m | T_q^{(k)} | \alpha'\, j'\, m' \rangle = C \, \langle \alpha\, j\, m | U_q^{(k)} | \alpha'\, j'\, m' \rangle$$

(details e.g. Joshi chapter 6)

Quadrupole effect

Classically, the *interaction energy* is given by the tensor scalar product

$$E_Q = \frac{1}{6} \sum_{i,j=x,y,z} V_{ij} Q_{ij} \,, \qquad (2.7)$$

where the two tensors must be expressed in the same coordinate system.

$$Q_{\alpha\beta} = \int (3x_\alpha x_\beta - \delta_{\alpha\beta} r^2) \rho dr$$

$$V_{\alpha\beta} = \frac{\partial^2 V}{\partial x_\alpha \partial x_\beta}$$

When written using quantum mechanical operators, the Hamiltonian $\mathcal{H}_Q$ for a nucleus of spin I expressed in the principal axis coordinate system is

$$\mathcal{H}_Q = \frac{e^2 qQ}{4I(2I-1)} \left[3I_z^2 - I^2 + \eta \left(I_x^2 - I_y^2 \right) \right] \quad ?$$

Quadrupole effect

$$E_Q = \frac{1}{6}\sum V_{\alpha\beta} Q_{\alpha\beta} \quad \left\{ \begin{array}{l} Q_{\alpha\beta} = \int (3x_\alpha x_\beta - \delta_{\alpha\beta} r^2)\rho dr \\ V_{\alpha\beta} = \frac{\partial^2 V}{\partial x_\alpha \partial x_\beta} \end{array} \right\} \quad \boxed{H_Q = \frac{1}{6}\sum V_{\alpha\beta} \hat{Q}_{\alpha\beta}}$$

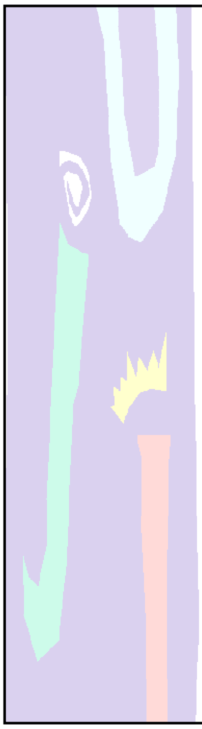
With the help of *Wigner-Eckart theorem*

$$\langle I, m | Q_{\alpha\beta} | I, m' \rangle = C \left\langle I, m \left| \frac{3}{2}\left(I_\alpha I_\beta + I_\beta I_\alpha\right) - \delta_{\alpha\beta} I^2 \right| I, m' \right\rangle$$

We will express constant, C, with matrix element for $m = m' = I$ and $\alpha = \beta = z$.

$$eQ \equiv \langle I, I | Q_{zz} | I, I \rangle = C\langle I, I | 3I_z{}^2 - \boldsymbol{I}^2 | I, I \rangle = C\langle I, I | I(2I-1) | I, I \rangle \longrightarrow C = \frac{eQ}{I(2I-1)}$$

$$\boxed{H_Q = \frac{eQ}{6I(2I-1)} \sum V_{\alpha\beta} \left[\frac{3}{2}\left(I_\alpha I_\beta + I_\beta I_\alpha\right) - \delta_{\alpha\beta} I^2\right]}$$



Symmetry and Structure in Chemistry

POINT SYMMETRY

Unit 11: Electrical Multipoles and Polarizability as basis set of group representations

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Multipole expansion of the electric potential

Multipole expansion for the potential of a finite static charge distribution

Energy associated to a static charge distribution and a potential acting on it:

$$E = \sum_j q_j \phi_j$$

Assume r_0 as coordinate origin and consider a Taylor expansion of the potential:

$$\phi_j = \phi_0 + \sum_{\alpha=x,y,z} \left(\frac{\partial \phi}{\partial \alpha}\right)_0 (\alpha_j - \alpha_0) + \frac{1}{2!} \sum_{\alpha,\beta=x,y,z} \left(\frac{\partial^2 \phi}{\partial \alpha \partial \beta}\right)_0 (\alpha_j - \alpha_0)(\beta_j - \beta_0) + \dots$$

The interaction energy:

$$E = \phi_0 \sum_j q_j + \sum_{\alpha=x,y,z} \left(\frac{\partial \phi}{\partial \alpha}\right)_0 \sum_j q_j (\alpha_j - \alpha_0) + \frac{1}{2!} \sum_{\alpha,\beta=x,y,z} \left(\frac{\partial^2 \phi}{\partial \alpha \partial \beta}\right)_0 \sum_j q_j (\alpha_j - \alpha_0)(\beta_j - \beta_0) + \dots$$

The moments of a statistical distribution f(x) are defined as:

$$\mu_k = \int (x-a)^k f(x) dx$$

μ_0 = 1, μ_1 is the average, μ_2 the variance, etc.

By analogy we define the moments of a static charge distribution:

monopole	$q = \sum_j q_j$
dipole	$\mu_\alpha = \sum_j q_j (\alpha_j - \alpha_0)$
quadrupole	$Q_{\alpha,\beta} = \sum_j q_j (\alpha_j - \alpha_0)(\beta_j - \beta_0)$
octupole	$R_{\alpha,\beta,\gamma} = \sum_j q_j (\alpha_j - \alpha_0)(\beta_j - \beta_0)(\gamma - \gamma_0)$
n − pole	...

By definition all these moments are symmetric, e.g. $Q_{xy}=Q_{yx}$, $R_{xyy}=R_{yxy}$

Laplace equation $\nabla^2\phi = 0$

Rewriting Laplace equation

$$\begin{cases} \sum_\alpha \delta_{\alpha,\beta}\frac{\partial^2\phi}{\partial\alpha\partial\beta} = 0 \\ \to \frac{1}{6}r'^2\sum_\alpha \delta_{\alpha,\beta}\frac{\partial^2\phi}{\partial\alpha\partial\beta} = 0 \\ \to \frac{1}{6}r'^2\sum_{\alpha,\beta} \delta_{\alpha,\beta}\frac{\partial^2\phi}{\partial\alpha\partial\beta} = 0 \end{cases}$$

Third term in the above equation

$$\frac{1}{2}\sum_{\alpha,\beta=x,y,z}\left(\frac{\partial^2\phi}{\partial\alpha\partial\beta}\right)_0\sum_j q_j\alpha'_j\beta'_j = \frac{1}{2}\sum_{\alpha,\beta=x,y,z}\left(\frac{\partial^2\phi}{\partial\alpha\partial\beta}\right)_0\sum_j q_j\alpha'_j\beta'_j - \frac{1}{6}\sum_{\alpha,\beta=x,y,z}\sum_j q_j r'^2_j\delta_{\alpha,\beta}\frac{\partial^2\phi}{\partial\alpha\partial\beta}$$

$$= \frac{1}{3}\sum_{\alpha,\beta=x,y,z}\left(\frac{\partial^2\phi}{\partial\alpha\partial\beta}\right)_0\sum_j \frac{1}{2}q_j\left[3\alpha'_j\beta'_j - r'^2_j\delta_{\alpha,\beta}\right]$$

$$= \frac{1}{3}\sum_{\alpha,\beta=x,y,z}\left(\frac{\partial^2\phi}{\partial\alpha\partial\beta}\right)_0\Theta_{\alpha\beta}$$

Laplace equation allows a convenient redefinition of these moments.

Monopole and dipole remain as they are.

Laplace equation though allows the following rewriting of the higher moments:

$$\text{quadrupole} \quad \Theta_{\alpha\beta} = \sum_j \frac{1}{2}q_j\left[3\alpha'_j\beta'_j - r'^2_j\delta_{\alpha,\beta}\right]$$

$$\text{octupole} \quad \Omega_{\alpha\beta\gamma} = \sum_j q_j\tfrac{1}{2}[5\alpha'_j\beta'_j\gamma'_j - \alpha'_j r'^2_j\delta_{\beta,\gamma} - \beta'_j r'^2_j\delta_{\alpha,\gamma} - \gamma'_j r'^2_j\delta_{\alpha,\beta}]$$

etc.

They are traceless tensors:

$$\sum_\alpha \Theta_{\alpha\alpha} = \Theta_{xx} + \Theta_{yy} + \Theta_{zz} = \sum_j \frac{q_j}{2}[3r'^2_j - 3r'^2_j] = 0$$

$$\sum_\beta \Omega_{x\beta\beta} = [\Omega_{xxx} + \Omega_{xyy} + \Omega_{xzz}] = 0$$

The interaction energy:

$$E = q\phi_0 - \sum_\alpha \mu_\alpha \nabla_\alpha \phi - \frac{1}{3}\sum_{\alpha,\beta} \Theta_{\alpha\beta}\nabla_\alpha\nabla_\beta\phi - \frac{1}{3\cdot 5}\sum_{\alpha,\beta,\gamma}\Omega_{\alpha\beta\gamma}\nabla_\alpha\nabla_\beta\nabla_\gamma\phi + \dots$$

$$\rightarrow \; E \; = \; q\phi_0 - \sum_{n=1}^{\infty}\frac{1}{1\cdot 3\cdot 5\cdot(2n-1)}\,\xi^{(n)}_{\alpha\beta\dots\nu}\,\nabla_\alpha\nabla_\beta\dots\nabla_\nu\phi$$

Dependence of electric multipole moments on origin

In general, electric multipole moments beyond the monopole depend on the choice of origin.

The dipole moment is independent of an arbitrary shift of origin if the monopole $\sum_j q_j$ is zero:

$$\mu = \sum_j q_j(\alpha_j - \alpha_0) = \sum_j q_j\alpha_j - \alpha_0\sum_j q_j$$
$$= \sum_j q_j\alpha_j$$

The quadrupole moment is independent of an arbitrary shift of origin if the dipole is zero.

$$Q_{\alpha\beta} = \sum_j q_j(\alpha_j - \alpha_0)\beta_j - \beta_0\sum_j q_j(\alpha_j - \alpha_0) = \sum_j q_j(\alpha_j - \alpha_0)\beta_j = \sum_j q_j\alpha_j\beta_j$$

The leading non-vanishing electric multipole moment is independent of the choice of origin of coordinates.

Multipole symmetry

Multipole moments are symmetric traceless tensors. Concerning inversion , like polynomials, odd multipoles are ungerade (e.g. dipole) while even multipoles are gerade (e.g. quadrupole).

Monopole moment (total charge) is an scalar, invariant under every symmetry transformation. Then it forms a basis for the irrep. D_{0g}.

Dipole moment transforms as the position vector r, then its component form a basis for the D_{1u} irrep.

*Quadrupole moment may be viewed as a r*r direct product. In particular the symmetric part of the direct product $D_{1u} \otimes D_{1u}$ (since it is symmetric with respect to the indexes exchange):*

$$\{D_{1u}^2|[2]\} = D_{0g} \oplus D_{2g}$$

Since quadrupole is traceless, it does not contains nonzero D_{0g} invariant component. Quadrupole has then D_{2g} symmetry

*Octupole moment may be viewed as the symmetric part of the direct product a r*r*r.*

$$\{D_{1u}^3|[3]\} = D_{1u} \oplus D_{3u}$$

Octupole moment is traceless.

$$\sum_\alpha \Omega_{\alpha\alpha\beta} = \sum_\alpha \Omega_{\alpha\beta\alpha} = \sum_\alpha \Omega_{\beta\alpha\alpha} = 0$$

Then, the octupole moment components form a basis for D_{3u}

Since traces are obtained be contraction, the trace of a tensor is another tensor of the same dimensions (the Euclidean space) but of an order two units less.

For example: octupole has three traces that are first order tensors, like the dipole moment. The remaining 7 components transforms as D_{3u}

Hexadecupole $\Phi_{\alpha\beta\gamma\delta}$ ***corresponds to*** $\{D^4_{1u}|[4]\} = D_{0g} \oplus D_{2g} \oplus D_{4g}$

Their zero traces, a tensor of an order two unit less, $\{D^2_{1u}|[2]\} = D_{0g} \oplus D_{2g}$ ***are zero. Then, hexadecupole has D_{4g} symmetry.***

etc.

To determine the irreps. in lower symmetries of the components of the multiploles we consider the symmetry lowering from the full rotation group:

	D_{0g}	D_{0u}	D_{1g}	D_{1u}	D_{2g}	D_{2u}
I_h	A_g	A_u	T_{1g}	T_{1u}	H_g	H_u
O_h	A_{1g}	A_{1u}	T_{1g}	T_{1u}	$E_g \oplus T_{2g}$	$E_u \oplus T_{2u}$
T_d	A_1	A_2	T_1	T_2	$E \oplus T_2$	$E \oplus T_1$
D_{6h}	A_{1g}	A_{1u}	$A_{2g} \oplus E_{1g}$	$A_{2u} \oplus E_{1u}$	$A_{1g} \oplus E_{1g} \oplus E_{2g}$	$A_{1u} \oplus E_{1u} \oplus E_{2u}$
D_{6d}	A_1	B_1	$A_2 \oplus E_5$	$B_2 \oplus E_1$	$A_1 \oplus E_2 \oplus E_5$	$B_1 \oplus E_1 \oplus E_4$
D_{5h}	A_1'	A_1''	$A_2' \oplus E_1''$	$A_2'' \oplus E_1'$	$A_1' \oplus E_2' \oplus E_1''$	$A_1'' \oplus E_1' \oplus E_2''$
D_{5d}	A_{1g}	A_{1u}	$A_{2g} \oplus E_{1g}$	$A_{2u} \oplus E_{1u}$	$A_{1g} \oplus E_{1g} \oplus E_{2g}$	$A_{1u} \oplus E_{1u} \oplus E_{2u}$
D_{4h}	A_{1g}	A_{1u}	$A_{2g} \oplus E_g$	$A_{2u} \oplus E_u$	$A_{1g} \oplus B_{1g} \oplus B_{2g} \oplus E_g$	$A_{1u} \oplus B_{1u} \oplus B_{2u} \oplus E_u$
D_{4d}	A_1	B_1	$A_2 \oplus E_3$	$B_2 \oplus E_1$	$A_1 \oplus E_2 \oplus E_3$	$B_1 \oplus E_1 \oplus E_2$
D_{3h}	A_1'	A_1''	$A_2' \oplus E''$	$A_2'' \oplus E'$	$A_1' \oplus E' \oplus E''$	$A_1'' \oplus E' \oplus E''$
D_{3d}	A_{1g}	A_{1u}	$A_{2g} \oplus E_g$	$A_{2u} \oplus E_u$	$A_{1g} \oplus 2E_g$	$A_{1u} \oplus 2E_u$
D_{2h}	A_g	A_u	$B_{1g} \oplus B_{2g} \oplus B_{3g}$	$B_{1u} \oplus B_{2u} \oplus B_{3u}$	$2A_g \oplus B_{1g} \oplus B_{2g} \oplus B_{3g}$	$2A_u \oplus B_{1u} \oplus B_{2u} \oplus B_{3u}$
D_{2d}	A_1	B_1	$A_2 \oplus E$	$B_2 \oplus E$	$A_1 \oplus B_1 \oplus B_2 \oplus E$	$A_1 \oplus A_2 \oplus B_1 \oplus E$
$D_{\infty h}$	Σ_g^+	Σ_u^-	$\Sigma_g^- \oplus \Pi_g$	$\Sigma_u^+ \oplus \Pi_u$	$\Sigma_g^+ \oplus \Pi_g \oplus \Delta_g$	$\Sigma_u^- \oplus \Pi_u \oplus \Delta_u$

Polarizability

If the charge distribution is not static, it may be polarized (deformed) by the field.

Then, multipoles change with the field and its gradients:

$$
\begin{aligned}
\mu_\alpha &= \mu_\alpha^0 + \sum_\beta \alpha_{\alpha\beta} F_\beta + \frac{1}{2}\sum_{\beta,\gamma} \beta_{\alpha\beta\gamma} F_\beta F_\gamma + \ldots + \frac{1}{3}\sum_{\beta,\gamma} A_{\alpha;\beta\gamma} F'_{\beta\gamma} + \frac{1}{3}\sum_{\beta,\gamma,\delta} B_{\alpha\beta;\gamma\delta} F_\beta F'_{\gamma\delta} + \ldots \\
\Theta_{\alpha\beta} &= \Theta_{\alpha\beta}^0 + \sum_\gamma A_{\gamma;\alpha\beta} F_\gamma + \sum_{\gamma,\delta} C_{\alpha\beta;\gamma\delta} F'_{\gamma\delta} + \frac{1}{2}\sum_{\gamma,\delta} B_{\gamma\delta;\alpha\beta} F_\gamma F_\delta + \ldots \\
\Omega_{\alpha\beta\gamma} &= \Omega_{\alpha\beta\gamma}^0 + \sum_\delta E_{\delta;\alpha\beta\gamma} F_\delta + \ldots
\end{aligned}
$$

Define polarizability and hyperpolarizabilities:

$$\alpha_{\alpha\beta} = \left(\frac{\partial \mu_\alpha}{\partial F_\beta}\right)_0 = \left(\frac{\partial^2 E}{\partial F_\alpha \partial F_\beta}\right)_0$$

$$A_{\gamma;\alpha\beta} = \left(\frac{\partial \Theta_{\alpha\beta}}{\partial F_\gamma}\right)_0 = \left(\frac{\partial^3 E}{\partial F_\gamma \partial F'_{\alpha\beta}}\right)_0$$

$$\beta_{\alpha\beta\gamma} = \left(\frac{\partial^3 E}{\partial F_\alpha \partial F_\beta \partial F_\gamma}\right)_0$$

etc.

By definition polarizability α and hyperpolarizabilities β, γ, etc are symmetric with respect to the indexes exchange. Hyperpolarizabilities $A_{\gamma;\alpha\beta}$, $C_{\alpha\beta;\gamma\delta}$ are symmetric with respect to index exchange within each subset of indexes.

By definition they are not traceless tensors (e.g. always the field polarizes an atom, i.e. the D_{0g} trace of α cannot be zero)

Symmetry

Polarizability α components form a basis set for $\{D_{1u}^2|[2]\} = D_{0g} \oplus D_{2g}$

The isotropic D_{0g} trace of α is responsible for Rayleig dispersion.

The anisotropic D_{2g} components of α are responsible for Raman dispersion

$$\beta_{\alpha\beta\gamma} \longrightarrow \{D_{1u}^3|[3]\} = D_{1u} \oplus D_{3u}$$

etc.

Other hyperpolarizabilities

Let's consider $A_{\gamma;\alpha\beta} = \left(\frac{\partial^3 E}{\partial F_\gamma \partial F'_{\alpha\beta}}\right)_0$

The electric field F has D_{1u} symmetry while its second derivative $F'_{\alpha\beta}$ is a traceless D_{2g} tensor. Then, the symmetry of $A_{\gamma;\alpha\beta}$ must be:

$$D_{1u} \otimes D_{2g} = D_{1u} \oplus D_{2u} \oplus D_{3u}$$

Symmetry of the larger polarizabilities

Polarizability	*Components*	*Reducible*	*Sum of irreps.*
$\alpha_{\alpha\beta}$	6	$\{D_{1u}^2|[2]\}$	$D_{0g} \oplus D_{2g}$
$\beta_{\alpha\beta\gamma}$	10	$\{D_{1u}^3|[3]\}$	$D_{1u} \oplus D_{3u}$
$\gamma_{\alpha\beta\gamma\delta}$	15	$\{D_{1u}^4|[4]\}$	$D_{0g} \oplus D_{2g} \oplus D_{4g}$
$A_{\alpha;\beta\gamma}$	15	$D_{1u} \otimes D_{2g}$	$D_{1u} \oplus D_{2u} \oplus D_{3u}$
$B_{\alpha\beta;\gamma\delta}$	30	$\{D_{1u}^2|[2]\} \otimes D_{2g}$	$D_{0g} \oplus D_{1g} \oplus 2D_{2g} \oplus D_{3g} \oplus D_{4g}$
$C_{\alpha\beta;\gamma\delta}$	15	$\{D_{2g}^2|[2]\}$	$D_{0g} \oplus D_{2g} \oplus D_{4g}$
$E_{\alpha;\beta\gamma\delta}$	21	$D_{1u} \otimes D_{3u}$	$D_{2g} \oplus D_{3g} \oplus D_{4g}$

Symmetry and Structure in Chemistry

POINT SYMMETRY

Unit 12: Theory of invariants

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Theory of invariants

1. Perturbation theory becomes more complex for many-band models

2. Nobody calculate the huge amount of integrals involved

grup them $\Rightarrow$ and fit to experiment

Alternative (simpler and deeper) to perturbation theory:

Determine the Hamiltonian H by symmetry considerations

Theory of invariants (basic ideas)

1. Second order perturbation: H second order in k: $H = \sum_{i \geq j}^{3} M_{ij} k_i k_j$

2. H must be an invariant under point symmetry (T_d ZnBl, D_{6h} wurtzite)

A·B is invariant (A_1 symmetry) if A and B are of the same symmetry

e.g. (x, y, z) basis of T_2 of T_d: $x \cdot x + y \cdot y + z \cdot z = r^2$ basis of A_1 of T_d

Theory of invariants (machinery)

1. k basis of T_2

2. k_i k_j basis of $T_2 \otimes T_2 = A_1 \oplus E \oplus T_2 \oplus [T_1]$

3. Character Table:

$$A_1 \rightarrow k_x^2 + k_y^2 + k_z^2$$
$$E \rightarrow \{2k_z^2 - k_x^2 - k_y^2, k_x^2 - k_y^2\}$$
$$T_2 \rightarrow \{k_x k_y, k_x k_z, k_y k_z\}$$
$$T_1 \rightarrow NO(k_i k_j \text{ symmetric tensor})$$

notation: elements of these basis: k_i^Γ.

4. Invariant: sum of invariants:

$$H = \sum_i^{\dim(\Gamma)} \sum_\Gamma a_\Gamma N_i^\Gamma k_i^\Gamma$$

irrep

basis element

fitting parameter (not determined by symmetry)

Machinery (cont.)

How can we determine the N_i^Γ matrices?

(J_x, J_y, J_z) *basis of* T_1, *and* $T_2 \otimes T_2 = T_1 \otimes T_1$

$\rightarrow$ we can use symmetry-adapted $J_i J_j$ products

Example: 4-th band model: $\{|3/2, 3/2>, |3/2, 1/2>, |3/2, -1/2>, |3/2, -3/2>\}$

$$\mathbb{J}_x = \begin{bmatrix} 0 & \sqrt{3}/2 & 0 & 0 \\ \sqrt{3}/2 & 0 & 1 & 0 \\ 0 & 1 & 0 & \sqrt{3}/2 \\ 0 & 0 & \sqrt{3}/2 & 0 \end{bmatrix}$$

$$\mathbb{J}_z = \begin{bmatrix} 3/2 & 0 & 0 & 0 \\ 0 & 1/2 & 0 & 0 \\ 0 & 0 & -1/2 & 0 \\ 0 & 0 & 0 & -3/2 \end{bmatrix}$$

$$\mathbb{J}_y = \begin{bmatrix} 0 & -i\sqrt{3}/2 & 0 & 0 \\ i\sqrt{3}/2 & 0 & -i & 0 \\ 0 & i & 0 & -i\sqrt{3}/2 \\ 0 & 0 & i\sqrt{3}/2 & 0 \end{bmatrix}$$

$$\mathbb{J}^2 = \tfrac{3}{2}(\tfrac{3}{2}+1)\mathbb{I}_{4x4} = \tfrac{15}{4}\mathbb{I}_{4x4}$$

$$\{\mathbb{J}_x, \mathbb{J}_y\} = \tfrac{1}{2}(\mathbb{J}_x\mathbb{J}_y + \mathbb{J}_y\mathbb{J}_x)$$

$$\mathbb{J}_x^2 \quad \mathbb{J}_y^2 \quad \mathbb{J}_z^2$$

Machinery (cont.)

We form the following invariants

$$A_1: \quad X_{A_1} = \mathbb{I}\cdot(k_x^2+k_y^2+k_z^2) = k^2 \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} k^2 & 0 & 0 & 0 \\ 0 & k^2 & 0 & 0 \\ 0 & 0 & k^2 & 0 \\ 0 & 0 & 0 & k^2 \end{bmatrix}$$

$$E: \quad X_E = \frac{1}{\sqrt{6}}(2\mathbb{J}_z^2 - \mathbb{J}_y^2 - \mathbb{J}_x^2)\frac{1}{\sqrt{6}}(2k_z^2 - k_y^2 - k_x^2) + \frac{1}{\sqrt{2}}(\mathbb{J}_x^2 - \mathbb{J}_y^2)\frac{1}{\sqrt{2}}(k_x^2 - k_y^2)$$

$$T_2: \quad X_{T_2} = \frac{1}{2}(\mathbb{J}_x\mathbb{J}_y + \mathbb{J}_y\mathbb{J}_x)k_xk_y + \frac{1}{2}(\mathbb{J}_y\mathbb{J}_z + \mathbb{J}_z\mathbb{J}_y)k_yk_z + \frac{1}{2}(\mathbb{J}_z\mathbb{J}_x + \mathbb{J}_x\mathbb{J}_z)k_zk_x$$

Finally we build the Hamiltonian

$$\mathbb{H} = -\frac{\hbar^2}{2m_0}\left[(\gamma_1 + \frac{5}{2}\gamma_2)X_{A_1} - 2\gamma_2 X_E + 4\gamma_3 X_{T_2}\right]$$

Luttinger parameters: determined by fitting

Four band Hamiltonian:

$$\mathbb{H} = -\frac{\hbar^2}{2m_0}\begin{bmatrix} \gamma_1 k^2 + \gamma_2(k_x^2+k_y^2-2k_z^2) & -2\sqrt{3}\gamma_3 k_z(k_x - i\,k_y) & -\sqrt{3}\gamma_2(k_x^2-k_y^2) + 2\,i\,\sqrt{3}\,\gamma_3\,k_xk_y & 0 \\ -2\sqrt{3}\gamma_3 k_z(k_x + i\,k_y) & \gamma_1 k^2 - \gamma_2(k_x^2+k_y^2-2k_z^2) & 0 & -\sqrt{3}\gamma_2(k_x^2-k_y^2) + 2\,i\,\sqrt{3}\,\gamma_3\,k_xk_y \\ -\sqrt{3}\gamma_2(k_x^2-k_y^2) - 2\,i\,\sqrt{3}\,\gamma_3\,k_xk_y & 0 & \gamma_1 k^2 - \gamma_2(k_x^2+k_y^2-2k_z^2) & 2\sqrt{3}\gamma_3 k_z(k_x - i\,k_y) \\ 0 & -\sqrt{3}\gamma_2(k_x^2-k_y^2) - 2\,i\,\sqrt{3}\,\gamma_3\,k_xk_y & 2\sqrt{3}\gamma_3 k_z(k_x + i\,k_y) & \gamma_1 k^2 + \gamma_2(k_x^2+k_y^2-2k_z^2) \end{bmatrix}$$

Exercise: Show that the 2-bands {|1/2,1/2>,|1/2,-1/2>} conduction band k·p Hamiltonian reads H= *a* k² I, where I is the 2x2 unit matrix, k the modulus of the linear momentum and *a* is a fitting parameter (that we cannot fix by symmetry considerations)

Hints: 1. $T_2 \otimes T_2 = T_1 \otimes T_1 = A_1 \oplus E \oplus T_2 \oplus [T_1]$

2. Angular momentum components in the ±1/2 basis: $S_i = 1/2\, \sigma_i$, with

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

3. Character tables and basis of irreps

Character table for T_d point group

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	linear, rotations	quadratic
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	-1	1	-1	(L_x, L_y, L_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

$$A_1 \rightarrow k_x^2 + k_y^2 + k_z^2$$
$$E \rightarrow \{2k_z^2 - k_x^2 - k_y^2, k_x^2 - k_y^2\}$$
$$T_2 \rightarrow \{k_x k_y + k_y k_x, k_x k_z + k_z k_x, k_y k_z + k_z k_y\}$$
$$T_1 \rightarrow \{k_x k'_y - k_y k'_x, k_x k'_z - k_z k'_x, k_y k'_z - k_z k'_y\}$$

Answer:

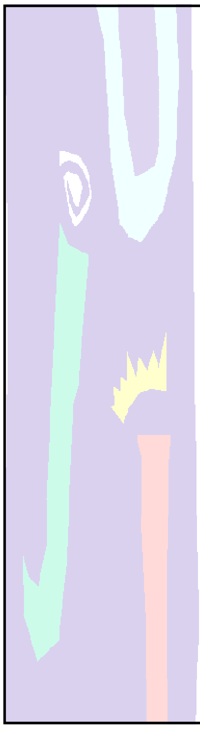
$$A_1 \rightarrow k_x^2 + k_y^2 + k_z^2$$
$$E \rightarrow \{2k_z^2 - k_x^2 - k_y^2, k_x^2 - k_y^2\}$$
$$T_2 \rightarrow \{k_x k_y + k_y k_x, k_x k_z + k_z k_x, k_y k_z + k_z k_y\}$$
$$T_1 \rightarrow \{k_x k'_y - k_y k'_x, k_x k'_z - k_z k'_x, k_y k'_z - k_z k'_y\}$$

1. Disregard T_1: $k_i k_j - k_j k_i = 0$

2. Disregard E: $\boldsymbol{\sigma}_x^2 = \boldsymbol{\sigma}_y^2 = \boldsymbol{\sigma}_z^2 = \mathbf{I}$(2x2)

3. Disregard T_2: $\boldsymbol{\sigma}_i \boldsymbol{\sigma}_j + \boldsymbol{\sigma}_j \boldsymbol{\sigma}_i = 0$

4. A_1: $\rightarrow k_x^2 + k_y^2 + k_z^2 = k^2$
$\rightarrow \boldsymbol{\sigma}_x^2 + \boldsymbol{\sigma}_y^2 + \boldsymbol{\sigma}_z^2 = 3\mathbf{I}$ $\mapsto$ $\boxed{\mathbf{H} = a\, k^2\, \mathbf{I}}$



Symmetry and Structure in Chemistry

POINT SYMMETRY

k·p Theory and the effective mass

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k·p Theory

How do we calculate realistic band diagrams?
- Tight-binding
- Pseudopotentials
- k·p theory

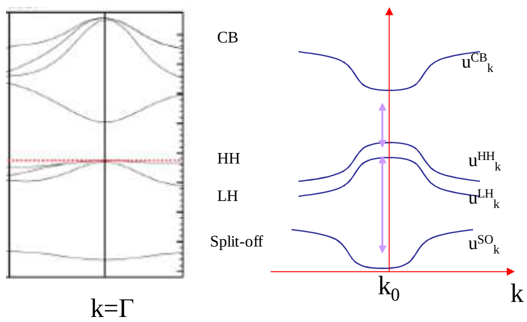
$$\hat{H} = \left(\frac{\vec{p}^{\,2}}{2m} + V_c(\vec{r}) \right) \qquad \Psi_k(\vec{r}) = e^{i\vec{k}\vec{r}}\, u_k(\vec{r})$$

$$e^{-i\vec{k}\vec{r}}\, \hat{H}\, \Psi_k(\vec{r}) = \varepsilon_k\, e^{-i\vec{k}\vec{r}}\, \Psi_k(\vec{r})$$

$$\left(\frac{\vec{p}^{\,2}}{2m} + V_c(\vec{r}) + \frac{\hbar^2 k^2}{2m} + \hbar \frac{\vec{k}\cdot\vec{p}}{m} \right) u_k(\vec{r}) = \varepsilon_k\, u_k(\vec{r})$$

The k·p Hamiltonian

MgO



$$\left(\frac{\vec{p}^2}{2m}+V_c(\vec{r})+\frac{\hbar^2 k^2}{2m}+\hbar\frac{\vec{k}\cdot\vec{p}}{m}\right)u_k(\vec{r})=\varepsilon_k u_k(\vec{r})$$

$$u_k^n(\vec{r})=\sum_n^{\infty} c_{nk}\, u_{k0}^n(\vec{r})$$

gap

k~ k0

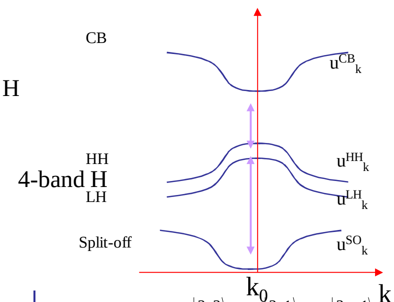
$$\langle u_{k0}^n|\hat{H}_{kp}|u_{k0}^{n'}\rangle=\left(\varepsilon_{k0}^n+\frac{\hbar^2(\vec{k}-\vec{k}_0)^2}{2m}\right)\delta_{n,n'}+\hbar\frac{\vec{k}}{m}\langle u_{k0}^n|\vec{p}|u_{k0}^{n'}\rangle$$

Kane parameter

8-band H

1-band H

4-band H



	$\|s\uparrow\rangle$	$\|s\downarrow\rangle$	$\|\frac{3}{2},\frac{3}{2}\rangle$	$\|\frac{3}{2},\frac{1}{2}\rangle$	$\|\frac{3}{2},\frac{-1}{2}\rangle$	$\|\frac{3}{2},\frac{-3}{2}\rangle$	$\|\frac{1}{2},\frac{1}{2}\rangle$	$\|\frac{1}{2},\frac{-1}{2}\rangle$
$\langle s\uparrow\|$	$\frac{k^2}{2m}$	0	Pk_+	$-\sqrt{\frac{2}{3}}Pk_z$	$-\sqrt{\frac{1}{3}}Pk_-$	0	$\sqrt{\frac{1}{3}}Pk_z$	$-\sqrt{\frac{2}{3}}Pk_-$
$\langle s\downarrow\|$	0	$\frac{k^2}{2m}$	0	$\sqrt{\frac{1}{3}}Pk_-$	$-\sqrt{\frac{2}{3}}Pk_z$	Pk_-	$\sqrt{\frac{2}{3}}Pk_-$	$\sqrt{\frac{1}{3}}Pk_z$
$\langle\frac{3}{2},\frac{3}{2}\|$	Pk_+	0	$-\varepsilon_0+\frac{k^2}{2m}$	0	0	0	0	0
$\langle\frac{3}{2},\frac{1}{2}\|$	$-\sqrt{\frac{2}{3}}Pk_z$	$\sqrt{\frac{1}{3}}Pk_-$	0	$-\varepsilon_0+\frac{k^2}{2m}$	0	0	0	0
$\langle\frac{3}{2},\frac{-1}{2}\|$	$-\sqrt{\frac{1}{3}}Pk_-$	$-\sqrt{\frac{2}{3}}Pk_z$	0	0	$-\varepsilon_0+\frac{k^2}{2m}$	0	0	0
$\langle\frac{3}{2},\frac{-3}{2}\|$	0	Pk_-	0	0	0	$-\varepsilon_0+\frac{k^2}{2m}$	0	0
$\langle\frac{1}{2},\frac{1}{2}\|$	$\sqrt{\frac{1}{3}}Pk_z$	$\sqrt{\frac{2}{3}}Pk_-$	0	0	0	0	$-\varepsilon_0-\Delta+\frac{k^2}{2m}$	0
$\langle\frac{1}{2},\frac{-1}{2}\|$	$-\sqrt{\frac{2}{3}}Pk_-$	$\sqrt{\frac{1}{3}}Pk_z$	0	0	0	0	0	$-\varepsilon_0-\Delta+\frac{k^2}{2m}$

$$u_k^n(\vec{r})=\sum_n^{\infty} c_{nk}\, u_{k0}^n(\vec{r})$$

One-band Hamiltonian for the conduction band

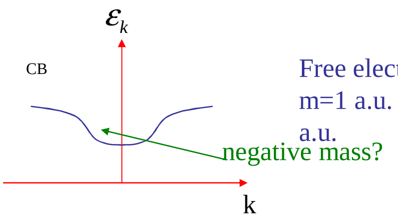
$$\left\langle u_{k0}^{n} \right| \hat{H}_{kp} \left| u_{k0}^{n'} \right\rangle = \left(\varepsilon_{k0}^{n} + \frac{\hbar^2 (\vec{k} - \vec{k}_0)^2}{2m} \right) \delta_{n,n'} + \hbar \frac{\vec{k}}{m} \left\langle u_{k0}^{n} \right| \vec{p} \left| u_{k0}^{n'} \right\rangle$$

$$\varepsilon_k^{cb} = \varepsilon_{k0}^{cb} + \frac{\hbar^2 (\vec{k} - \vec{k}_0)^2}{2m}$$

This is a crude approximation... Let's include remote bands perturbationally

$$\varepsilon_k^{cb} = \varepsilon_{k0}^{cb} + \sum_{\alpha = x,y,z} \frac{\hbar^2 (k_\alpha - k_{0\alpha})^2}{2m} + \frac{\hbar}{m} k_\alpha \sum_{n \neq cb} \frac{\left| \left\langle u_{k0}^{cb} \right| p_\alpha \left| u_{k0}^{n} \right\rangle \right|^2}{\varepsilon_{k0}^{cb} - \varepsilon_{k0}^{n}}$$

1/m*



Free electron
m=1 a.u.

InAs
m*=0.025 a.u.

Effective mass

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{\partial \varepsilon_k^{cb}}{\partial k^2}$$

$$\varepsilon_k^{cb} = \varepsilon_{k0}^{cb} + \frac{\hbar^2 (k_\alpha - k_{0\alpha})^2}{2m_\alpha^*}$$