# Notes on Group Theory

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## Contents



Note that this document is not self-contained and does not constitute an introduction to group theory in quantum chemistry, but rather serves as a summary to one that has had a course on group theory.

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## 1 Motivation

The symmetry informations gathered on a model and on a system give a framework to make exact statements on the physics of the problem. Remember that the application of a crude approximation such as mean-field Hartree-Fock yields suprising good results because it includes symmetry considerations (anti-symmetry of the wavefunction).

In our case here, the spatial symmetry informations can be used to construct symmetric molecular orbitals from atomic orbitals and provide arguments to infer whether a given matrix element (monoelectronic and bielectronic integrals, dipole moment, vibration element, ...) vanishes or not.

## 2 Group Theory

Let $G$ be the group of all the space symmetry operations. We are actually interested in particular subgroups of $G$, containing $g$ elements, that describe a molecule. The symmetry group of a molecule is called a *point group* (the set of symmetry operations leaves at least one point fixed, to oppose to the symmetry of a crystal which is described by a *space group* of symmetry operations, which includes translations in space).

Remember that the symmetry operations of a group can be gathered into $c$ disjoint *equivalence classes* formed of operations that are similarly transformed from one another.

> We will work throughout the document on the example of the ammonia molecule $NH_3$. It belongs to the group called $C_{3v}$, for which $g = 6$ and $c = 3$, which symmetry operations are $\{E, C_3^1, C_3^2, \sigma_v(a), \sigma_v(b), \sigma_v(c)\}$ assembled in the $\{E\}$, $\{C_3\}$ and $\{\sigma_v\}$ equivalence classes.

Let $GL$ be the group of the inversible linear applications of a vector space $\mathbb{V}$ of dimension $n$ unto itself ($\mathbb{V}$ will often be $\mathbb{R}^3$) ; we can of course identify $GL$ with the group of the non-singular associated matrices of $\mathbb{C}$:

$$GL(\mathbb{V}) \sim GL_n(\mathbb{C}) \tag{1}$$

Note that the dimension $n$ of the space and associated matrices have nothing to do with the group, it's cardinal, *etc.*

## 2.1 Representation

A *linear representation* $\Gamma$ of $G$ is a morphism of $G$ into $GL$, *i.e.* it is a correspondance between each symmetry operation of $G$ and an element of $GL$ (or an associated matrix in $GL_n$) so that the composition operation $o$ of $G$ is represented by the product . of $GL$:

$$\Gamma_{(R_1 o R_2)} = \Gamma_{R_1}.\Gamma_{R_2} \tag{2}$$

We actually denote the representations $\Gamma^{\mathbb{V}}$ to stress out the dependance to the space $\mathbb{V}$ ; $\Gamma^{\mathbb{V}}$ is composed of all the representations of the symmetry operations of $G$: $\Gamma^{\mathbb{V}} = \{\Gamma^{\mathbb{V}}_{R_1}, \dots \Gamma^{\mathbb{V}}_{R_g}\}$.

> In $\mathbb{R}^3$ with the canonical orthogonal basis $\{i, j, k\}$, the matrices associated with the symmetry operations $E, C_3, \sigma_v$ are :
>
> $$\Gamma^{\mathbb{R}^3}_E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \Gamma^{\mathbb{R}^3}_{C_3} = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \qquad \Gamma^{\mathbb{R}^3}_{\sigma_v} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} \tag{3}$$
>
> Another view can be in a sub-space of functions of $\mathbb{R}^3$, with for example a basis composed of the atomic orbitals $\{s_N, s_1, s_2, s_3\}$. In this case, we have the following representations:
>
> $$\Gamma^{\mathbb{V}}_E = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \qquad \Gamma^{\mathbb{V}}_{C_3} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} \qquad \Gamma^{\mathbb{V}}_{\sigma_v} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \tag{4}$$

## 2.2 Reduction

Remember that two sup-spaces $\mathbb{V}_1$ and $\mathbb{V}_2$ of $\mathbb{V}$ are said to be *supplementary spaces* (written $\mathbb{V} = \mathbb{V}_1 \oplus \mathbb{V}_2$) if for any $v \in \mathbb{V}$ there exist $w_1 \in \mathbb{V}_1$ and $w_2 \in \mathbb{V}_2$ so that $v = w_1 + w_2$. Note that for a given $\mathbb{V}$ and $\mathbb{V}_1$, $\mathbb{V}_2$ is not unique (consider in $\mathbb{R}^3$ the $xy$ plane for $\mathbb{V}_1$ and any vector not in the plane for $\mathbb{V}_2$). Moreover, a sub-space $\mathbb{V}_1$ is said to be stable by $G$ if the image of any element of $\mathbb{V}_1$ by any operation of $G$ remains in $\mathbb{V}_1$.

One can prove that if a sub-space $\mathbb{V}_1$ of $\mathbb{V}$ is stable by $G$, then there exist a supplementary sub-space $\mathbb{V}_2$ that is also stable by $G$. The matrices $\Gamma^{\mathbb{V}}_R$ associated with the symmetry operations $R$ constructed using for $\mathbb{V}$ a basis composed of basis of $\mathbb{V}_1$ and $\mathbb{V}_2$ are then block-diagonal and can be written as direct sums of matrices:

$$\begin{aligned}
\Gamma^{\mathbb{V}} &= \left\{\Gamma^{\mathbb{V}}_{R_1}, \ldots, \Gamma^{\mathbb{V}}_{R_g}\right\} \\
&= \left\{\begin{pmatrix}\Gamma^{\mathbb{V}_1}_{R_1} & 0 \\ 0 & \Gamma^{\mathbb{V}_2}_{R_1}\end{pmatrix}, \ldots, \begin{pmatrix}\Gamma^{\mathbb{V}_1}_{R_g} & 0 \\ 0 & \Gamma^{\mathbb{V}_2}_{R_g}\end{pmatrix}\right\} \\
&= \left\{\Gamma^{\mathbb{V}_1}_{R_1} \oplus \Gamma^{\mathbb{V}_2}_{R_1}, \ldots, \Gamma^{\mathbb{V}_1}_{R_g} \oplus \Gamma^{\mathbb{V}_2}_{R_g}\right\} \\
&= \Gamma^{\mathbb{V}_1} \oplus \Gamma^{\mathbb{V}_2}
\end{aligned} \tag{5}$$

Inversely, if the matrices of *all* the elements of $G$ are block-diagonal together, then $\mathbb{V}$ can be written as a direct sum.

From this point of view: a representation $\Gamma^{\mathbb{V}}$ is said to be *irreductible* if $\mathbb{V}$ contains no stable sub-space (the space $\mathbb{V}$ is also said to be irreducible). One can show that the vector space can be decomposed into at most $c$ irreducible sub-spaces, and the representation $\Gamma^{\mathbb{V}}$ into at most $c$ irreducible representations (this means among other things that the character tables, that will we encountered later, are square). We have:

$$\mathbb{V} = \bigoplus_{i=1}^{c} \mathbb{V}_i \qquad \text{and} \qquad \Gamma^{\mathbb{V}} = \bigoplus_{i=1}^{c} \Gamma^{\mathbb{V}_i} \tag{6}$$

(note that in these summations, the index $i$ does go from 1 to at most $c$ but not all irreducible sub-spaces and irreducible representations are present in the summations)

An alternative way to see the reducing of a representation is to consider that, given a representation $\Gamma^{\mathbb{V}} = \{\Gamma^{\mathbb{V}}_{R_1}, \ldots, \Gamma^{\mathbb{V}}_{R_g}\}$, we search for a transformation $X$ so that $\Gamma^{\mathbb{V}} = \{X\Gamma^{\mathbb{V}}_{R_1}X^{-1}, \ldots, X\Gamma^{\mathbb{V}}_{R_g}X^{-1}\}$ is formed from matrices that are block-diagonal with the same structure of blocks.

In the previous example, the matrix $X = \begin{pmatrix}1/\sqrt{3} & 1/\sqrt{3} & 1/\sqrt{3} \\ 1/\sqrt{2} & -1/\sqrt{2} & 0 \\ 2/\sqrt{6} & -1/\sqrt{6} & -1/\sqrt{6}\end{pmatrix}$ transforms the representation into:

$$\Gamma^{\mathbb{R}^3}_{E} = \begin{pmatrix}1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1\end{pmatrix} \qquad \Gamma^{\mathbb{R}^3}_{C_3} = \begin{pmatrix}1 & 0 & 0 \\ 0 & 1 & -\sqrt{3} \\ 0 & \sqrt{3} & -2\end{pmatrix} \qquad \Gamma^{\mathbb{R}^3}_{\sigma_v} = \begin{pmatrix}1 & 0 & 0 \\ 0 & -1 & \sqrt{3} \\ 0 & 0 & 1\end{pmatrix} \tag{7}$$

and we can see that $\mathbb{R}^3 = span\{i\} \oplus span\{j,k\}$ and that:

$$\Gamma^{\{i\}}_{E} = \begin{pmatrix}1\end{pmatrix} \qquad \Gamma^{\{i\}}_{C_3} = \begin{pmatrix}1\end{pmatrix} \qquad \Gamma^{\{i\}}_{\sigma_v} = \begin{pmatrix}1\end{pmatrix} \tag{8}$$

and:

$$\Gamma^{\{j,k\}}_{E} = \begin{pmatrix}1 & 0 \\ 0 & 1\end{pmatrix} \qquad \Gamma^{\{j,k\}}_{C_3} = \begin{pmatrix}1 & -\sqrt{3} \\ \sqrt{3} & -2\end{pmatrix} \qquad \Gamma^{\{j,k\}}_{\sigma_v} = \begin{pmatrix}-1 & \sqrt{3} \\ 0 & 1\end{pmatrix} \tag{9}$$

In the space of the functions of $\mathbb{R}^3$, the transformation $X = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1/\sqrt{3} & 1/\sqrt{3} & 1/\sqrt{3} \\ 0 & 2/\sqrt{6} & -1/\sqrt{6} & -1/\sqrt{6} \\ 0 & 0 & 1/\sqrt{2} & -1/\sqrt{2} \end{pmatrix}$ yields:

$$\Gamma_E^{\mathbb{V}} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \qquad \Gamma_{C_3}^{\mathbb{V}} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1/2 & \sqrt{3}/2 \\ 0 & 0 & -\sqrt{3}/2 & -1/2 \end{pmatrix} \qquad \Gamma_{\sigma_v}^{\mathbb{V}} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \tag{10}$$

which has the same irreducible representations as the $\mathbb{R}^3$ example.

Note that the number of representation for $G$ is unlimited (one can always similarly transform a representation), and although the irreducible representations are the building blocks of all representations, like the representations themselves, they are not unique!

## 2.3 Character

We define the *character* $\chi_R^{\mathbb{V}}$ of $\Gamma_R^{\mathbb{V}}$ as the trace of the matrix associated to $\Gamma_R^{\mathbb{V}}$. Of course, the character does not depend on the basis, which is the whole point. In particular, the characters of all the symmetry operations in an equivalence class are all the same. The character of a representation $\Gamma^{\mathbb{V}}$ is the list (the *character vector*) of the characters of the symmetry operations : $\chi^{\mathbb{V}} = \{\chi_{R_1}^{\mathbb{V}}, \ldots, \chi_{R_g}^{\mathbb{V}}\}$.

In the example of the representation $\Gamma^{\mathbb{R}^3}$, the characters are:

$$\chi_E^{\mathbb{R}^3} = 3 \qquad \chi_{C_3}^{\mathbb{R}^3} = 0 \qquad \chi_{\sigma_v}^{\mathbb{R}^3} = 1 \tag{11}$$

The characters of the irreducible representations are :

$$\begin{aligned} &\chi_E^{\{i\}} = 2 \quad &\chi_{C_3}^{\{i\}} = -1 \quad &\chi_{\sigma_v}^{\{i\}} = 0 \\ &\chi_E^{\{j,k\}} = 1 \quad &\chi_{C_3}^{\{j,k\}} = 1 \quad &\chi_{\sigma_v}^{\{j,k\}} = 1 \end{aligned} \tag{12}$$

The characters of all the irreducible representations of a group $G$ form an orthonormal basis of the vector space of the central functions on $G$, $(\mathcal{F}(G,\mathbb{C}), \langle . | . \rangle)$, and the *character table* is the data of the character vectors of the irreducible representations. The lines and columns of the character table of a group have properties inherited from the properties of the irreducible representations and of the characters (orthogonality relations,...) ; these can among other things help to construct the table.

The $C_{3v}$ group has the following character table:

| | $E$ | $2C_3$ | $3\sigma_v$ |
|---|---|---|---|
| $A_1$ | 1 | 1 | 1 |
| $E$ | 2 | $-1$ | 0 |
| $A_2$ | 1 | 1 | $-1$ |

(13)

(The denominations $A_1, E, A_2$ are just a question of nomenclature and are not treated here.) Note the the previous example basis only spanned $A_1 \oplus E$ and $2A_1 \oplus E$, respectively. The exploration of $A_2$ isn't treated here.

## 2.4 Decomposition

A very important use of the characters and their properties is the decomposition of a general representation into irreducible representations. Since the irreductible representations form a basis of the space of functions of $\mathbb{V}$, this manipulation is similar to the projection of a vector on a complete set of basis vectors.

Consider the following scalar product in the space of the function on $G$:

$$\langle f^1 | f^2 \rangle = \frac{1}{g} \sum_{R=1}^{g} f_R^1 f_R^2 = \frac{1}{g} \sum_{R=1}^{c} c_R f_R^1 f_R^2 \tag{14}$$

where, in the second expression, the summation runs on the classes and accounts for the number $c_R$ of equivalent symmetry operations in each class.

We have:

$$\langle \chi^{\mathbb{V}_i} | \chi^{\mathbb{V}} \rangle = \langle \chi^{\mathbb{V}_i} | \chi^{\bigoplus_{j=1}^{c} \mathbb{V}_j} \rangle = \sum_{j=1}^{c} \langle \chi^{\mathbb{V}_i} | \chi^{\mathbb{V}_j} \rangle \tag{15}$$

The elemental scalar products $\langle \chi^{\mathbb{V}_i} | \chi^{\mathbb{V}_j} \rangle$ are non-zero (equal to one) only if the representations $\Gamma^{\mathbb{V}_i}$ and $\Gamma^{\mathbb{V}_j}$ are isomorph. Hence the scalar product $a_i = \langle \chi^{\mathbb{V}_i} | \chi^{\mathbb{V}} \rangle$ gives the number of representations isomorph to $\Gamma^{\mathbb{V}_i}$ in $\Gamma^{\mathbb{V}}$.

In other word, more than $\mathbb{V} = \bigoplus_{i=1}^{c} \mathbb{V}_i$, we have that the space can be decomposed into $s$ sub-spaces that share the same symmetry properties (they are isomorph and so have the same characters). This decomposition is called the *canonical decomposition of* $\mathbb{V}$:

$$\mathbb{V} = \bigoplus_{i=1}^{s} a_i \mathbb{V}_i \tag{16}$$

In this canonical decomposition, each $a_i \mathbb{V}_i$ is a space that is the direct sum of $a_i$ spaces of irreducible representations isomorph to $\Gamma^{\mathbb{V}_i}$. Note that the spaces $a_i \mathbb{V}_i$ are in general no longer irreducible, but understand that, on the other hand, while the decomposition $\mathbb{V} = \bigoplus_{i=1}^{c} \mathbb{V}_i$ is not unique, the canonical decomposition is (the spaces $a_i \mathbb{V}_i$ are well-defined).

We search the decomposition of $\mathbb{R}^3$ and of $\mathbb{R}^3 \otimes \mathbb{R}^3$ into irreducible representations of $C_{3v}$. Remember that $\chi^{\mathbb{R}^3} = \{3, 0, 1\}$ ; we also have $\chi^{\mathbb{R}^3 \otimes \mathbb{R}^3} = \{9, 0, 1\}$ (we will encounter later the direct products of spaces and their characters).
We know that $\mathbb{R}^3 = a_1 A_1 \oplus a_2 E \oplus a_3 A_2$ and are loooking for $a_i$ using Eqs. [14,15]:

$$\begin{aligned} a_1 &= \langle \chi^{A_1} | \chi^{\mathbb{R}^3} \rangle = \frac{1}{6} (1*1*3 + 2*1*0 + 3*1*1) = 1 \\ a_2 &= \langle \chi^{E} | \chi^{\mathbb{R}^3} \rangle = \frac{1}{6} (1*2*3 + 2*-1*0 + 3*0*1) = 1 \\ a_3 &= \langle \chi^{A_2} | \chi^{\mathbb{R}^3} \rangle = \frac{1}{6} (1*1*3 + 2*1*0 + 3*-1*1) = 0 \end{aligned} \tag{17}$$

(the first number is the cardinal $c_R$ of the class represented by the current symmetry operation $R$ in the sum, the second is the character $\chi^i_R$, for the current class, of the irreducible representation of which we search $a_i$, the third term is the character $\chi^{\mathbb{R}^3}_R$ for the current class.)
We obtained that $\mathbb{R}^3 = A_1 \oplus E$, as earlier, but without the need to block-diagonalize or manipulate $\Gamma^{\mathbb{R}^3}$ in any way: the knowledge of the characters is all we need.
For $\mathbb{R}^3 \otimes \mathbb{R}^3$, we have:

$$\begin{aligned} a_1 &= \langle \chi^{A_1} | \chi^{\mathbb{R}^3 \otimes \mathbb{R}^3} \rangle = \frac{1}{6} (1*1*9 + 2*1*0 + 3*1*1) = 2 \\ a_2 &= \langle \chi^{E} | \chi^{\mathbb{R}^3 \otimes \mathbb{R}^3} \rangle = \frac{1}{6} (1*2*9 + 2*-1*0 + 3*0*1) = 3 \\ a_3 &= \langle \chi^{A_2} | \chi^{\mathbb{R}^3 \otimes \mathbb{R}^3} \rangle = \frac{1}{6} (1*1*9 + 2*1*0 + 3*-1*1) = 1 \end{aligned} \tag{18}$$

which yields $\mathbb{R}^3 \otimes \mathbb{R}^3 = 2A_1 \oplus 3E \oplus A_2$.

Because of the uniqueness of the canonical decomposition of the space $\mathbb{V}$, there exist a unique decomposition of a vector $\mathbf{v} \in \mathbb{V}$ as $\mathbf{v} = \sum_{i=1}^{s} \mathbf{v}_i$ where $\mathbf{v}_i \in a_i \mathbb{V}_i$, and one can show that the projection of $\mathbf{v}$ on a sub-space $a_i \mathbb{V}_i$ of the decomposition reads:

$$\mathbf{v}_i = \hat{P}^{a_i \mathbb{V}_i} \mathbf{v} = \left( \frac{d_i}{g} \sum_{R=1}^{g} \chi^{\mathbb{V}_i}_R \Gamma^{\mathbb{V}}_R \right) \mathbf{v} \tag{19}$$

where $d_i$ is the dimension of $\mathbb{V}_i$.

## 2.5 Summary

A good point of view on reduction and characters is found by thinking that we are looking for *characteristics* of groups and symmetry operations. A reverse way of seeing the direct sum and the reduction is to think that, given $\Gamma^{\mathbb{V}_1}$ a representation of dimension $n_1$ of $G$, and $\Gamma^{\mathbb{V}_2}$ a representation of dimension $n_2$ of $G$, one can always construct $\Gamma^{\mathbb{V}_1} \oplus \Gamma^{\mathbb{V}_2}$, a representation of dimension $n_1 + n_2$ of $G$ *without adding any information on the group*. The reduction is an effort to find representations that are somehow minimal and characteristic of the group.

Of course, even with *irreducible* representations, similarly transformations are always possible and leads to none-uniqueness of the representations at hand : this is dealt with by using characters rather than entire representations. The characters of the irreducible representations of the group *are* characteristic of the group.

## 3 In quantum mechanics

### 3.1 Hamiltonian group

An operation $R$ is a symmetry operation of the Hamiltonian $H$ if $H$ is left invariant by $R$ ($H = RHR^{-1}$) *i.e.* if $H$ and $R$ commute ($HR = RH$). The group $G$ of the Hamiltonian is formed by the ensemble of all symmetry operations of the Hamiltonian: $G = \{R_1, \ldots, R_g\}$.

A good representation of this group is achieved in the Hilbert space $\mathbb{V} = \mathcal{H}$ by looking at the transformation under symmetry operations of the Hamiltonian of a set of orthonormal eigenstates $\psi = \{\phi_i\}$ of $H$. A transformation of a $\phi_i$ is written as a decomposition on the basis $\{\phi_i\}$:

$$R_1\phi_i = \sum_{j=1}^{n} \phi_j [\Gamma^{\mathcal{H}}_{R_1}]_{ji} \tag{20}$$

so that successive application yields:

$$\begin{aligned}
R_2 o R_1 \phi_i &= R_2 \left( \sum_{j=1}^{n} \phi_j [\Gamma^{\mathcal{H}}_{R_1}]_{ji} \right) \\
&= \sum_{j=1}^{n} (R_2\phi_j)\, [\Gamma^{\mathcal{H}}_{R_1}]_{ji} \\
&= \sum_{j,k=1}^{n} \phi_k [\Gamma^{\mathcal{H}}_{R_2}]_{kj} [\Gamma^{\mathcal{H}}_{R_1}]_{ji} \\
&= \sum_{k=1}^{n} \phi_k [\Gamma^{\mathcal{H}}_{R_2} \Gamma^{\mathcal{H}}_{R_1}]_{ki}
\end{aligned} \tag{21}$$

which can otherwise be written:

$$R_2 o R_1 \phi_i = \sum_{k=1}^{n} \phi_k [\Gamma^{\mathcal{H}}_{(R_2 o R_1)}]_{ki} \tag{22}$$

*i.e.* $\Gamma^{\mathcal{H}}_{(R_1 o R_2)} = \Gamma^{\mathcal{H}}_{R_1}\Gamma^{\mathcal{H}}_{R_2}$ and $\Gamma^{\mathcal{H}} = \{\Gamma^{\mathcal{H}}_{R_1}, \ldots, \Gamma^{\mathcal{H}}_{R_g}\}$ is a representation of the Hamiltonian group. It happens to be an irreducible one.

### 3.2 Diagonalize the Hamiltonian

An immediate result gained from the previous derivations is that one can easily block-diagonalize the Hamiltonian $H$.

Indeed, the canonical decomposition of the Hilbert space $\mathcal{H}$ can be done by the procedure described earlier, with only knowledge of the group $G$ of the Hamiltonian, and not of the Hamiltonian itself. Remember that we are capable of finding the following canonical decomposition:

$$\mathcal{H} = \bigoplus_{i=1}^{s} a_i \mathcal{H}_i \tag{23}$$

One can prove that each $a_i\mathcal{H}_i$ is invariant by $H$ and that $H$ can then be represented by a block-diagonal matrix. Diagonalizing $H$ becomes only the procedure of diagonalizing it's diagonal blocks.

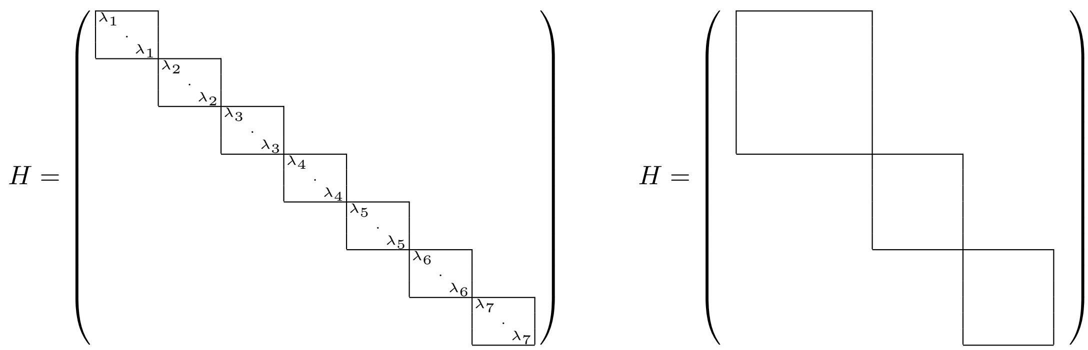
In the simple case where $a_i = 1$, the space $\mathcal{H}_i$ is of the symmetry of the $i^{th}$ irreducible representation and is a least included in an eigenspace of $H$. This shows that the knowledge of the symmetry of $H$ is enough to know some of it's eigenspaces.

When one of the spaces of the decomposition is a reducible space $a_i\mathcal{H}_i$, to obtain the eigenspaces of $H$ one must diagonalize the corresponding diagonal block. The resulting eigenspaces are one of the possible decomposition in isomorph irreductible spaces of $a_i\mathcal{H}_i$.

Consider the following representation of both decompositions of the Hilbert space:

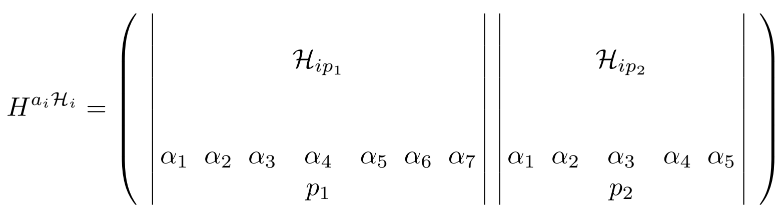
$$\mathcal{H} = \bigoplus_{i=1}^{c} \mathcal{H}_i \qquad\qquad \mathcal{H} = \bigoplus_{i=1}^{s} a_i\mathcal{H}_i$$

$$\text{where } \mathcal{H}_i = \underbrace{\mathcal{H}_{i1} \oplus \mathcal{H}_{i2} \oplus \dots}_{a_i}$$




On the left, each block is diagonal with the same eigenvalue and represents one eigenspace of $H$ (the decomposition is into fully irreducible spaces). Some of the blocks, randomly arranged, are eigenspaces of the same symmetry.

On the right, each block $H^{a_i\mathcal{H}_i}$ of the Hamiltonian contains several eigenspaces ($a_i\mathcal{H}_i$ is reducible except when $a_i = 1$) of the same symmetry. The eigenspaces of $H$ are labelled by $(i,p)$, $i$ being the number of the irreducible representation corresponding to the $a_i\mathcal{H}_i$ it belongs to (all spaces in $a_i\mathcal{H}_i$ are isomorph and have the same characters), and $p \in [1, a_i]$ labels the different eigenspaces in $a_i\mathcal{H}_i$, found for example by diagonalizing the block $a_i\mathcal{H}_i$. If the space $\mathcal{H}_{ip}$ is of dimension greater than one, the eigenvectors of the space need to be further labelled with $\alpha$, as shown here:




## 3.3 Direct product

Consider the action of a symmetry operation on a *product* of eigenstates:

$$\begin{aligned} R(\phi_i\phi_j) &= R(\phi_i)R(\phi_j) \\ &= \sum_{k=1}^{n} \phi_k [\Gamma_R^{\mathcal{H}}]_{ki} \sum_{l=1}^{n} \phi_l [\Gamma_R^{\mathcal{H}}]_{lj} \\ &= \sum_{k,l=1}^{n} \phi_k\phi_l [\Gamma_R^{\mathcal{H}}]_{kl,ij} \end{aligned} \tag{24}$$

The first line is easy to understand if we consider that $R$ is a coordinate transformation, its action on any function of the coordinates is to transform each occurrence of the coordinates.

The result here is that the product of eigenstates transforms as the direct product of the (irreducible) representations associated with each function: $[\Gamma_R^{\mathcal{H}}]_{kl,ij} = [\Gamma_R^{\mathcal{H}}]_{ki}[\Gamma_R^{\mathcal{H}}]_{lj}$.

Direct products have many interesting properties, in this context we specifically mention:

1. the direct product of irreducible representations of two groups is an irreducible representation of the direct product of those groups

2. the characters of the representations of a direct product group can be computed directly from the characters of the representations of the two groups forming the direct product

3. the character table of a direct product group is constructed as the direct product of the character tables of the constituing groups

### 3.4 Selection rules

We aim at an insight into the following example of integrals:

$$\begin{aligned} &\text{Hamiltonian expectation value: } \int \phi_i(\mathbf{x})\ \hat{H}\ \phi_j(\mathbf{x})d\mathbf{x} \\ &\text{overlap: } \int \phi_i(\mathbf{x})\phi_j(\mathbf{x})d\mathbf{x} \\ &\dots \end{aligned} \tag{25}$$

where $\phi_i, \phi_j$ and $\hat{H}$ are associated with representations $\Gamma^i, \Gamma^j$ and $\Gamma^H$. As seen earlier the product of functions will transform according to the direct product of the associated representations, so rather than looking at the conditions for the vanishing of the integrals in terms of each representation involved, we can look at:

$$I = \int f(\mathbf{x})d\mathbf{x} \tag{26}$$

and find condition on $f$ ($f$ will be the product of functions in the integrals).

Consider the change of variables $\mathbf{x}' = \Gamma_R^{\mathbb{V}}\mathbf{x}$ that leaves invariant the differential element $d\mathbf{x}$. The integral is then:

$$I = \int f((\Gamma_R^{\mathbb{V}})^{-1}\mathbf{x}')d\mathbf{x}' = \int \Gamma_R^{\mathcal{H}} f(\mathbf{x}')d\mathbf{x}' \tag{27}$$

which can be done for the $g$ symmetry operations of $G$, each time leaving $I$ unchanged. Summing these equivalent $I$ gives:

$$\int \frac{1}{g}\sum_{R=1}^{g} \Gamma_R^{\mathcal{H}} f(\mathbf{x}')d\mathbf{x}' = \int \hat{P}^{a_1 A_1} f(\mathbf{x}')d\mathbf{x}' \tag{28}$$

where we recognized the projector on the representation whose characters are all 1 (see Eq. [19]), *i.e.* $A_1$.

With this at hand, it is easy to say that the integral $I$ vanishes when the function $f$ belongs to a representation whose canonical decomposition does not contain $A_1$ (the representation entierely symmetric). In other words, the integrals in Eq. [25] vanish when the decomposition of the direct product of the representations associated with the function involved does not contain $A_1$.

Consider the integrals involving the dipole moment $I = \int \phi_i(\mathbf{x})\mu_{[x/y/z]}(\mathbf{x})\phi_j(\mathbf{x})d\mathbf{x}$.
The components of the vector field $\boldsymbol{\mu}(\mathbf{x})$ transform into each other and so they span a representation isomorph to the $\mathbb{R}^3$ space : their representation is that of $\mathbb{R}^3$, $\Gamma^{\mathbb{R}^3}$.
The product of functions in $I$ hence transforms as $\Gamma^i \otimes \Gamma^{\mathbb{R}^3} \otimes \Gamma^j$ and the number of irreducible $A_1$ representations contained in this representation is:

$$\begin{aligned} a_{A_1} &= \frac{1}{6}\sum_{R=1}^{3} c_R \chi_R^{A_1} \chi_R^{(\Gamma^i \otimes \Gamma^{\mathbb{R}^3} \otimes \Gamma^j)} \\ &= \frac{1}{6}\sum_{R=1}^{3} c_R \chi_R^{A_1} \chi_R^{\Gamma^i} \chi_R^{\Gamma^{\mathbb{R}^3}} \chi_R^{\Gamma^j} \\ &= \frac{1}{6}(1 * 1 * \chi_{A_1}^{\Gamma^i} * 3 * \chi_{A_1}^{\Gamma^j} + 2 * 1 * \chi_E^{\Gamma^i} * 0 * \chi_E^{\Gamma^j} + 3 * 1 * \chi_{A_2}^{\Gamma^i} * 1 * \chi_{A_2}^{\Gamma^j}) \end{aligned} \tag{29}$$

In a particular case, with known $\phi_i$ and $\phi_j$, one can infer the vanishing of the integral.

Another way to tackle this problem is to decompose all the direct products of representations $\Gamma^{\phi_i}$ and $\Gamma^{\mathbb{R}^3}$. This will indicate which representations $\Gamma^{\phi_j}$ will yield a vanishing integral (it will be those who are *not* included in $\Gamma^{\phi_i} \otimes \Gamma^{\mathbb{R}^3}$).
Remembering that $\Gamma^{\mathbb{R}^3} = A_1 \oplus E$, we have that (use the character table):

$$\begin{array}{r|ccc} & E & 2C_3 & 3\sigma_v \\ \hline A_1 \otimes \Gamma^{\mathbb{R}^3} & 3 & 0 & 1 \\ E \otimes \Gamma^{\mathbb{R}^3} & 6 & 0 & 0 \\ A_2 \otimes \Gamma^{\mathbb{R}^3} & 3 & 0 & -1 \end{array} \tag{30}$$

which decompositions are:

$$\begin{aligned} A_1 \otimes \Gamma^{\mathbb{R}^3} &= A_1 \oplus E \\ E \otimes \Gamma^{\mathbb{R}^3} &= A_1 \oplus 2E \oplus A_2 \\ A_2 \otimes \Gamma^{\mathbb{R}^3} &= A_2 \oplus E \end{aligned} \tag{31}$$

With that information in hand, we can say that if $\phi_i$ is of representation $A_1$, $\phi_j$ cannot be of representation $A_2$ for the integral to be non-zero. Similarly, if $\phi_i$ is of representation $A_2$, $\phi_j$ cannot be of representation $A_1$, and there is no condition on $\phi_j$ when $\phi_i$ is of representation $E$.

This also gives us the following insight into the two interesting particular integrals of Eq. [25] : the overlap and the Hamiltonian expectation value. The Hamiltonian $H$ has the full symmetry of the molecule, and both these integrals are non-zero if $\Gamma^i \otimes \Gamma^j$ contains $A_1$ in its decomposition, *i.e.* if $\phi_i$ and $\phi_j$ belong to the same representation. A good way to see this is to look at the calculation of $a_{A_1}$ and realize that it yields the orthonormality formula for the characters:

$$\begin{aligned} a_{A_1} &= \frac{1}{g} \sum_{R=1}^{g} \chi_R^{A_1} \chi_R^{\Gamma^i \otimes \Gamma^j} \\ &= \frac{1}{g} \sum_{R=1}^{g} \chi_R^{\Gamma^i} \chi_R^{\Gamma^j} \\ &= \delta_{\Gamma^i \Gamma^j} \end{aligned} \tag{32}$$

Hence, an overlap integral vanishes unless the two orbitals transforms as the same symmetry, and in the same manner, an Hamiltonian expectation value is non-zero only if the functions involved belong to the same irreducible representation. Those are very important informations obtained at little cost.

### 3.5 Molecular symmetry orbitals

The selection rules are applicable with any functions of which we know the representations, but they are best used in a context where the functions *are* irreducible representations of the Hamiltonian group. In the same way, the Hamiltonian is block-diagonal with basis functions that *are* irreducible representations.

It is then preferable to construct a basis of molecular orbitals from atomic orbitals in a way that ensures that they are irreducible representations, so that the Hamiltonian will naturally be in block-diagonal form and the selection rules will be easy to use.

/First of all, as a reminder : why are we using and talking about molecular orbitals? In quantum chemistry, we usually modelize the poly-electronic problem (the poly-electronic Hamiltonian) by the superposition of mono-electronic problems (a sum of mono-electronic Hamiltonians). The eigenstates of the initial problem are found from the eigenstates of the mono-electronic Hamiltonians, which are mono-electronic functions called the molecular orbitals. We can show that an infinite ensemble of molecular orbitals form an orthonormal basis of $\mathcal{L}^2(\mathbb{R}^3, \mathbb{C})$ (the space of the square-integrable functions of $\mathbb{R}^3$

in $\mathbb{C}$), possibly of $\mathcal{L}^2(\mathbb{R}^3 \otimes \mathbb{S}, \mathbb{C})$, when using spin-orbitals that exist in a space-spin space. We form our functions of $\mathcal{L}^2(\mathbb{R}^{3N}, \mathbb{C})$ or of $\mathcal{L}^2((\mathbb{R}^3 \otimes \mathbb{S})^N, \mathbb{C})$ as (eventually anti-symmetrized) products of these molecular orbitals. The molecular orbitals are the basis of our treatments in quantum chemistry and a lot is gained when they are constructed with symmetry informations built-in./

The way this is done is to use intermediary functions called Symmetry Adapted Linear Combinations (SALCs). The SALCs are linear combinations of atomic orbitals that each span a given irreducible representation. From a given set of chosen atomic orbitals (that must span a space invariant by $G$), the SALCs are the set of linear combiations that put the matrices associated with the representations into block-diagonal form.

The powerful tool is that these SALCs are found by projecting each atomic orbital on the irreducible representations of the group. The projector on an irreducible representation $\Gamma^i$ is:

$$\hat{P}^{\Gamma^i} = \frac{1}{g} \sum_{R=1}^{g} \chi_R^{\Gamma^i} R \tag{33}$$

This projector, for each symmetry operation $R$, acts on a given function and multiplies the result by the character of the target irreducible representation.

This is probably best understood through example. Let us construct the table of the $Rf_i$ for the basis of the $s$ valence orbitals of $NH_3$ :

$$\begin{array}{c|cccc} & s_N & s_1 & s_2 & s_3 \\ \hline E & s_N & s_1 & s_2 & s_3 \\ C_3 & s_N & s_2 & s_3 & s_1 \\ C_3^2 & s_N & s_3 & s_1 & s_2 \\ \sigma_a & s_N & s_1 & s_3 & s_2 \\ \sigma_b & s_N & s_2 & s_1 & s_3 \\ \sigma_c & s_N & s_3 & s_2 & s_1 \end{array} \tag{34}$$

For a brute construction of the SALCs, for each irreducible representations $A_1$, $E$ and $A_2$, one needs to multiply the table by the appropriate characters and sum the columns.
For $A_1$, all the characters are 1, so that we obtain:

$$\begin{aligned} s_N &\to 6\,(s_N) \\ s_1 &\to 2\,(s_1 + s_2 + s_3) \\ s_2 &\to 2\,(s_1 + s_2 + s_3) \\ s_3 &\to 2\,(s_1 + s_2 + s_3) \end{aligned}$$

*i.e.* , we obtain two linearly independent SALCs from the projection of the atomic orbial basis on $A_1$: $\phi_1 = s_N$ and $\phi_2 = s_1 + s_2 + s_3$ (we do not bother with orthonormalization here).

For $E$, the table multiplied by the characters $\Gamma_R^E$ yields:

$$\begin{array}{c|cccc} & s_N & s_1 & s_2 & s_3 \\ \hline E & 2s_N & 2s_1 & 2s_2 & 2s_3 \\ C_3 & -s_N & -s_2 & -s_3 & -s_1 \\ C_3^2 & -s_N & -s_3 & -s_1 & -s_2 \\ \sigma_a & 0 & 0 & 0 & 0 \\ \sigma_b & 0 & 0 & 0 & 0 \\ \sigma_c & 0 & 0 & 0 & 0 \end{array} \tag{35}$$

and we obtain:

$$\begin{aligned} s_N &\to 0 \\ s_1 &\to 2s_1 - s_2 - s_3 \\ s_2 &\to 2s_2 - s_1 - s_3 \\ s_3 &\to 2s_3 - s_1 - s_2 \end{aligned}$$

which are not linearly independent. Two linear dependent combinations of these functions are $\phi_3 = 2s_1 - s_2 - s_3$ and $\phi_4 = 2_2 - s_3$.

The table multiplied by the characters of $A_2$ is:

$$\begin{array}{c|cccc} & s_N & s_1 & s_2 & s_3 \\ \hline E & s_N & s_1 & s_2 & s_3 \\ C_3 & s_N & s_2 & s_3 & s_1 \\ C_3^2 & s_N & s_3 & s_1 & s_2 \\ \sigma_a & -s_N & -s_1 & -s_3 & -s_2 \\ \sigma_b & -s_N & -s_2 & -s_1 & -s_3 \\ \sigma_c & -s_N & -s_3 & -s_2 & -s_1 \end{array} \tag{36}$$

which yields no SALCs. This could have been predicted from various reasons:

1. We already otained four SALCs, which is the dimension of the irreducible representation space (the sum of the column $E$ in the character table), so the SALCs set is complete.
2. We already know that the space $\mathbb{R}^3$ does not contain $A_2$.
3. More generally, we need only to search for SALCs in the irreducible representations that are in the decomposition of the atomic basis set chosen. Here $\{s_n, s_1, s_2, s_3\}$ decomposes into $2A_1 \oplus E$.

(Note that you still need to Schmidt-orthonormalize the set of SALCs.)

Remember that we worked with this atomic orbital basis before, and that the matrix $X$ (around Eq. [10]) was the one putting the matrix representations in common block-diagonal form. Indeed:

$$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1/\sqrt{3} & 1/\sqrt{3} & 1/\sqrt{3} \\ 0 & 2/\sqrt{6} & -1/\sqrt{6} & -1/\sqrt{6} \\ 0 & 0 & 1/\sqrt{2} & -1/\sqrt{2} \end{pmatrix} \begin{pmatrix} s_N \\ s_1 \\ s_2 \\ s_3 \end{pmatrix} = \begin{pmatrix} s_N \\ 1/\sqrt{3}(s_1 + s_2 + s_3) \\ 1/\sqrt{6}(2s_1 - s_2 - s_3) \\ 1/\sqrt{2}(s_2 - s_3) \end{pmatrix} \tag{37}$$

are the orthonormalized SALCs.