Basic notions of linear representations of symmetry groups for electronic structure theory

Emmanuel Giner

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1 General purpose and introduction

The use of group theory in quantum mechanics is extremely intensive: it ranges from molecular spectroscopy to particle physics. The application of group theory in quantum mechanics relies on the general concept of symmetries: if the Hamiltonian commutes with some operator S it means that some quantity is conserved, or in other words that there exists a good "quantum label" to distinguish between the eigenstates of the Hamiltonian. Group theory (or more precisely the theory of linear representation of the groups) is the natural framework to perform the link between symmetries and conservation. The global picture is the following.

1.1 Our goal

Consider a physical system which is invariant with respect to certain operations, such as rotations, translations, spatial inversions and so on. The operations leaving the system unchanged are then called *symmetries*. The system is described by a Hamiltonian H and our goal is to obtain the eigenvectors and eigenvalues of this Hamiltonian

$$H |\Psi_i\rangle = E_i |\Psi_i\rangle . \tag{1}$$

This Hamiltonian could be for instance the non relativistic Born Oppenheimer Hamiltonian, which is the general Hamiltonian describing electrons in matter. In general, the solutions of such an equation are extremely complex. Thanks to the symmetry of the system, we can strongly reduce the complexity of the solutions by carrying out the math of *linear representations of groups* which is at the heart of this lecture.

As a simple and pictorial example, we consider that H is just a one-electron Hamiltonian. The main idea is to find a *symmetry adapted* (SA) basis which will *block diagonalize the Hamiltonian*. To be more specific, thanks to the theory of linear representations we will be able to find the "intrinsic symmetry labels" of the problem which represents how basis functions are changed by the applications of the symmetry operations. For instance, even or odd functions with respect to a reflection plane are two different symmetry labels, and for spherically symmetrical problem, the angular momentum quantum number l of the spherical harmonics is the symmetry label. We call $\mathcal{B}^\alpha = \{|\chi_i^\alpha\rangle , i = 1, d_\alpha\}$ the SA basis for the symmetry label α which might contain d_α basis functions (for instance $\alpha = p$, $d_\alpha = 3$). In the language of group theory, the label α referred to the *irreducible representations* α and the d_α functions $|\chi_i^\alpha\rangle$ are called the *basis* for the irreducible representations.

A fundamental result of the theory of linear representation of groups (the so-called Schur's Lemma) is that the *Hamiltonian matrix elements are zero between two different symmetry labels*

$$\left\langle \chi_j^\beta \middle| H \middle| \chi_i^\alpha \right\rangle = 0 \quad \text{if } \alpha \neq \beta. \tag{2}$$

For instance, the Hamiltonian of a system with a reflection plane symmetry does not couple even or odd functions. The Hamiltonian of a spherically symmetrical system does not couple functions of different l. Therefore, we know that written on the SA basis, the Hamiltonian has a block-diagonal form

$$H = \begin{pmatrix} (H^\alpha) & 0 & 0 & \dots & 0 \\ 0 & (H^{\alpha'}) & 0 & \dots & 0 \\ 0 & 0 & (H^{\alpha''}) & \dots & 0 \end{pmatrix} \tag{3}$$

where H^α is the Hamiltonian matrix written in the basis of the irreducible representations of the symmetry label α. As a consequence, once found the irreducible representations and their basis functions, we have much smaller matrices to diagonalize and we can directly target a given symmetry sector by focusing only on a given irreducible representation.

For some symmetry groups the basis functions $|\chi_i^\alpha\rangle$ do not depend on the system as the spherical harmonics for the rotational group for instance. These are typically continuous groups for which a differential equation can be set up and therefore explicit analytical solutions can be obtained. Nevertheless, for symmetry groups with a finite number of elements (which are the most common in chemistry), the symmetry adapted basis functions χ_i^α have to be determined for each system, and to do so, we represent them in a given basis $\mathcal{B} = \{|\phi_i\rangle, i = 1, d\}$ which is not symmetry adapted. As a typical example, in electronic structure we usually take $\mathcal{B}$ to be a set of atomic orbitals (AO), which is a set of hydrogen-like functions centered on each atomic center of the molecular or solid-state system under study. Each of the AO is not symmetry adapted, but we look for linear combinations of such AOs which are symmetry adapted

$$|\chi_i^\alpha\rangle = \sum_{j=1,d} U_{ij}^\alpha |\phi_j\rangle, \tag{4}$$

where the U_{ij}^α are the coefficients that we are looking for. Therefore, we want to find a rotation between the basis $\mathcal{B}$ and $\mathcal{B}_{\text{SA}} = \cup_\alpha \mathcal{B}^\alpha$.

The Hamiltonian matrix written in the basis $\mathcal{B}$ is then

$$H_{ij} = \langle\phi_i|H|\phi_j\rangle, \tag{5}$$

$$H = \begin{pmatrix} & |\phi_1\rangle & |\phi_2\rangle & \dots & |\phi_n\rangle \\ \langle\phi_1| & H_{11} & H_{12} & \dots & H_{1n} \\ \langle\phi_2| & H_{21} & H_{22} & \dots & H_{2n} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \langle\phi_n| & H_{n1} & H_{n2} & \dots & H_{nn} \end{pmatrix}, \tag{6}$$

where the general expression of the eigenvectors $|\Psi_i\rangle$ onto the basis set $\mathcal{B}$ is

$$|\Psi_i\rangle = \sum_{j=1,d} c_{ij} |\phi_j\rangle, \tag{7}$$

and the dimension of the matrix often makes the solutions very hard to find. But when written in the whole SA basis $\mathcal{B}_{\text{SA}}$ made of the union of all the symmetry adapted basis $\mathcal{B}^\alpha$, one obtains a block diagonal form

$$H = \begin{pmatrix} (H^\alpha) & 0 & 0 & \dots & 0 \\ 0 & (H^{\alpha'}) & 0 & \dots & 0 \\ 0 & 0 & (H^{\alpha''}) & \dots & 0 \end{pmatrix}, \tag{8}$$

which makes the problem much easier. Another interesting aspect of group theory is to be able to give a *symmetry label* to each states of the Hamiltnonian, which is very important in spectroscopy for instance in order to identify each state.

1.2 Bonus: using symmetry for perturbation theory

Another fundamental application of group theory is to then study the system *perturbed by an operator V* and the associated *selection rules*.

- You assume that you have diagonalized H_0 and found the associated eigenvectors $|\Psi_i\rangle$
- If H_0 contains some spatial symmetries, then each $|\Psi_i\rangle = |\Psi_i^\alpha\rangle$ can be associated with a given symmetry label α.
- Assume that you want to compute the eigenvectors of $H = H_0 + V$ where V is some operator (spin-orbit, electric-dipole interaction, etc ...)
- Because of the results of group theory, you can write V as a sum of symmetry adapted operators

$$V = \sum_\alpha v_\alpha V^\alpha.$$

- Then you can *predict* if the operator V can couple two $|\Psi_i^\alpha\rangle$ and $\left|\Psi_j^\beta\right\rangle$, *i.e.* you can anticipate when $\left\langle\Psi_j^\alpha\middle|V\middle|\Psi_i^\beta\right\rangle$ is zero or not.
- You can then reduce the dimension of your problem and/or identify the *selection rules* (for instance two s functions of an atom are not coupled through the electric dipole moment).

Decomposing the Hamiltonian matrix in a block diagonal structure or the symmetry of some functions and operators turns out in applying the so-called *theory of linear representations of groups*. Such a theory allows to perform the link between the abstract definition of group axioms to actual mathematical tools which can be used in linear algebra.

2 Definition of symmetries in quantum mechanics

2.1 Symmetries as commuting operators

We say that our system is symmetric under the application of a symmetry transformation if their exists an *invertible* operator S associated with it which *leaves the Hamiltonian unchanged*, *i.e.* for which the corresponding operator commute with the Hamiltonian

$$\boxed{[H,S]=0 \text{ and } S \text{ is invertible} \Leftrightarrow S \textit{ represents a symmetry operation of the system.}} \tag{9}$$

Another useful way to see the commutation relation is to notice that

$$[H,S]=0 \Rightarrow HS=SH \Rightarrow S^{-1}HS=H. \tag{10}$$

This definition can be actually related to the concept of a *quantity which is constant in time*. Indeed, using the Heisenberg representation for a time independent Hamiltonian H and an operator S which is also time independent, the evolution of the expectation value of

$$\langle S(t)\rangle = \langle\psi|e^{iHt}Se^{-iHt}|\psi\rangle$$

where $|\psi\rangle = |\psi(t=0)\rangle$ is the initial wave function, is given by

$$i\hbar\frac{\partial}{\partial t}\langle S(t)\rangle = \langle\psi|\big[S,H\big]|\psi\rangle\,. \tag{11}$$

Therefore one sees that if $\big[S,H\big]=0$, one has

$$\langle S(t)\rangle = \langle S(t=0)\rangle, \tag{12}$$

and therefore that the expectation value is a constant of the motion.

As we are going to see later on, the relation of commutation of two operators as in Eq. (9) has three major implications:

- we can *assign to each eigenvector* of H an eigenvalue of S and therefore *a physical quantum number*,
- the set of operators commuting with H *forms a group in the mathematical sense*,
- we can use *the eigenvectors of S to block diagonalize the Hamiltonian H*.

Now suppose that there exists a set of operators $\mathcal{S}=\{S_i, i=1,g\}$ which commute with the Hamiltonian, but do not commute between each other (think about rotations of a spherical systems for instance). If we choose the eigenvector of a given operator S_i as a basis for the Hamiltonian, these functions will not be eigenvectors of another operator S_j if $[S_i,S_j]\neq 0$. Therefore what operator shall we choose as a basis ? As we shall see later on, group theory proposes a very nice solution to that: the irreducible representations.

2.2 A few examples of symmetries

According to the system under study, one might find different kind of symmetries. Here is a brief non exhaustive list of the kind of symmetries one can find in quantum mechanics.

- Non relativistic quantum mechanics:
  - Permutations between particles: defines the fermions/bosons symmetry together with the spin symmetry.
  - $[n, H] = 0$ where n is the "number" operator: the number of particles is necessary fixed.
  - Translational symmetry in solids: the momentum is conserved.
  - Rotational symmetry in atoms: the angular momentum is conserved.
  - Specific spatial rotations in molecules: not so clear what physical observable is it.
- Relativistic quantum mechanics:
  - Charge operator: the number of particles is not fixed but the charge is fixed.

2.3 Spatial symmetries as unitary spatial transformations

In the present lecture we will focus on groups of spatial symmetry which are made of three types of symmetry operations

- inversion with respect to a point, labelled I,
- rotations labelled C_n of an angle $\theta = 2\pi/n$ around an axis (by default z),
- reflection with respect to a plane *horizontal* (which means orthogonal) to the axis of the rotation and labelled σ_h,
- reflection with respect to a plane *vertical* (which means coplanar) to the axis of the rotation and labelled σ_v.

The group of translations will not be covered here.

These spatial symmetries belong to the general class of *unitary spatial transformations*. Let us consider a vector $\boldsymbol{r}$ of $\mathbb{R}^3$ and a spatial transformation which transforms $\boldsymbol{r}$ to $\boldsymbol{r'}$. We can represent such a transformation by a linear map (or a linear "application" in "frenglish") s such that

$$s\boldsymbol{r} = \boldsymbol{r'}. \tag{13}$$

Assuming an orthonormal basis $\{\boldsymbol{e}_x, \boldsymbol{e}_y, \boldsymbol{e}_z\}$ of $\mathbb{R}^3$, we can therefore obtain the matrix representation of s as

$$s_{ij} = \boldsymbol{e}_i \cdot s\boldsymbol{e}_j. \tag{14}$$

For the sake of lightness of notations, we will use the same notations for the linear map s and its matrix elements s_{ij}.

An important point that we require is that this spatial transformation is *unitary*, which means that it *preserves the scalar product*, which mathematically translates as

$$\begin{aligned} s\boldsymbol{r}_1 &= \boldsymbol{r'}_1 \\ s\boldsymbol{r}_2 &= \boldsymbol{r'}_2 \\ \Rightarrow \boldsymbol{r}_1 \cdot \boldsymbol{r}_2 &= \boldsymbol{r'}_1 \cdot \boldsymbol{r'}_2. \end{aligned} \tag{15}$$

This necessary implies that

$$s^{-1} = s^{\dagger}, \tag{16}$$

and therefore that the matrix elements fulfill

$$\sum_{i=1,n} s^*_{ij} s_{il} = \delta_{jl}. \tag{17}$$

2.4 How spatial transformations change functions

Knowing the matrix representation s_{ij} of a given symmetry operation s on $\mathbb{R}^3$, we want now to know how such an operator acts on functions $f(\mathbf{r}) = \langle \mathbf{r}|f\rangle$ (using Dirac's bra-ket notations)

$$\begin{aligned} |f_S\rangle &= S\,|f\rangle \\ \Leftrightarrow f_S(\mathbf{r}) &= \langle \mathbf{r}|f_S\rangle = \langle \mathbf{r}|S|f\rangle\,. \end{aligned} \tag{18}$$

A natural thing to require is that if we evaluate the function $|f_S\rangle$ at the point $\mathbf{r}' = s\mathbf{r}$, then it should give the same value as the original function $|f\rangle$ evaluated at the original point $\boldsymbol{r}$

$$\begin{aligned} f_S(\mathbf{r}') &= f(\mathbf{r}) \\ \Leftrightarrow f_S(s\mathbf{r}) &= f(\mathbf{r}) \end{aligned} \tag{19}$$

Since $\mathbf{r} = s^{-1}\mathbf{r}'$, then one obtains

$$f_S(\mathbf{r}') = f(s^{-1}\mathbf{r}'), \tag{20}$$

which is of course valid for any points $\mathbf{r}'$ which can then be relabelled $\mathbf{r}$

$$\boxed{f_S(\mathbf{r}) = f(s^{-1}\mathbf{r}).} \tag{21}$$

Thanks to these relations, we can then compute the matrix elements of symmetry operators on vector spaces made of functions. In the rest of the lecture we will be often using the same notation for the operator s acting in $\mathbb{R}^3$ and S which acts in a finite vector space made of functions.

2.4.1 Examples for point group symmetries

As an example, let us consider the H_2 molecule which is symmetrical with respect to a mirror plane symmetry operation σ_h orthogonal to the bonding axis which is taken along z. The two nuclei, labelled by H_A and H_B, have coordinates $\mathbf{R}_A = (0, 0, -R)$ and $\mathbf{R}_B = (0, 0, +R)$.

Such a symmetry operation σ_h sends a point (x, y, z) to $(x, y, -z)$. Therefore, the representation of the σ_h symmetry operation on $\mathbb{R}^3$ is

$$\sigma_h = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}. \tag{22}$$

You can notice that $\sigma_h = {\sigma_h}^{-1}$ as $(\sigma_h)^2 = \mathbb{1}$.

We want to know how such a symmetry operator acts on atomic functions centered on each atom. As an example, we take a vector space of dimension 2 spanned by the $1s$-like function for each atom

$$\begin{aligned} \phi^A_{1s}(\mathbf{r}) &= Ne^{-|\mathbf{r}-\mathbf{R}_A|} = Ne^{-\sqrt{x^2+y^2+(z-R)^2}}, \\ \phi^B_{1s}(\mathbf{r}) &= Ne^{-|\mathbf{r}-\mathbf{R}_B|} = Ne^{-\sqrt{x^2+y^2+(z+R)^2}}, \end{aligned} \tag{23}$$

N being a normalization factor.

If we apply σ_h on $\phi_{1s}(\mathbf{r})$, applying Eq. (21), one obtains

$$\begin{aligned} \sigma_h\phi^A_{1s}(\mathbf{r}) &= \phi^A_{1s}({\sigma_h}^{-1}\mathbf{r}) = \phi^A_{1s}(\sigma_h\mathbf{r}) \\ &= Ne^{-\sqrt{x^2+y^2+((-z)-R)^2}} \\ &= Ne^{-\sqrt{x^2+y^2+(z+R)^2}} \\ &= \phi^B_{1s}(\mathbf{r}). \end{aligned} \tag{24}$$

Therefore we see that σ_h "sends" $\phi_{1s}^A(\mathbf{r})$ to $\phi_{1s}^B(\mathbf{r})$, just as σ_h "sends" the vector $\mathbf{R}_A$ into $\mathbf{R}_B$. We can then represent the σ_h operator in a matrix form on the basis of $\left|\phi_{1s}^A\right\rangle$ and $\left|\phi_{1s}^B\right\rangle$ by

$$\sigma_h = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \tag{25}$$

We shall find this example many times in the lecture.

2.4.2 Example with rotations in $\mathbb{R}^3$

Let us take the example of a rotation r_θ around the z axis in the trigonometric direction of angle θ. The matrix representation of r_θ on $\mathbb{R}^3$ is

$$r_\theta = \begin{pmatrix} \cos(\theta) & -\sin(\theta) & 0 \\ \sin(\theta) & \cos(\theta) & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{26}$$

Suppose now that we want to represent the rotation on the vector space spanned by the three following orthonormal functions

$$\begin{aligned} f_x(\boldsymbol{r}) &= Nxe^{-(x^2+y^2+z^2)} \\ f_y(\boldsymbol{r}) &= Nye^{-(x^2+y^2+z^2)} \\ f_z(\boldsymbol{r}) &= Nze^{-(x^2+y^2+z^2)} \end{aligned} \tag{27}$$

where N is the normalization factor such that $\langle f_i | f_i \rangle = 1$ for $i = x, y, z$. This means that we want to find how such a rotation transforms these functions in order to set up a *matrix representation*.

We define the rotation operator R_θ acting on vector spaces made of functions as

$$\left| f^\theta \right\rangle = R_\theta \left| f \right\rangle, \tag{28}$$

then we know from Eq. (21) that

$$f^\theta(\boldsymbol{r}) = f({r_\theta}^{-1}\boldsymbol{r}). \tag{29}$$

As the operator r_θ is unitary and real one obtains that

$${r_\theta}^{-1} = \begin{pmatrix} \cos(\theta) & \sin(\theta) & 0 \\ -\sin(\theta) & \cos(\theta) & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{30}$$

and therefore that

$${r_\theta}^{-1}\boldsymbol{r} = \begin{pmatrix} \cos(\theta)x + \sin(\theta)y \\ -\sin(\theta)x + \cos(\theta)y \\ z \end{pmatrix}. \tag{31}$$

Evaluating the original function $f(\boldsymbol{r})$ at the point ${r_\theta}^{-1}\boldsymbol{r}$ yields the expression for the rotated function

$$f^\theta(x, y, z) = f(\cos(\theta)x + \sin(\theta)y,\, -\sin(\theta)x + \cos(\theta)y,\, z). \tag{32}$$

Let us apply such a result on the basis functions $f_x(\boldsymbol{r})$, $f_y(\boldsymbol{r})$ and $f_z(\boldsymbol{r})$

$$\begin{aligned}
f_x^\theta(\boldsymbol{r}) &= R_\theta f_x(\boldsymbol{r}) \\
&= N\big(\cos(\theta)x + \sin(\theta)y\big) \exp\Big(-\big(\cos(\theta)x + \sin(\theta)y\big)^2 - \big(-\sin(\theta)x + \cos(\theta)y\big)^2 - z^2\Big) \\
&= N\big(\cos(\theta)x + \sin(\theta)y\big) e^{-(x^2+y^2+z^2)} \\
&= \cos(\theta) f_x(\boldsymbol{r}) + \sin(\theta) f_y(\boldsymbol{r}), \\
f_y^\theta(\boldsymbol{r}) &= R_\theta f_y(\boldsymbol{r}) \\
&= N\big(-\sin(\theta)x + \cos(\theta)y\big) e^{-(x^2+y^2+z^2)} \\
&= -\sin(\theta) f_x(\boldsymbol{r}) + \cos(\theta) f_y(\boldsymbol{r}), \\
f_z^\theta(\boldsymbol{r}) &= R_\theta f_z(\boldsymbol{r}) \\
&= N z e^{-(x^2+y^2+z^2)} \\
&= f_z(\boldsymbol{r}).
\end{aligned} \tag{33}$$

We can then obtain the matrix representation of R_θ on the three basis function as

$$R_\theta = \begin{pmatrix} \cos(\theta) & -\sin(\theta) & 0 \\ \sin(\theta) & \cos(\theta) & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{34}$$

The reason why the matrix representations on two different vector spaces turn out to be exactly the same matrix is because the functions are transformed exactly as the basis vectors of $\mathbb{R}^3$.

3 Definitions of groups

3.1 Definitions of the notion of group and a few examples

Definition:*Composition law*
A *composition law* is a correspondence between any couple of elements (G, B) belonging to a set $\mathcal{G}$ and another element C, not necessarily belonging to $\mathcal{G}$. In the case of groups we will use the notation: $C = AB$. If the composition law is such that $\forall\ (A, B) \in \mathcal{G}$, $C = AB \in \mathcal{G}$ then the composition law is said to be *internal*.

Definition:*Group*
A *group* is a set of elements, endorsed with an *internal composition law*, verifying the following properties:

- the composition law is *associative*:

$$\forall (A, B, C) \in \mathcal{G} \text{ the composition law verifies } A(BC) = (AB)C, \tag{35}$$

- there exists a *neutral element* E in the set $\mathcal{G}$:

$$\exists E \in \mathcal{G} \quad \text{such that } \forall A \in \mathcal{G}, \quad EA = A\ E = A, \tag{36}$$

- all elements $A \in \mathcal{G}$ has an *inverse*:

$$\forall A \in \mathcal{G}, \quad \exists\, A^{-1} \in \mathcal{G} : \text{such that} \quad AA^{-1} = A^{-1}A = E \tag{37}$$

In the rest of the lecture I will be using the symbol G.
Definition:*Order of the group*
The order of the group $\mathcal{G}$, labelled g, is simply the number of elements of $\mathcal{G}$.

Definition:*Multiplication table*
A group is totally determined by its *multiplication table*, *i.e.* the list of relations between the different elements of the group with the composition law:

$$G_i G_j = G_k \quad \forall (G_i, G_j) \in \mathcal{G}. \tag{38}$$

Definition:*Commutative group, or Abelian group*
A group $\mathcal{G}$ is said to be *Abelian* or *commutative* if:

$$\forall\ (A, B) \in \mathcal{G},\ AB = BA. \tag{39}$$

Examples:

1) $\mathbb{Z}$ endorsed with the composition law "addition" is a commutative group of infinite order,
2) $\mathbb{Z}^*$ endorsed with the composition law "multiplication" is not a group,
3) The set of invertible matrices, endorsed with the composition law "addition" is not a group,
4) The set of real valued invertible matrices, endorsed with the composition law "multiplication" is a non-commutative group of infinite order called $\mathrm{GL}(n; \mathbb{R})$
5) The set of 3 clockwise rotations of $2\pi/3$ of a equilateral triangle is a commutative group of order 3, it is the point group $\mathcal{C}_3$,
6) The set of 3 clockwise rotations of $2\pi/3$ together with the set of 3 reflections by the 3 medians is a non commutative group of order 6 it is the $\mathcal{C}_{3v}$ group,
7) The set of rotations in dimension 2 of angle ϕ is an Abelian continuous group,
8) The set of rotations in dimension 3 of angles (θ, ϕ) in a non Abelian continuous group, the SO(3) group.

3.2 Why symmetry operators necessarily form a group?

Let $\mathcal{S} = \{S_i, i = 1, g\}$ be the set of invertible operators commuting with a Hamiltonian H, *except for H itself*

$$\mathcal{S} = \Big\{ S_i, i = 1, g \text{ s.t } [S_i, H] = 0 \text{ and } \exists\, {S_i}^{-1}\, \forall\, S_i, H \text{ excluded} \Big\}. \tag{40}$$

Any element S of $\mathcal{S}$ is a symmetry operator and the commuting relation implies that

$$SHS^{-1} = S^{-1}HS = H \Leftrightarrow S \in \mathcal{S}. \tag{41}$$

A very interesting property of this relationship is that it induces *a group structure*. Indeed, one has that

- For two elements S_i and $S_j \in \mathcal{S}$, the product of such an element is $S_j S_i$ and we have that

$$\begin{aligned} S_j S_i H \big(S_j S_i\big)^{-1} &= S_j \underbrace{S_i H {S_i}^{-1}}_{=H} {S_j}^{-1} \\ &= S_j H {S_j}^{-1} \\ &= H, \end{aligned} \tag{42}$$

  therefore the product of two elements of the set remains in the set, and therefore *the composition law is internal.*

- Operators defined on Hilbert space fulfill

$$\big(S_k S_j\big) S_i \left|\Psi\right\rangle = S_k \big(S_j S_i\big) \left|\Psi\right\rangle , \tag{43}$$

  Therefore the *composition law is associative.*

- The identity operator $\mathbb{1}$ is *the neutral element.*

- Also, for a given operator $S \in \mathcal{S}$ we postulate that there exists an inverse element S^{-1}, and such element S^{-1} satisfies

$$S^{-1} H \big(S^{-1}\big)^{-1} = S^{-1} H S = H, \tag{44}$$

  and therefore S^{-1} is also in the set.

Therefore, the rest of the lecture will be devoted to the study of the linear representation of group in order to take advantage of this nice structure.

3.3 Examples of groups

3.3.1 The group of order 2

Group of order 2
We consider the group of order 2. Because of the very definition of the group one must have

$$\mathcal{G} = \{E, A\ \}, \tag{45}$$

with $A = A^{-1}$, or equivalently $AA = E$. The multiplication table of such a group is trivial

G_j \ G_i	E	A
E	E	A
A	A	E

The group of order 2 is isomorph to various symmetry groups called $\mathcal{C}_s$, $\mathcal{C}_i$ or $\mathcal{C}_2$. For instance, the group $\mathcal{C}_s$ is defined by the two elements $\mathcal{C}_s = \{E, \sigma_h\ \}$, where σ_h is the orthogonal symmetry plane of a homonuclear diatomic molecule, and the multiplication table of $\mathcal{C}_s$ is

G_j \ G_i	E	σ_h
E	E	σ_h
σ_h	σ_h	E

Therefore, any results obtained on the group of order 2 is transferable on the group $\mathcal{C}_s$. We can also notice that the group of order 2 is isomorph to the group of permutations of two elements called Sym(2) which is composed of $\text{Sym}(2) = \{E, p_{12}\}$ where p_{12} exchanges the two elements.

3.3.2 The group $\mathcal{C}_{3v}$

The group $\mathcal{C}_{3v}$ is the group of all elements leaving unchanged an equilateral triangle, which contains

- the identity,
- two rotations which are C_3 and ${C_3}^{-1}$,
- three reflections called σ_1, σ_2 and σ_3 through axes which are the three medians of the triangle.

As any of these operations leave the triangle unchanged, any composition of these operations is also in the set, and therefore the set

$$\mathcal{C}_{3v} = \{ E, C_3, {C_3}^{-1}, \sigma_1, \sigma_2, \sigma_3\} \tag{46}$$

is closed. One can establish the multiplication table of $\mathcal{C}_{3v}$ as follows

G_j \ G_i	E	C_3	${C_3}^{-1}$	σ_1	σ_2	σ_3
E	E	C_3	${C_3}^{-1}$	σ_1	σ_2	σ_3
C_3	C_3	${C_3}^{-1}$	E	σ_3	σ_1	σ_2
${C_3}^{-1}$	${C_3}^{-1}$	E	C_3	σ_2	σ_3	σ_1
σ_1	σ_1	σ_2	σ_3	E	C_3	${C_3}^{-1}$
σ_2	σ_2	σ_3	σ_1	${C_3}^{-1}$	E	C_3
σ_3	σ_3	σ_1	σ_2	C_3	${C_3}^{-1}$	E

We can notice that for instance $C_3\sigma_1 = \sigma_3$ and $\sigma_1 C_3 = \sigma_2$. Therefore the $\mathcal{C}_{3v}$ group is non Abelian.

The group $\mathcal{C}_{3v}$ is isomorph to the group of permutations of three elements called Sym(3) which is composed of the identity, two cyclic permutations (which can be referred to as the C_3 and ${C_3}^{-1}$ in $\mathcal{C}_{3v}$) and three non cyclic permutations (the σ_1, σ_2 and σ_3 in $\mathcal{C}_{3v}$). In general, all finite groups are subgroups of a permutation group.

3.4 Conjugate elements, classes

3.4.1 Conjugate element

Two elements A and B are said to be *conjugate* if there exists a group element G such that $A = GBG^{-1}$. We also say that A is obtained from B through a transformation by G.
Remark:
The neutral (or the identity) E is necessarily a class, and is the only element in that class.

The set of all elements that are conjugated with each other is called a *conjugate class*, noted $\mathcal{C}$. In an Abelian group, as all elements commute through the multiplication, one obtains that

$$GAG^{-1} = AGG^{-1} = A, \tag{47}$$

and therefore that *each element consists in a class in an Abelian group.*

The $\mathcal{C}_{3v}$ group is a good example to see conjugated elements. Indeed, from the multiplication table of C_{3v} one can notice that

$$C_3\sigma_1 = \sigma_3 \Rightarrow {\sigma_1}^{-1}C_3\sigma_1 = {\sigma_1}^{-1}\sigma_3 \tag{48}$$

but as all reflections σ_i are their one inverse as $\sigma_i\sigma_i = E$, one obtains that

$${\sigma_1}^{-1}C_3\sigma_1 = \sigma_1\sigma_3 = {C_3}^{-1}, \tag{49}$$

and therefore one can see that the two elements C_3 and ${C_3}^{-1}$ are *conjugated* and form a *class* because they are linked by σ_1. Inversely, one can show that the σ_i are also conjugated (through the C_3 and ${C_3}^{-1}$ elements) and form another class.

In general, the "geometrically equivalent" operations belong to the same class (*i.e.* rotations with rotations, inversions with inversions and so on).

4 Basic concepts about the theory of linear representation of groups

As it was introduced before, the spatial symmetries of a given system obey to the abstract notions of the axioms of group theory. In order to be able to take advantage of the consequences of these axioms in practice, one needs a mathematical representation of these groups, *i.e.* a way to know how to transform the abstract notions of symmetry operation into the concrete notion of operators acting on the vector spaces we use in quantum mechanics. The theory of group representation is a powerful general mathematical framework able to provide important theorems which will be used to obtain a systematic way of representing the symmetry operators.

4.1 The definition of a representation of a group

Definition:*Linear representation of groups*
A *linear representation* of a group $\mathcal{G}$ of order g (g being finite or not) *on a vector space* $\mathcal{V}$ of dimension d is *a set of* g *matrices of dimension* $d \times d$ *which have the same multiplication table than the group* $\mathcal{G}$

$$\begin{aligned}\Gamma^{\mathcal{V}} = & \{\Gamma^{\mathcal{V}}(G_i) \text{ is a matrix } d \times d; i = 1, g \\ & \text{such that if } G_i G_j = G_k \text{ then } \Gamma^{\mathcal{V}}(G_i)\Gamma^{\mathcal{V}}(G_j) = \Gamma^{\mathcal{V}}(G_k)\}.\end{aligned} \tag{50}$$

We say that $\mathcal{V}$ *is a representation space* of $\mathcal{G}$. When no ambiguity is found, we will drop the upper index $\mathcal{V}$.
If all the matrices are different, we say that the group representation $\Gamma^{\mathcal{V}}$ is *true* or *faithful*.
Given this definition, there exists an infinite number of representations of a group $\mathcal{G}$ because

- by changing of vector space $\mathcal{V}$ one changes the representation of the group,
- within the same vector space $\mathcal{V}$ one has an infinite number of possible similarity transformations (*i.e.* change of the basis) which provide matrices with the same multiplication table.

The *dimension* of a representation is the dimension of the vector space $\mathcal{V}$, or in other terms the *rank of the matrices used to represent the various elements of the group.*
Remark:
You can also use a more conceptual definition for linear representations which do not use the notion of the basis for $\mathcal{V}$, but that uses only a set of g linear maps $\{\Gamma(G_i)\}$ from $\mathcal{V}$ to $\mathcal{V}$ fulfilling the group multiplication table

$$(\Gamma, \mathcal{V}) = \{\Gamma(G_i) : \mathcal{V} \to \mathcal{V},\ \Gamma(G_i)\Gamma(G_j)\,|u\rangle = \Gamma(G_k)\,|u\rangle \quad \text{if } G_i\,G_j = G_k \quad \forall\,|u\rangle \in \mathcal{V} \text{ and } \forall G_i, G_j \in \mathcal{G}\}. \tag{51}$$

Definition:*Equivalent representations*
We say that two representations $\Gamma^{\mathcal{V}_1}$ and $\Gamma^{\mathcal{V}_2}$ are *equivalent* if the g matrices of $\Gamma^{\mathcal{V}_2}$ can be obtained by applying *a unique* similarity transformation on *all matrices of* $\Gamma^{\mathcal{V}_1}$

$$\Gamma^{\mathcal{V}_1} \text{ and } \Gamma^{\mathcal{V}_2} \text{ are equivalent if } \exists! T \text{ such that } \Gamma^{\mathcal{V}_2}(G_i) = T^{-1}\Gamma^{\mathcal{V}_1}(G_i)T, \quad \forall G_i \in \mathcal{G}, \tag{52}$$

where T is an invertible matrix. Therefore equivalent representations differ by a change of basis, which implies that the vector spaces $\Gamma^{\mathcal{V}_1}$ and $\Gamma^{\mathcal{V}_2}$ must be isomorph, *i.e.* of the same dimension.
Theorem: *Unitary representations*
Any representation $\Gamma^{\mathcal{V}}$ is equivalent to a unitary representation, *i.e.* a representation where all matrices $\Gamma^{\mathcal{V}}(G_i)$ are unitary. Therefore, from thereon we can only focus on the unitary representations.
Definition:*basis for a representation*
Let $\{|e_i\rangle, i = 1, d'\ \}$ with $d' \leq d$ be a set of linearly independent vectors of $\mathcal{V}$. We say that this set of vector forms a *basis for the representation of* $\mathcal{G}$ *in* $\mathcal{V}$ if

$$\Gamma^{\mathcal{V}}(G_k)\,|e_i\rangle = \sum_{j=1,d} c_j\,|e_j\rangle \quad \forall G_k\, \in \mathcal{G}, \tag{53}$$

i.e. if the set $\{|e_i\rangle, i = 1, d'\ \}$ is closed under the application of any matrix $\Gamma^{\mathcal{V}}(G_k)$.

4.2 Summary of the general strategy to obtain a representation of a group

The general strategy to represent a group $\mathcal{G} = \{G_i, i = 1, g\}$ of order g is the following

1) Choose a vector space $\mathcal{V}$ of dimension d,
2) Choose a basis set $\mathcal{B}$ of $\mathcal{V}$,
3) Find a set of g linear maps $\mathcal{V} \to \mathcal{V}$ whose matrix representations $\Gamma^{\mathcal{V}} = \{\Gamma^{\mathcal{V}}(G_i), i = 1, g\}$ are such that these matrices reproduce the multiplication table of the group.

It should be pointed here that having a faithful representation is not necessary to obtain a representation, which means that some matrices can be the same.

4.3 A pictorial and simple example: the group of order 2

4.3.1 Example of representation on $\mathbb{R}^2$

The group of order 2 composed of two elements E and A is isomorph with different symmetry groups (like $\mathcal{C}_s$ or $\mathcal{C}_2$ for instance). To represent the group of order 2, we will choose the $\mathbb{R}^2$ vector space which will then give us matrices of rank 2. We assume that we take a basis $\mathcal{B} = \{|e_1\rangle, |e_2\rangle\}$ of $\mathbb{R}^2$ (which do not need to be orthonormal by the way). We then just need to take two matrices of rank 2 which admit the same multiplication table which is

$G_j \backslash G_i$	E	A
E	E	A
A	A	E

(54)

A first faithful representation of the group of order 2 is

$$\Gamma_1^{\mathbb{R}^2} = \{\Gamma_1^{\mathbb{R}^2}(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \Gamma_1^{\mathbb{R}^2}(A) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\}. \tag{55}$$

Indeed we have that

$$\Gamma_1^{\mathbb{R}^2}(E)\Gamma_1^{\mathbb{R}^2}(A) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \Gamma_1^{\mathbb{R}^2}(A), \tag{56}$$

and of course that

$$\Gamma_1^{\mathbb{R}^2}(A)\Gamma_1^{\mathbb{R}^2}(E) = \Gamma_1^{\mathbb{R}^2}(A). \tag{57}$$

Eventually, we also have that

$$\Gamma_1^{\mathbb{R}^2}(A)\Gamma_1^{\mathbb{R}^2}(A) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \Gamma_1^{\mathbb{R}^2}(E). \tag{58}$$

Another non faithful representation in $\mathbb{R}^2$ could be

$$\Gamma_2^{\mathbb{R}^2} = \{\Gamma_2^{\mathbb{R}^2}(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \Gamma_1^{\mathbb{R}^2}(A) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\}, \tag{59}$$

which obviously reproduces the multiplication table. As one cannot obtain $\Gamma_1^{\mathbb{R}^2}$ from $\Gamma_2^{\mathbb{R}^2}$ by a similarity transformation, these two representations *are not equivalent* although they live in the same vector space and the same basis.

4.3.2 Equivalent representations: change of basis

The basis $\mathcal{B}$ is therefore the basis for our representation $\Gamma_1^{\mathbb{R}^2}$, but you can notice that $|e_1\rangle$ itself (or $|e_2\rangle$) does not form a basis for the representation $\Gamma_1^{\mathbb{R}^2}$. Indeed, as $\Gamma_1^{\mathbb{R}^2}(A)$ has extra diagonal elements one obtains that

$$\Gamma_1^{\mathbb{R}^2}(A)\,|e_1\rangle \neq \lambda\,|e_1\rangle\,, \;\; \lambda \in \mathbb{R}. \tag{60}$$

An equivalent representation to $\Gamma_1^{\mathbb{R}^2}$ would be obtained by a change of basis. For instance one can define the basis $\mathcal{B}_\theta = \{|u_1\rangle, |u_2\rangle\}$ obtained from the rotation of an angle θ of the original basis $\mathcal{B}$

$$\begin{aligned} |u_1\rangle &= \cos(\theta)\,|e_1\rangle + \sin(\theta)\,|e_2\rangle\,, \\ |u_2\rangle &= -\sin(\theta)\,|e_1\rangle + \cos(\theta)\,|e_2\rangle\,. \end{aligned} \tag{61}$$

If we re express the matrices of $\Gamma_1^{\mathbb{R}^2}$ in the basis $\mathcal{B}_\theta = \{|u_1\rangle, |u_2\rangle\}$, we can obtain a new representation noted here $\Gamma_\theta^{\mathbb{R}^2}$

$$\Gamma_\theta^{\mathbb{R}^2} = \{\Gamma_\theta^{\mathbb{R}^2}(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \Gamma_\theta^{\mathbb{R}^2}(A) = \begin{pmatrix} \sin(2\theta) & 1 - 2\big(\sin(\theta)\big)^2 \\ 1 - 2\big(\sin(\theta)\big)^2 & \sin(2\theta) \end{pmatrix}\}, \tag{62}$$

and you can of course verify that it fulfills also the multiplication table of the group. You can also notice that for $\theta = \pi/4$, as $\cos(\pi/4) = \sin(\pi/4) = \frac{1}{\sqrt{2}}$, one obtains a block diagonal representation

$$\Gamma^{\mathbb{R}^2}_{\pi/4} = \{\Gamma^{\mathbb{R}^2}_{\pi/4}(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \Gamma^{\mathbb{R}^2}_{\pi/4}(A) = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\}. \tag{63}$$

This corresponds to the change of basis

$$\begin{aligned} |u_1\rangle &= \frac{1}{\sqrt{2}}\big(\,|e_1\rangle + |e_2\rangle\,\big), \\ |u_2\rangle &= \frac{1}{\sqrt{2}}\big(\,|e_1\rangle - |e_2\rangle\,\big). \end{aligned} \tag{64}$$

It is interesting to see that $|u_1\rangle$ and $|u_2\rangle$ form two basis of dimension 1 to the representation $\Gamma^{\mathbb{R}^2}_{\pi/4}$ of dimension 2 as now the matrix $\Gamma^{\mathbb{R}^2}_{\pi/4}(A)$ is diagonal

$$\begin{aligned} &\Gamma^{\mathbb{R}^2}_{\pi/4}(A)\,|u_1\rangle \propto |u_1\rangle \\ &\Gamma^{\mathbb{R}^2}_{\pi/4}(A)\,|u_2\rangle \propto |u_2\rangle\,. \end{aligned} \tag{65}$$

Therefore we have identified two smaller basis for the representation of the group, so we feel that we have "reduced" the information.

4.3.3 Other examples of representations

One can also obtain a smaller non faithful representation $\Gamma^{\mathbb{R}}_g$ by representing the group on $\mathbb{R}$ as follows

$$\Gamma^{\mathbb{R}}_g = \{\Gamma^{\mathbb{R}}_g(E) = 1,\, \Gamma^{\mathbb{R}}_g(A) = 1\}, \tag{66}$$

because indeed these one-by-one matrices fulfill the multiplication table of the group. Another one-dimensional *faithful* representation could be the following

$$\Gamma^{\mathbb{R}}_u = \{\Gamma^{\mathbb{R}}_u(E) = 1,\, \Gamma^{\mathbb{R}}_u(A) = -1\}, \tag{67}$$

because indeed these one-by-one matrices fulfill the multiplication table of the group. These two representations *are not equivalent* as there do not exist any similarity transformation that can connect them.

One can also do the opposite and enlarge the representation $\Gamma^{\mathbb{R}^2}_1$ from $\mathbb{R}^2$ to $\mathbb{R}^3$ by just adding one extra dimension which is not coupled. To be more specific we can for instance obtain a representation $\Gamma^{\mathbb{R}^3}_1$ as the following two matrices

$$\Gamma^{\mathbb{R}^3}_1 = \{\Gamma^{\mathbb{R}^3}_1(E) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \Gamma^{\mathbb{R}^3}_1(A) = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}\}, \tag{68}$$

as the fact of adding an uncoupled dimension to the previous matrices does not affect the multiplication table. Therefore the two representations $\Gamma^{\mathbb{R}^2}_1$ and $\Gamma^{\mathbb{R}^3}_1$ are truly different as they cannot be obtained one from another by a similarity transformation because the vector spaces on which these representations are defined do not have the same dimension. Therefore they are *non equivalent*.

4.3.4 Application to H_2^+

As we know that the group of order 2 and $\mathcal{C}_s = \{E, \sigma_h\}$ have the same multiplication table, we can now apply the results of the abstract group of order 2 to the symmetry group and use it to describe the H_2^+ molecule.

The Born Oppenheimer Hamiltonian for H_2^+ is

$$H(R) = -\frac{1}{2}\Delta_{\mathbf{r}} - (\frac{1}{|\mathbf{r}_i - \mathbf{R}_A|} + \frac{1}{|\mathbf{r}_i - \mathbf{R}_B|}), \tag{69}$$

and we use the set of two functions $\mathcal{B} = \{|\phi_{1s}^A\rangle, |\phi_{1s}^B\rangle\}$ previously described as a basis for the for our problem, which defines the vector space $\mathcal{V} = \{|v\rangle = c_A|\phi_{1s}^A\rangle + c_B|\phi_{1s}^B\rangle,\ (c_A, c_B) \in \mathbb{R}^2\} \equiv \text{span}(|\phi_{1s}^A\rangle, |\phi_{1s}^B\rangle)$ in which we look for approximate solutions of the Schrödinger equation. The Hamiltonian matrix can be therefore written as

$$H(R) = \begin{pmatrix} \epsilon(R) & t(R) \\ t(R) & \epsilon(R) \end{pmatrix}, \tag{70}$$

where

$$\begin{aligned} \epsilon(R) &= \langle\phi_{1s}^A|H(R)|\phi_{1s}^A\rangle = \langle\phi_{1s}^B|H(R)|\phi_{1s}^B\rangle \\ t(R) &= \langle\phi_{1s}^B|H(R)|\phi_{1s}^A\rangle = \langle\phi_{1s}^A|H(R)|\phi_{1s}^B\rangle < 0, \end{aligned} \tag{71}$$

are the matrix elements of our problem which depends parametrically of the distance $2R$ between the two protons. For the sake of simplicity of notations, we omit the R dependence.

We choose the same vector space $\mathcal{V}$ spanned by the two $1s$ functions of the hydrogen atoms to represent the $\mathcal{C}_s$ group. As we previously found a matrix representation of σ_h on $\mathcal{V}$ and that the representation of E is always the identity matrix, we simply obtain

$$\Gamma^{\mathcal{V}} = \{\Gamma^{\mathcal{V}}(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \Gamma^{\mathcal{V}}(\sigma_h) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\}, \tag{72}$$

which is exactly the same representation than $\Gamma_1^{\mathbb{R}^2}$. One can notice that the representation matrices of $\Gamma^{\mathcal{V}}$ commute with the Hamiltonian matrix as

$$\begin{pmatrix} \epsilon & t \\ t & \epsilon \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} \epsilon & t \\ t & \epsilon \end{pmatrix} = \begin{pmatrix} t & \epsilon \\ \epsilon & t \end{pmatrix}, \tag{73}$$

and therefore the spatial transformation σ_h is indeed a symmetry of our system. Nevertheless, one can notice that because the σ_h operator is not diagonal in $\Gamma^{\mathcal{V}}(\sigma_h)$, it physically means that none of the basis function has a proper symmetry with respect to σ_h.

But by doing the following change of basis

$$\begin{aligned} |A_g\rangle &= \frac{1}{\sqrt{2}}(|\phi_{1s}^A\rangle + |\phi_{1s}^B\rangle) \\ |A_u\rangle &= \frac{1}{\sqrt{2}}(|\phi_{1s}^A\rangle - |\phi_{1s}^B\rangle), \end{aligned} \tag{74}$$

we obtain two orthogonal functions for which the σ_h symmetry operation has the form

$$\Gamma^{\mathcal{V}}(\sigma_h) = \begin{pmatrix} & |A_g\rangle & |A_u\rangle \\ \langle A_g| & 1 & 0 \\ \langle A_u| & 0 & -1 \end{pmatrix}, \tag{75}$$

which means that each function has well defined value of the symmetry with respect to the action of σ_h:

$$\begin{aligned} \Gamma^{\mathcal{V}}(\sigma_h)|A_g\rangle &= +1|A_g\rangle \\ \Gamma^{\mathcal{V}}(\sigma_h)|A_u\rangle &= -1|A_u\rangle. \end{aligned} \tag{76}$$

Writing the Hamiltonian is the new basis leads to new expression

$$H = \begin{pmatrix} & |A_g\rangle & |A_u\rangle \\ \langle A_g| & \epsilon + t & 0 \\ \langle A_u| & 0 & \epsilon - t \end{pmatrix}, \tag{77}$$

which means that by diagonalizing the matrix $\Gamma^{\mathcal{V}}(\sigma_h)$ we also diagonalized the Hamiltonian. As $t < 0$, we obtain that the ground state of H_2^+ is $|A_g\rangle$ and the delocalization of the electron between atom A and B allows for a stabilization due to t with respect to the diagonal elements ϵ.

4.3.5 Application to the permutation group

As mentioned before, another manifestation of the group of order 2 is the group of permutation of two elements, Sym(2). Let us consider a general Hamiltonian for a system of two identical particles

$$H = -\frac{1}{2}\Delta_{\mathbf{r}_1} - \frac{1}{2}\Delta_{\mathbf{r}_2} + v(\mathbf{r}_1) + v(\mathbf{r}_2) + W(|\mathbf{r}_1 - \mathbf{r}_2|), \tag{78}$$

where v and W are two general real-valued functions. Here we do not consider the spin of particles. Such a Hamiltonian commutes with the *permutation operator* p_{12} which acts on a function $f : \mathbb{R}^6 \to \mathbb{R}$ as follows

$$p_{12} f(\mathbf{r}_1, \mathbf{r}_2) = f(\mathbf{r}_2, \mathbf{r}_1). \tag{79}$$

The permutation operator applied twice returns of course the identity

$$\left(p_{12}\right)^2 f(\mathbf{r}_1, \mathbf{r}_2) = f(\mathbf{r}_1, \mathbf{r}_2), \tag{80}$$

and therefore the permutation group Sym(2) has exactly the same multiplication table as the group of order 2, therefore it is the same group. Let us now design a representation of such a group on the vector space $\mathcal{V}_{\text{FCI}}$ spanned by the four functions $\mathbb{R}^6 \to \mathbb{R}$ corresponding to a Full configuration interaction (FCI) of two particles in two orthonormal orbitals $a(\mathbf{r})$ and $b(\mathbf{r})$

$$\mathcal{V}_{\text{FCI}} = \text{span}\{|a\rangle \otimes |a\rangle\,, |a\rangle \otimes |b\rangle\,, |b\rangle \otimes |a\rangle\,, |b\rangle \otimes |b\rangle\}, \tag{81}$$

where $\langle \mathbf{r}_1 | a\rangle \otimes \langle \mathbf{r}_2 | b\rangle = a(\mathbf{r}_1) b(\mathbf{r}_2)$ and correspondingly for the other functions. To obtain the representation of the group Sym(2), we just need to understand how p_{12} acts on each function

$$\begin{aligned} p_{12} a(\mathbf{r}_1) a(\mathbf{r}_2) &= a(\mathbf{r}_1) a(\mathbf{r}_2), \\ p_{12} a(\mathbf{r}_1) b(\mathbf{r}_2) &= b(\mathbf{r}_1) a(\mathbf{r}_2), \\ p_{12} b(\mathbf{r}_1) a(\mathbf{r}_2) &= a(\mathbf{r}_1) b(\mathbf{r}_2), \\ p_{12} b(\mathbf{r}_1) b(\mathbf{r}_2) &= b(\mathbf{r}_1) b(\mathbf{r}_2), \end{aligned} \tag{82}$$

which can be written in a matrix form as

$$\Gamma^{\mathcal{V}_{\text{FCI}}}(p_{12}) = \begin{pmatrix} & |a\rangle \otimes |a\rangle & |a\rangle \otimes |b\rangle & |b\rangle \otimes |a\rangle & |b\rangle \otimes |b\rangle \\ \langle a| \otimes \langle a| & 1 & 0 & 0 & 0 \\ \langle a| \otimes \langle b| & 0 & 0 & 1 & 0 \\ \langle b| \otimes \langle a| & 0 & 1 & 0 & 0 \\ \langle b| \otimes \langle b| & 0 & 0 & 0 & 1 \end{pmatrix}, \tag{83}$$

and we obtain a four-dimensional representation of the group of order 2

$$\Gamma^{\mathcal{V}_{\text{FCI}}} = \left\{ \Gamma^{\mathcal{V}_{\text{FCI}}}(E) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \quad \Gamma^{\mathcal{V}_{\text{FCI}}}(p_{12}) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \right\}. \tag{84}$$

We know that the eigenfunctions of the Hamiltonian will be necessarily also eigenfunctions of the p_{12} operator. We can already see that the two functions $a(\mathbf{r}_1)a(\mathbf{r}_1)$ and $b(\mathbf{r}_1)b(\mathbf{r}_1)$ have a well defined parity (+1) with respect to the exchange of two particles, and therefore one only needs to worry about the two other functions $a(\mathbf{r}_1)b(\mathbf{r}_2)$ and $b(\mathbf{r}_1)a(\mathbf{r}_2)$. One can notice that within the subspace $\mathcal{V}_{ab}$ spanned by these two functions, one obtains exactly the same representation of the group of order 2 than before

$$\Gamma^{\mathcal{V}_{ab}} = \{\Gamma^{\mathcal{V}_{ab}}(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \Gamma^{\mathcal{V}_{ab}}(p_{12}) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\}, \tag{85}$$

and therefore that by doing the same change of basis one obtains functions that will diagonalize the $\Gamma^{\mathcal{V}_{ab}}(p_{12})$ matrix

$$\begin{aligned} B(\mathbf{r}_1,\mathbf{r}_2) &= \frac{1}{\sqrt{2}}(a(\mathbf{r}_1)b(\mathbf{r}_2)+b(\mathbf{r}_1)a(\mathbf{r}_2)), \\ F(\mathbf{r}_1,\mathbf{r}_2) &= \frac{1}{\sqrt{2}}(a(\mathbf{r}_1)b(\mathbf{r}_2)-b(\mathbf{r}_1)a(\mathbf{r}_2)), \end{aligned} \tag{86}$$

with the corresponding eigenvalues for the p_{12} operator

$$\begin{aligned} p_{12}B(\mathbf{r}_1,\mathbf{r}_2) &= +S(\mathbf{r}_1,\mathbf{r}_2), \\ p_{12}F(\mathbf{r}_1,\mathbf{r}_2) &= -T(\mathbf{r}_1,\mathbf{r}_2). \end{aligned} \tag{87}$$

We therefore see that we have two different class of functions in the vector space: three "bosonic" and one "ferminonic". Because of the commutation between p_{12} and H, we know that these functions do not mix.

4.4 A more involved example: the $\mathcal{C}_{3v}$ group

Our goal here is to present the representation of a non Abelian group: the $\mathcal{C}_{3v}$ group.

4.4.1 Representation in $\mathbb{R}^2$

The $\mathcal{C}_{3v}$ group is the set of all symmetry elements of an equilateral triangle. A natural representation of this symmetry group is then on the vector space $\mathbb{R}^2$. We set the barycentre at the origin and one vertex on the x axis, and after some basic geometry (matrix representation of rotations and reflections in $\mathbb{R}^2$) one obtains the following representation of $\mathcal{C}_{3v}$ in $\mathbb{R}^2$

$$\begin{aligned} \Gamma^{\mathbb{R}^2} = \Bigg\{ \Gamma^{\mathbb{R}^2}(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \Gamma^{\mathbb{R}^2}(C_3) = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}, \Gamma^{\mathbb{R}^2}({C_3}^{-1}) = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}, \\ \Gamma^{\mathbb{R}^2}(\sigma_1) = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \Gamma^{\mathbb{R}^2}(\sigma_2) = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}, \Gamma^{\mathbb{R}^2}(\sigma_3) = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix} \Bigg\}. \end{aligned} \tag{88}$$

These matrices represent the group because they have the same multiplication table than $\mathcal{C}_{3v}$.

4.4.2 Extension to $\mathbb{R}^3$

We wish now to extend the representation of $\mathcal{C}_{3v}$ to $\mathbb{R}^3$, and we therefore just need to know how the vector $|e_z\rangle$ is changed by the six operations of $\mathcal{C}_{3v}$. Being orthogonal to the plane, you can easily convince yourself that $|e_z\rangle$ is unchanged by the action of any symmetry operation of $\mathcal{C}_{3v}$. This also means that it does not mix with $|e_x\rangle$ nor $|e_y\rangle$ when any symmetry operation is applied. Therefore a representation in $\mathbb{R}^3$ is

$$\begin{aligned} \Gamma_1^{\mathbb{R}^3} = \Bigg\{ \Gamma_1^{\mathbb{R}^3}(E) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \Gamma_1^{\mathbb{R}^3}(C_3) = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}, \Gamma_1^{\mathbb{R}^3}({C_3}^{-1}) = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}, \\ \Gamma_1^{\mathbb{R}^3}(\sigma_1) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \Gamma_1^{\mathbb{R}^3}(\sigma_2) = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}, \Gamma_1^{\mathbb{R}^3}(\sigma_3) = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \Bigg\}. \end{aligned} \tag{89}$$

One can notice that this representation, unlike $\Gamma^{\mathbb{R}^2}$, has a natural block diagonal structure.

4.4.3 Representation on functions

Let us now move closer to a representation on a vector space made of functions. Suppose that we have a molecular system such as H_3 which we aim at describing in a minimal basis (*i.e.* one AO function per atom). The atomic centers H_1, H_2 and H_3 are spotted by the vectors $\mathbf{R}_1$, $\mathbf{R}_2$ and $\mathbf{R}_3$ which are at the vertices of an equilateral triangle of side 1. We choose the following coordinate system

$$\mathbf{R}_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \quad \mathbf{R}_2 = \begin{pmatrix} -\frac{1}{2} \\ \frac{\sqrt{3}}{2} \\ 0 \end{pmatrix}, \quad \mathbf{R}_3 = \begin{pmatrix} -\frac{1}{2} \\ -\frac{\sqrt{3}}{2} \\ 0 \end{pmatrix}. \tag{90}$$

Each AO centered on H_i is an s-like function

$$s_i(\mathbf{r}) = Ne^{-|\mathbf{r}-\mathbf{R}_i|}, \tag{91}$$

where N is a normalization factor. This yields this explicit expression for the three AOs

$$\begin{aligned} s_1(\mathbf{r}) &= Ne^{-\sqrt{(x-1)^2+y^2+z^2}}, \\ s_2(\mathbf{r}) &= Ne^{-\sqrt{(x+\frac{1}{2})^2+(y-\frac{\sqrt{3}}{2})^2+z^2}}, \\ s_3(\mathbf{r}) &= Ne^{-\sqrt{(x+\frac{1}{2})^2+(y+\frac{\sqrt{3}}{2})^2+z^2}}. \end{aligned} \tag{92}$$

We want now to represent the group $\mathcal{C}_{3v}$ on the vector space $\mathcal{V} = \text{span}(|s_1\rangle, |s_2\rangle, |s_3\rangle)$. Therefore we need to find how each function s_i is changed by each of the symmetry operations. We know that, for a general symmetry element S represented on $\mathbb{R}^3$ by $\Gamma^{\mathbb{R}^3}(S)$, its action on a function $f(\mathbf{r})$ is

$$\Gamma^{\mathcal{V}} f(\mathbf{r}) = f(\Gamma^{\mathbb{R}^3}(S^{-1})\mathbf{r}) = f(\mathbf{r}'). \tag{93}$$

For simplicity, we will most of time write the previous equation as

$$Sf(\mathbf{r}) = f((S^{-1})\mathbf{r}) = f(\mathbf{r}'), \tag{94}$$

as the only difference between the operator S on the left-hand side of the equation and that on the right-hand side of the equation is the vector space they act on: it is either the vector space of functions or the geometrical vector space $\mathbb{R}^3$. Therefore, as we know a representation on $\mathbb{R}^3$ of the group, it will be easy to obtain a representation of $\mathcal{C}_{3v}$ on functions. Let us take a detailed example with C_3. We need to compute first $\mathbf{r}' = \Gamma_1^{\mathbb{R}^3}({C_3}^{-1})\mathbf{r}$

$$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} -\frac{1}{2}x + \frac{\sqrt{3}}{2}y \\ -\frac{\sqrt{3}}{2}x - \frac{1}{2}y \\ z \end{pmatrix}. \tag{95}$$

Therefore, if we write

$$\begin{aligned} s_1(\mathbf{r}) &= Ne^{-\sqrt{f_1(\mathbf{r})}}, f_1(\mathbf{r}) = (\mathbf{r}-\mathbf{R}_1)^2 = (x-1)^2 + y^2 + z^2 \\ C_3 s_1(\mathbf{r}) &= C_3 N \exp\left\{-\sqrt{f_1(\mathbf{r})}\right\} \\ &= N \exp\left\{-C_3\sqrt{f_1(\mathbf{r})}\right\} \\ &= N \exp\left\{-\sqrt{f_1({C_3}^{-1}\mathbf{r})}\right\} \\ &= N \exp\left\{-\sqrt{f_1(\mathbf{r}')}\right\}, \end{aligned} \tag{96}$$

and therefore we just have to focus on $f_1(\mathbf{r}')$. We then need to replace $\mathbf{r} = (x, y, z)$ by $\mathbf{r}' = (-\frac{1}{2}x + \frac{\sqrt{3}}{2}y, -\frac{\sqrt{3}}{2}x - \frac{1}{2}y, z)$ in f_1:

$$
\begin{aligned}
C_3 f_1(\mathbf{r}) &= (x' - 1)^2 + y'^2 + z'^2 \\
&= \big(-\frac{1}{2}x + \frac{\sqrt{3}}{2}y - 1\big)^2 + \big(-\frac{\sqrt{3}}{2}x - \frac{1}{2}y\big)^2 + z^2.
\end{aligned}
\tag{97}
$$

After some (non interesting) math you get to

$$
C_3 f_1(\mathbf{r}) = (\mathbf{r} - \mathbf{R}_2)^2,
\tag{98}
$$

which therefore implies that

$$
\begin{aligned}
C_3 s_1(\mathbf{r}) &= N e^{-\sqrt{(\mathbf{r}-\mathbf{R}_2)^2}} \\
&= s_2(\mathbf{r}).
\end{aligned}
\tag{99}
$$

Therefore the function attached on atom H_1 transforms under C_3 in the function centered on H_2, just as the vectors of the vertices of the triangle. One can do exactly the same for the other functions and one will see that $s_2(\mathbf{r})$ transforms as $s_3(\mathbf{r})$, and that $s_3(\mathbf{r})$ transforms as $s_1(\mathbf{r})$. One can then represent the C_3 on this vector space by the following matrix

$$
\Gamma_2^{\mathcal{V}}(C_3) = \begin{pmatrix} & |s_1\rangle & |s_2\rangle & |s_3\rangle \\ \langle s_1| & 0 & 0 & 1 \\ \langle s_2| & 1 & 0 & 0 \\ \langle s_3| & 0 & 1 & 0 \end{pmatrix},
\tag{100}
$$

and as the vector space $\mathcal{V}$ is isomoprh to $\mathbb{R}^3$, we have inserted the index "2" in order to differentiate the representation from the other three-dimensional representation $\Gamma_1^{\mathbb{R}^3}$. As long as the functions depend only on the distance to the atomic center they are attached on (*i.e.* s functions), the conclusions will be exactly the same for the other symmetry operations. For other functions like p or d functions, the matrix would be more involved, but one could still obtain them based on the general strategy used here. Eventually, one can set up the representation of $\mathcal{C}_{3v}$ on the vector space $\mathcal{V}$ as

$$
\begin{aligned}
\Gamma_2^{\mathcal{V}} = \Big\{ \Gamma_2^{\mathcal{V}}(E) &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \Gamma_2^{\mathcal{V}}(C_3) = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}, \quad \Gamma_2^{\mathcal{V}}(C_3{}^{-1}) = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}, \\
\Gamma_2^{\mathcal{V}}(\sigma_1) &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad \Gamma_2^{\mathcal{V}}(\sigma_2) = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \quad \Gamma_2^{\mathcal{V}}(\sigma_3) = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \Big\}.
\end{aligned}
\tag{101}
$$

Therefore we have obtained a two-dimensional representation of $\mathcal{C}_{3v}$ in Sec. 4.4.1 and two three-dimensional representations in Sec. 4.4.2 and in the present section. The two-dimensional representation is of course non equivalent to any of the three-dimensional representations because of the different dimension. Nevertheless, in the case of the three-dimensional representations, it is less obvious to see wether they are equivalent or not. A way to see it would be to compute the trace of each matrix for the two different three-dimensioal representations, because the trace is invariant with respect to change of basis, or more generally with respect to a similarity transformation. In this way, we could identify easily of these representations are the same. This will be done later with the notion of *characters*.

4.5 A few useful notions of linear algebra and vector spaces

In order to continue our journey in the abstract world of linear representations, we will need to have some notions on linear algebra and vector spaces which will allow us to properly define the notion of irreducible representations. Thorough this section we will assume vector spaces of *finite dimension* endorsed with a *scalar product*.

4.5.1 Supplementary subspace and direct sum of vector spaces

Let V_1 and V_2 be two sub vector spaces, of dimension d_1 and d_2, of the vector space $\mathcal{V}$ of dimension d.
Definition:*supplementary vector spaces and direct sums of representations:*
V_1 and V_2 are said to be *supplementary* for $\mathcal{V}$, which is noted as $\mathcal{V} = V_1 \oplus V_2$, if any vector $|v\rangle \in \mathcal{V}$ has a unique decomposition $|v\rangle = |v_1\rangle + |v_2\rangle$ where $|v_1\rangle \in V_1$, $|v_2\rangle \in V_2$. We also said that $\mathcal{V}$ is the *direct sum of* V_1 *and* V_2.

If any vector in V_1 is orthogonal to any vector in V_2, we say that V_1 and V_2 are orthogonal, or that V_1 is the complement orthogonal to V_2 with respect to $\mathcal{V}$.

Examples:
As an example, if we take $\mathcal{V} = \mathbb{R}^3$, spanned by $\{|e_1\rangle, |e_2\rangle, |e_3\rangle\}$, we can choose $V_1 = \text{span}(|e_1\rangle)$ and $V_2 = \text{span}(|e_2\rangle, |e_3\rangle)$. It is here clear that any vector $|v\rangle \in \mathbb{R}^3$ can be decomposed as a sum of two vectors in V_1 and V_2. Therefore we can say that $\mathbb{R}^3 = V_1 \oplus V_2$. In that case V_1 and V_2 are orthogonal. Another example would be $\mathcal{V} = \mathbb{R}^2$ where one can take $V_1 = \text{span}(|e_1\rangle)$ and $V_2 = \{|v_2\rangle = \lambda(|e_1\rangle + |e_2\rangle), \lambda \in \mathbb{R}\}$. In that case, the supplementary subspaces are not orthogonal.

Regarding now the matrix representation of a linear map A on the whole vector space $\mathcal{V}$, provided a basis $\mathcal{B} = \{|e_i\rangle, i = 1, d\ \}$ for $\mathcal{V}$, one can write it as

$$A^{\mathcal{V}} = \sum_{i,j=1,d} \langle e_i|A|e_j\rangle |e_i\rangle \langle e_j| = \sum_{i,j=1,d} A_{ij} |e_i\rangle \langle e_j| . \tag{102}$$

If now V_1 and V_2 are two supplementary vector spaces of $\mathcal{V}$, with basis $\mathcal{B}^1 = \{\boldsymbol{v}_i^1, i = 1, d_1\}$ and $\mathcal{B}^2 = \{\boldsymbol{v}_i^2, i = 1, d_2\}$, respectively, we can therefore write the linear map as

$$A^{\mathcal{V}} = A^{V_1,V_1} + A^{V_1,V_2} + A^{V_2,V_1} + A^{V_2,V_2}, \tag{103}$$

$$A^{\mathcal{V}} = \begin{pmatrix} A^{V_1,V_1} & A^{V_1,V_2} \\ A^{V_2,V_1} & A^{V_2,V_2} \end{pmatrix}, \tag{104}$$

where for instance

$$A^{V_1,V_2} = \sum_{i=1,d_1} \sum_{j=1,d_2} \langle \boldsymbol{v}_i^1|A|\boldsymbol{v}_j^2\rangle |v_i^1\rangle \langle \boldsymbol{v}_j^2| . \tag{105}$$

Linear maps from V_1 to V_2 are called *intertwining maps* and this concept will be very useful to obtain the block diagonal structure of the Hamiltonian.

4.5.2 The notion of stable (or invariant) subspace

Let $\mathcal{G}$ be a group of order g, $\Gamma^{\mathcal{V}}$ a representation of that group on a vector space $\mathcal{V}$ of dimension d, and V be a subspace (of dimension $d' \leq d$) of $\mathcal{V}$.

Definition:*Stable subspace by the elements of the group $\mathcal{G}$:*
It is said that V is *stable by $\mathcal{G}$* (or invariant by any elements of $\mathcal{G}$) if the application of any matrix $\Gamma^{\mathcal{V}}(G_i)$ on any vector $|v\rangle$ in V remains in V

$$\Gamma^{\mathcal{V}}(G_i)\,|v\rangle \in V, \quad \forall\, \Gamma^{\mathcal{V}}(G_i) \in \Gamma^{\mathcal{V}}, \quad \forall\, |v\rangle\, \in V. \tag{106}$$

We can also say that the subspace V is closed under all elements of the group. Therefore, a stable subspace V necessarily defines a representation of dimension smaller or equal to d, labelled Γ^V, and any basis spanning V is a basis for the representation Γ^V.

Theorem : *Supplementary representations*
Let $\Gamma^{\mathcal{V}}$ be a representation of the group $\mathcal{G}$ on a vector space $\mathcal{V}$ and V be a stable subspace of $\mathcal{V}$ by $\mathcal{G}$. Then,

there exists a supplementary subspace, noted here as $\bar{V}$, which is stable by $\mathcal{G}$. An important consequence is that these subspaces are *orthogonal*. Therefore, the two supplementary subspaces V and $\bar{V}$ can be used as representations spaces for the group $\mathcal{G}$, and they are of lower dimension than the original representation on $\mathcal{V}$.

We also say that these two representations are *supplementary representations*, or that the representation $\Gamma^{\mathcal{V}}$ *is the direct sum of the two sub representations* Γ^{V} *and* $\Gamma^{\bar{V}}$:

$$\mathcal{V} = V \oplus \bar{V} \text{ and } V, \bar{V} \text{ are stable subspaces of } \mathcal{V} \text{ by } \mathcal{G} \Leftrightarrow \Gamma^{\mathcal{V}} = \Gamma^{V} \oplus \Gamma^{\bar{V}}. \tag{107}$$

This means that, because V is a stable subspace of $\mathcal{V}$ by $\mathcal{G}$, the matrices $\Gamma^{V,\bar{V}}(G_i) = 0\ \forall G_i \in \mathcal{G}$, or in other terms that the intertwining maps between $\mathcal{V}_1$ and $\mathcal{V}_2$ are zero in the representation $\Gamma^{\mathcal{V}}$.

As a consequence of the stability of the two subspaces V and $\bar{V}$, one can rewrite all matrices $\Gamma^{\mathcal{V}}(G_i)$ such that they have all *the same block diagonal structure*

$$\Gamma^{\mathcal{V}}(G_i) = \begin{pmatrix} \left(\Gamma^{V}(G_i)\right) & 0 \\ 0 & \left(\Gamma^{\bar{V}}(G_i)\right) \end{pmatrix} \forall G_i \in \mathcal{G}. \tag{108}$$

Such a block diagonal structure can be in general obtained by performing a similarity transformation of the original basis $\mathcal{B}$ spanning the vector space $\mathcal{V}$. By doing so, one obtains an equivalent representation.

Examples: the group of order 2

Let us consider the representation $\Gamma_1^{\mathbb{R}^2}$ defined on $\mathbb{R}^2$ and obtained in the basis $\mathcal{B} = \{|e_1\rangle, |e_2\rangle\}$

$$\Gamma_1^{\mathbb{R}^2} = \{\Gamma_1^{\mathbb{R}^2}(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \Gamma_1^{\mathbb{R}^2}(A) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\}. \tag{109}$$

From the basis $\mathcal{B} = \text{span}(|e_1\rangle, |e_2\rangle)$ we can build the corresponding subspaces $V_1 = \text{span}(|e_1\rangle)$ and $V_2 = \text{span}(|e_2\rangle)$ which are necessarily supplementary as any vector of $\mathbb{R}^2$ can be decomposed on V_1 and V_2. Nevertheless, as the matrices are not block diagonal on the basis $\mathcal{B} = \{|e_1\rangle, |e_2\rangle\}$, the subspaces V_1 and V_2 are not stable (or invariant) subspaces. Indeed one sees that for instance

$$\Gamma_1^{\mathbb{R}^2}(A)\,|e_1\rangle = |e_2\rangle, \tag{110}$$

and therefore for any $|v\rangle \in V_1$, one has

$$\Gamma_1^{\mathbb{R}^2}(A)\,|v\rangle \in V_2, \tag{111}$$

and therefore V_1 or V_2 are of course not stable by $\mathcal{G}$.

If one performs the following change of basis

$$\begin{aligned} |u_1\rangle &= \frac{1}{\sqrt{2}}\big(\,|e_1\rangle + |e_2\rangle\,\big), \\ |u_2\rangle &= \frac{1}{\sqrt{2}}\big(\,|e_1\rangle - |e_2\rangle\,\big), \end{aligned} \tag{112}$$

one obtains an equivalent representation $\Gamma_2^{\mathbb{R}^2}$

$$\Gamma_2^{\mathbb{R}^2} = \{\Gamma_2^{\mathbb{R}^2}(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \Gamma_2^{\mathbb{R}^2}(A) = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\}. \tag{113}$$

Therefore, as all matrices of $\Gamma_2^{\mathbb{R}^2}$ are block diagonal in that basis, we know that the subspaces $V_1' = \text{span}(|u_1\rangle)$ and $V_2' = \text{span}(|u_2\rangle)$ *are invariant subspaces.* For instance

$$\begin{aligned} \Gamma_2^{\mathbb{R}^2}(A)\,|v_1\rangle &= (+1)\,|v_1\rangle \\ \Gamma_2^{\mathbb{R}^2}(A)\,|v_2\rangle &= (-1)\,|v_2\rangle, \end{aligned} \tag{114}$$

and therefore we see that the two subspaces are indeed stable. We also see that the two supplementary invariant subspaces V_1' and V_2' are orthogonal as they are spanned by orthonormal vectors.

Also, we can define two representations associated with V_1' and V_2' which are one dimensional representations

$$\Gamma^{V_1'} = \{\Gamma^{V_1'}(E) = 1, \Gamma^{V_1'}(A) = 1\}, \tag{115}$$

$$\Gamma^{V_2'} = \{\Gamma^{V_2'}(E) = 1, \Gamma^{V_2'}(A) = -1\}. \tag{116}$$

These representations are exactly the one dimensional representations we found before $\Gamma_g^{\mathbb{R}}$ and $\Gamma_u^{\mathbb{R}}$.

We can write the original representation $\Gamma_2^{\mathbb{R}^2}$ as a *direct sum* of $\Gamma_g^{\mathbb{R}}$ and $\Gamma_u^{\mathbb{R}}$

$$\Gamma_2^{\mathbb{R}^2} = \Gamma_g^{\mathbb{R}} \oplus \Gamma_u^{\mathbb{R}}. \tag{117}$$

Examples: the $\mathcal{C}_{3v}$ group

Let us reconsider the representation obtained in a vector space isomorph to $\mathbb{R}^3$ of the $\mathcal{C}_{3v}$ group written in the basis $\mathcal{B} = \{|e_x\rangle, |e_y\rangle, |e_z\rangle\}$

$$\begin{aligned}\Gamma_1^{\mathbb{R}^3} = \Bigg\{ \Gamma_1^{\mathbb{R}^3}(E) = \begin{pmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{pmatrix}, \Gamma_1^{\mathbb{R}^3}(C_3) = \begin{pmatrix}-\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0\\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0\\ 0 & 0 & 1\end{pmatrix}, \Gamma_1^{\mathbb{R}^3}({C_3}^{-1}) = \begin{pmatrix}-\frac{1}{2} & \frac{\sqrt{3}}{2} & 0\\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0\\ 0 & 0 & 1\end{pmatrix},\\ \Gamma_1^{\mathbb{R}^3}(\sigma_1) = \begin{pmatrix}1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 1\end{pmatrix}, \Gamma_1^{\mathbb{R}^3}(\sigma_2) = \begin{pmatrix}-\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0\\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0\\ 0 & 0 & 1\end{pmatrix}, \Gamma_1^{\mathbb{R}^3}(\sigma_3) = \begin{pmatrix}-\frac{1}{2} & \frac{\sqrt{3}}{2} & 0\\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0\\ 0 & 0 & 1\end{pmatrix}\Bigg\}.\end{aligned} \tag{118}$$

We can notice that all matrices $\Gamma_1^{\mathbb{R}^3}(G_i)$ have the same block diagonal structure: the vector space $V_{xy} = \text{span}(|e_x\rangle, |e_y\rangle)$ is uncoupled to the vector sapce $V_z = \text{span}(|e_z\rangle)$. Therefore these V_{xy} and V_z are two stable subspaces, which are of course supplementary for $\mathbb{R}^3$. We can then write that the representation $\Gamma_1^{\mathbb{R}^3}$ is a direct sum of the representation obtained within V_{xy} and that on V_z. The former is exactly the representation obtained on $\mathbb{R}^2$ (called $\Gamma^{\mathbb{R}^2}$, see Eq. (88)) and the latter being a one-dimensional representation where all the elements are represented by 1 (the totally symmetrical representation, labelled Γ_{A_1} in the litterature)

$$\Gamma_{A_1} = \{\Gamma_{A_1}(G_i) = 1, \forall G_i \in \mathcal{G}\}. \tag{119}$$

Therefore we can write that

$$\Gamma_1^{\mathbb{R}^3} = \Gamma^{\mathbb{R}^2} \oplus \Gamma_{A_1}. \tag{120}$$

4.6 Definition of reducible and irreducible representations

In group representation theory, there exists a special type of representations which are particularly interesting: the irreducible representations. These representations can be thought as finding a kind of common set of eigenvectors for the whole group of matrices representing the group, even if these matrices do not commute.

Definition:*Reducible and irreducible representations*

We say that a representation $\Gamma^{\mathcal{V}}$ is *irreducible* if there exists no smaller stable subspaces of $\mathcal{V}$ than $\mathcal{V}$ itself or $\{0\}$. We also say that $\mathcal{V}$ is an *irreducible space*.

In other terms, an irreducible representation is a set of g matrices representing the group which cannot be simultaneously further block diagonalized by a unique similarity transformation.

4.6.1 Reduction of a representation: "iterative" block diagonalization

The goal here is to show that any representation can be decomposed as a direct sum of irreducible representations. Let us consider a group $\mathcal{G} = \{G_i,\, i = 1, g\}$ and a *reducible representation* $\Gamma^{\mathcal{V}}$ of dimension d expressed in a basis $\mathcal{B} = \{|e_i\rangle, i = 1, d\}$. One can identify some *invariant subspaces* $\{V_1, V_2, \dots V_n\}$ which are supplementary in the sense that

$$\mathcal{V} = V_1 \oplus V_2 \dots \oplus V_n. \tag{121}$$

The invariant subspace V_i of dimension d_i is spanned by a basis $\mathcal{B}_i = \{|u_j^i\rangle, j = 1, d_i\}$. Therefore, by a change of basis from $\mathcal{B}$ to the new basis $\mathcal{B}'$ formed by the union of the basis of each individual subspaces

$$\mathcal{B}' = \{\mathcal{B}_1, \mathcal{B}_2, \dots, \mathcal{B}_n\}, \tag{122}$$

one can obtain a new equivalent representation where *all matrices have the same block diagonal structures*. Therefore, each of the individual subspaces V_i is a representation space of lower dimension d_i: we can therefore write that $\Gamma^{V_i} = \{\Gamma^{V_i}(G_k), k = 1, g\}$ is indeed a representation of the group.

Then one can do exactly the same reduction on each of the individual invariant subspace $\{V_1, V_2, \dots V_n\}$ just previously found: for a given subspace V_i,

- if there is not a smaller invariant subspace other than V_i itself, then V_i is an irreducible subspace and $\Gamma^{V_i} = \{\Gamma^{V_i}(G_k), k = 1, g\}$ is an irreducible representation,
- if there exists indeed a smaller invariant subspace, then the representation $\Gamma^{V_i} = \{\Gamma^{V_i}(G_k), k = 1, g\}$ can be further decomposed into a direct sum of smaller dimension representations and therefore one has to iterate for these representations.

When the process is finished, *i.e.* that we found the *all the invariant subspaces which cannot be further block diagonalized*, we know that we found the irreducible subspaces, labelled here $\{\tilde{V}_1, \tilde{V}_2, \dots \tilde{V}_m\}$, and therefore the corresponding irreducible representations $\Gamma^{\tilde{V}_i}$. We can then write the original representation $\Gamma^{\mathcal{V}}$ as *a direct sum of these irreducible representations*

$$\Gamma^{\mathcal{V}} = \Gamma^{\tilde{V}_1} \oplus \Gamma^{\tilde{V}_2} \oplus \dots \oplus \Gamma^{\tilde{V}_n}. \tag{123}$$

In terms of vocabulary, we will say that the reducible representation $\Gamma^{\mathcal{V}}$ *is composed of* the irreducible representations $\Gamma^{\tilde{V}_1}$, $\Gamma^{\tilde{V}_2}$ etc, or also that $\Gamma^{\tilde{V}_1}$ is contained in $\Gamma^{\mathcal{V}}$, that we will note as $\Gamma^{\tilde{V}_1} \in \Gamma^{\mathcal{V}}$.

Here the notion of *direct sum of representations* means that all matrices in $\Gamma^{\mathcal{V}}$ can be written in a block diagonal through a similarity transformation. With this qualitative reasoning we can state that *any representation can be decomposed into the direct sum of irreducible representations.*

Remark:

Notice that a much more general and rigorous proof of the possibility of writing any representation as a direct sum of irreducible representations is formulated as the Maschke's theorem.

The irreducible decomposition calls some remarks:

1) As the identification of the irreducible subspaces does not depend on the basis chosen for $\mathcal{V}$, *equivalent representations have the same irreducible representations decomposition.* Therefore we will say that two representations are *equal* when they are *equivalent*, and we will say $\Gamma_1^{\mathcal{V}_1} \cong \Gamma_2^{\mathcal{V}_2}$.
2) Two *non equivalent* representations *do not have the same* irreducible decompositions.
3) Therefore a representation is *completely* characterized by its irreducible decomposition.
4) A given irreducible representation can occur several time in the same reducible representation (see later for examples).

5) As any finite dimension vector spaces of dimension n is isomorph to $\mathbb{R}^n$, the specific vector space on which a representation is obtained does not really mater, but only its dimension. Therefore we could also drop the explicit reference to the vector space $\mathcal{V}$ on which it is obtained.

Theorem:*Abelian groups*
All irreducible representations of Abelian groups are one-dimensional.
Qualitative proof
As all elements of an Abelian group commute, the matrices of any representation $\Gamma^{\mathcal{V}}$ of such group also commute. Therefore, as commuting matrices share a common set of eigenvectors, they can all be diagonalized simultaneously. Therefore there exists a basis $\mathcal{B}_{\text{SA}} = \{|\chi_i\rangle, i = 1, d\}$ where all matrix $\Gamma^{\mathcal{V}}(G)$ of the representation can be written as

$$\Gamma^{\mathcal{V}}(G) = \begin{pmatrix} & |\chi_1\rangle & |\chi_2\rangle & \dots & |\chi_i\rangle & \dots & |\chi_d\rangle \\ \langle\chi_1| & \lambda_1^G & 0 & \dots & 0 & \dots & 0 \\ \langle\chi_2| & 0 & \lambda_2^G & \dots & 0 & \dots & 0 \\ \vdots & \vdots & \vdots & & \vdots & & \vdots \\ \langle\chi_i| & 0 & 0 & \dots & \lambda_i^G & \dots & \dots \\ \vdots & \vdots & \vdots & \dots & \vdots & \vdots & \dots \\ \langle\chi_d| & 0 & 0 & \dots & 0 & \dots & \lambda_d^G \end{pmatrix} \quad \forall G \in \mathcal{G}. \tag{124}$$

Therefore, any vector $|\chi_i\rangle$ spans an ***invariant sub vector space*** $\mathcal{V}_i = \text{span}(|\chi_i\rangle)$ because all off diagonal elements of $\Gamma^{\mathcal{V}}(G)$ are zero and therefore

$$\Gamma^{\mathcal{V}}(G)\,|\chi_i\rangle = \lambda_i^G\,|\chi_i\rangle \in \mathcal{V}_i. \tag{125}$$

Also you can easily verify that if three elements $G, K, L \in \mathcal{G}$ are connected by the multiplication table by

$$GK = L, \tag{126}$$

then of course the matrices $\Gamma^{\mathcal{V}}(G)$ fulfill such a relation

$$\Gamma^{\mathcal{V}}(G)\Gamma^{\mathcal{V}}(K) = \Gamma^{\mathcal{V}}(L), \tag{127}$$

but also do the one-dimensional representations which are *numbers*

$$\lambda_i^G \lambda_i^K = \lambda_i^L. \tag{128}$$

As these sub vector spaces $\mathcal{V}_i$ are one-dimensional, they cannot be further reduced and are therefore irreducible representations

$$\Gamma^{\mathcal{V}_i} = \{\Gamma^{\mathcal{V}_i}(G) = \lambda_i^G, \forall G \in \mathcal{G}\}. \tag{129}$$

Examples: the group of order 2
Let us take the representation $\Gamma_1^{\mathbb{R}^3}$ on $\mathbb{R}^3$

$$\Gamma_1^{\mathbb{R}^3} = \{\Gamma_1^{\mathbb{R}^3}(E) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \Gamma_1^{\mathbb{R}^3}(A) = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}\}, \tag{130}$$

where the basis is $\mathcal{B} = \{|e_1\rangle, |e_2\rangle, |e_3\rangle\}$. We can identify two invariant subspaces:

- $V_1 = \text{span}(|e_1\rangle, |e_1\rangle)$ of dimension 2,
- $V_2 = \text{span}(|e_3\rangle)$ of dimension 1.

Therefore, one can express the representation $\Gamma_1^{\mathbb{R}^3}$ as a direct sum (in the sense of representations) of two representations: one of dimension 2 which is $\Gamma_1^{\mathbb{R}_2^2}$

$$\Gamma_1^{\mathbb{R}_2^2} = \{\Gamma_1^{\mathbb{R}_2^2}(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \Gamma_1^{\mathbb{R}_2^2}(E) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\}, \tag{131}$$

and one of dimension 1 which is $\Gamma_g^{\mathbb{R}}$

$$\Gamma_g^{\mathbb{R}} = \{\Gamma_g^{\mathbb{R}}(E) = 1, \Gamma_g^{\mathbb{R}}(A) = 1\}, \tag{132}$$

and therefore we can write

$$\Gamma_1^{\mathbb{R}^3} = \Gamma_1^{\mathbb{R}^2} \oplus \Gamma_g^{\mathbb{R}}. \tag{133}$$

The one-dimensional representation $\Gamma_g^{\mathbb{R}}$ is necessarily *irreducible* as it cannot be further reduced. This representation is called the *totally symmetric representation* and happens in any group: all elements are represented by 1.

We will then try to see if there are invariant subspaces of smaller dimension than 2 for $\Gamma_1^{\mathbb{R}^2}$ in order to see if we can decompose $\Gamma_1^{\mathbb{R}^2}$ in smaller irreducible representations.

We know that if one performs the following change of basis within $\mathbb{R}^2$

$$\begin{aligned} |u_1\rangle &= \frac{1}{\sqrt{2}}\big(\,|e_1\rangle + |e_2\rangle\,\big), \\ |u_2\rangle &= \frac{1}{\sqrt{2}}\big(\,|e_1\rangle - |e_2\rangle\,\big), \end{aligned} \tag{134}$$

one obtains the corresponding representation $\Gamma_2^{\mathbb{R}^2}$ which is block diagonal

$$\Gamma_2^{\mathbb{R}^2} = \{\Gamma_2^{\mathbb{R}^2}(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \Gamma_2^{\mathbb{R}^2}(A) = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\}. \tag{135}$$

Therefore, the representation $\Gamma_1^{\mathbb{R}^2}$ can be indeed decomposed into two irreducible representations of dimension 1. The first representation is actually $\Gamma_g^{\mathbb{R}}$, and the second is

$$\Gamma_u^{\mathbb{R}} = \{\Gamma_u^{\mathbb{R}}(E) = 1, \quad \Gamma_u^{\mathbb{R}}(A) = -1\}, \tag{136}$$

and such a representation is here the antisymmetric representation.

Therefore by moving to the basis $\mathcal{B}_{\text{SA}} = \{|u_1\rangle, |u_2\rangle, |e_3\rangle\}$ one obtains the following representation

$$\Gamma^{\mathbb{R}^3} = \{ \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{137}$$

which is of course *equivalent* to the original representation $\Gamma_1^{\mathbb{R}^3}$

$$\Gamma^{\mathbb{R}^3} \cong \Gamma_1^{\mathbb{R}^3},$$

which means that the $\Gamma^{\mathbb{R}^3}$ can be decomposed as

$$\Gamma_1^{\mathbb{R}^3} = \Gamma_g^{\mathbb{R}} \oplus \Gamma_g^{\mathbb{R}} \oplus \Gamma_u^{\mathbb{R}} = 2\Gamma_g^{\mathbb{R}} \oplus \Gamma_u^{\mathbb{R}}, \tag{138}$$

where we have noted $2\Gamma_g^{\mathbb{R}}$ to indicate that the irreducible representation $\Gamma_g^{\mathbb{R}}$ is twice in $\Gamma_1^{\mathbb{R}^3}$.

Examples: $\mathbf{H}_2^+$

As we have shown previously, the representation $\Gamma^{\mathcal{V}}$ of the symmetry group C_s on the basis of two s functions of hydrogen atoms is *exactly* the same than the representation $\Gamma^{\mathbb{R}^2}$. Therefore we know that the representation $\Gamma^{\mathcal{V}}$ can be written as a sum of two irreducible representations

$$\Gamma^{\mathcal{V}} = \Gamma^{\mathcal{V}_g} \oplus \Gamma^{\mathcal{V}_u}, \tag{139}$$

where $\mathcal{V}_g = \text{span}(|A_g\rangle)$ is the invariant vector space associated with the irreducible representation

$$\Gamma^{\mathcal{V}_g} = \{\Gamma^{\mathcal{V}_g}(E) = 1,\, \Gamma^{\mathcal{V}_g}(\sigma_h) = 1\} \equiv \Gamma_g^{\mathbb{R}}, \tag{140}$$

and $\mathcal{V}_u = (|A_u\rangle)$

$$\Gamma^{\mathcal{V}_u} = \{\Gamma^{\mathcal{V}_u}(E) = 1,\, \Gamma^{\mathcal{V}_u}(\sigma_h) = -1\} \equiv \Gamma_u^{\mathbb{R}}. \tag{141}$$

Therefore, the two irreducible representations $\Gamma^{\mathcal{V}_g}$ and $\Gamma^{\mathcal{V}_u}$ can be associated with *symmetry labels of orbitals* as one knows that

$$\Gamma^{\mathcal{V}}(\sigma_h)\,|A_g\rangle = +\,|A_g\rangle \tag{142}$$

$$\Gamma^{\mathcal{V}}(\sigma_h)\,|A_u\rangle = -\,|A_u\rangle\,. \tag{143}$$

Therefore we see that the orbitals of the irreducible representation A_g are unchanged when applied the σ_h symmetry operation, and are thefore "even" with respect to the z axis. The orbitals of the A_u irreducible representation are "odd" with respect to the σ_h.

In the general context of symmetry groups, a given irreducible representation represents how some functions are changed with respect to all the symmetry elements of the groups.

Examples: the rotation group and the $Y_{l,m}$

The group of rotations (called SO(3)) is the (continuous) group of all possible rotations in $\mathbb{R}^3$. Such a group has an infinite number of irreducible representations labelled by an integer $l \geq 0$ and whose dimensions are $2l+1$. The basis for each irreducible representation l is the set of $Y_{l,m}$ for agiven l, that we can labell as $\mathcal{B}^{(l)} = \{Y_{l,m}, -l \leq m \leq l\}$. The label l refers to how a function can be changed with respect to rotations. For instance, $l = 0$ is a one-dimensional representation of the group where all rotations are represented by 1. The functions belonging to that symmetry are such that they are completely unchanged by any rotation, and therefore which depends only on the modulus of $\mathbf{r}$. The $l = 1$ irreducible representation has dimension 3 and a basis for these functions is $\mathcal{B}^{(l=1)} = \{Y_{1,-1}, Y_{1,0}, Y_{1,+1}\}$. This implies that any rotation applied to a vector belonging to the vector space spaned by $\mathcal{B}^{l=1}$ generates another vector remaining within the same vector space. In general, as the $Y_{l,m}$ form a basis for the irreducible representation l, the application of any rotation on a $Y_{l,m}$ *stays within the same* l, or in other words, the set of functions $\mathcal{B}^{(l)} = \{Y_{l,m},\, -l \leq m \leq +l\ \}$ is closed under any rotation $R(\alpha,\beta,\gamma)$

$$R(\alpha,\beta,\gamma)Y_{l,m}(\mathbf{r}) = \sum_{m'=-l,+l} \Gamma^l(\alpha,\beta,\gamma)_{m',m} Y_{l,m'}(\mathbf{r}), \tag{144}$$

where $\Gamma^l(\alpha,\beta,\gamma)_{m',m}$ are the matrix elements of the irreducible representation l for the element $R(\alpha,\beta,\gamma)$ of the rotation group.

Examples: the C_{3v} group

Let us reconsider the representation obtained in $\mathbb{R}^3$ of the $\mathcal{C}_{3v}$ group written in the basis $\mathcal{B} = \{|e_x\rangle, |e_y\rangle, |e_z\rangle\}$

$$\Gamma^{\mathbb{R}^3} = \left\{ \Gamma^{\mathbb{R}^3}(E) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \Gamma^{\mathbb{R}^3}(C_3) = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}, \Gamma^{\mathbb{R}^3}(C_3{}^{-1}) = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}, \right.$$
$$\left. \Gamma^{\mathbb{R}^3}(\sigma_1) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \Gamma^{\mathbb{R}^3}(\sigma_2) = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}, \Gamma^{\mathbb{R}^3}(\sigma_3) = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \right\}. \quad (145)$$

We noticed that the subspaces V_{xy} and V_z are two stable subspaces, and as V_z is of dimension one, it is necessarily an irreducible space, and the corresponding representation matrices (*i.e.* $\Gamma_{A_1}(G_i) = 1$, $\forall G_i \in \mathcal{G}$) an irreducible representation. The subspace V_{xy} is also an irreducible space as one cannot find a unique unitary transformation that can further block diagonalize simultaneously all the matrices in that subspace. Therefore we know that there the following set of matrices is an irreducible representation of dimension 2 of the $\mathcal{C}_{3v}$ group

$$\Gamma^{\mathbb{R}^2} = \left\{ \Gamma^{\mathbb{R}^2}(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \Gamma^{\mathbb{R}^2}(C_3) = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}, \Gamma^{\mathbb{R}^2}(C_3{}^{-1}) = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}, \right.$$
$$\left. \Gamma^{\mathbb{R}^2}(\sigma_1) = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \Gamma^{\mathbb{R}^2}(\sigma_2) = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}, \Gamma^{\mathbb{R}^2}(\sigma_3) = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix} \right\}. \quad (146)$$

We will now consider another representation of dimension 3 obtained in 4.4.3 for a vector space $\mathcal{V} = \text{span}(|e_1\rangle, |e_2\rangle, |e_3\rangle)$ isomorph to $\mathbb{R}^3$. We recall here the representation obtained

$$\begin{aligned} &\Gamma^{\mathcal{V}} = \{\Gamma^{\mathcal{V}}(G_i), i = 1, g\} \\ &\Gamma^{\mathcal{V}}(E) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \Gamma^{\mathcal{V}}(C_3) = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}, \Gamma^{\mathcal{V}}(C_3^{-1}) = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}, \\ &\Gamma^{\mathcal{V}}(\sigma_1) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \Gamma^{\mathcal{V}}(\sigma_2) = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \Gamma^{\mathcal{V}}(\sigma_3) = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \end{aligned} \quad (147)$$

Here it is much less clear how to find the decomposition in terms of irreducible representations, or even if such a representation is equivalent to $\Gamma^{\mathbb{R}^3}$

4.7 Characters

As pointed previously, it is not easy to know if two representations of identical dimensions are equivalent or not. To solve this problem, we will introduce a very powerful object: the characters.

4.7.1 Definition of characters

From now on we will label the representations not necessarily with the vector space on which they are defined (because any finite dimension vector space of dimension n is isomorph to $\mathbb{R}^n$) but with an index α and call it Γ^α

$$\Gamma^{\mathcal{V}}_\alpha \equiv \Gamma^\alpha.$$

Definition: *Characters*
Let Γ^α be a representation of dimension d_α of a group $\mathcal{G}$. We call $\chi^\alpha(G)$ *the character of the element G in*

the representation Γ^α , and it is the trace of the matrix $\Gamma^\alpha(G)$

$$\boxed{\chi^\alpha(G) = \mathrm{tr}(\Gamma^\alpha(G)) = \sum_{j=1,d_\alpha} \Gamma^\alpha(G)_{jj}.} \tag{148}$$

Because of the property of the trace one has that

$$\boxed{\mathrm{tr}(T^{-1}AT) = \mathrm{tr}(AT^{-1}T) = \mathrm{tr}(A),} \tag{149}$$

which means that the *trace of a matrix is invariant with respect to any similarity transformation,* and therefore independent of the basis. The five fundamental properties of characters are the following:

1) $\chi^\alpha(E) = d_\alpha$ as the identity element is always represented by an identity matrix of dimension d_α, therefore the *character of the identity gives the dimension of the representation,*

2) As a consequence of Eqs. (149) and (148), the *characters of all equivalent representations are the same.*

3) Conjugated elements G_i and G_j (*i.e.* elements belonging to the same class $\mathcal{C}$) are related by $GG_iG^{-1} = G_j$ (where G is an element in $\mathcal{G}$).
This implies that the *characters of all elements of the same class are identical.*

4) As the matrix $\Gamma^\alpha(G_i)$ is unitary, then $\Gamma^\alpha({G_i}^{-1}) = \Gamma^\alpha(G_i)^{-1} = \big(\Gamma^\alpha(G_i)\big)^\dagger$ and therefore

$$\chi^\alpha({G_i}^{-1}) = \sum_j \big(\Gamma^\alpha(G_i)\big)^\dagger_{jj} = \sum_j \big(\Gamma^\alpha(G_i)\big)^*_{jj} = \left(\sum_j \Gamma^\alpha(G_i)_{jj}\right)^* = \chi^\alpha(G_i)^*$$

5) As the dimension of the irreducible representations for Abelian group is 1, the matrices of irreducible representations are equal to their characters.

4.7.2 Intuitive approach to use characters for reducible representations

We know that any representation Γ^α can be decomposed into a direct sum of irreducible representations

$$\Gamma^\alpha = \Gamma^{\alpha_1} \oplus \Gamma^{\alpha_2} \oplus \ldots \oplus \Gamma^{\alpha_n}, \tag{150}$$

and that such a decomposition is unique. Therefore, any matrix $\Gamma^\alpha(G_i)$ can be written in a block diagonal form

$$\Gamma^\alpha(G_i) = \Gamma^{\alpha_1}(G_i) \oplus \Gamma^{\alpha_2}(G_i) \oplus \ldots \oplus \Gamma^{\alpha_n}(G_i), \tag{151}$$

where we used the same symbol $\oplus$ to introduce the "direct sum of matrices" similarly to the direct sum of vector spaces or representations. If one computes the character of such a matrix $\Gamma^{\mathcal{V}}(G_i)$ one therefore obtains

$$\boxed{\chi^\alpha(G_i) = \sum_{m=1,n} \chi^{\alpha_m}(G_i).} \tag{152}$$

Therefore the character of the reducible representation $\chi^\alpha(G_i)$ for an element G_i is equal to *the sum of the characters for the same element* G_i *of the irreducible representations composing* Γ^α.

Examples: the group of order 2

We found two irreducible representations $\Gamma_g = \{\Gamma_g(E) = 1, \Gamma_g(A) = 1\}$ and $\Gamma_u = \{\Gamma_u(E) = 1, \Gamma_u(A) = -1\}$. As these are one dimensional representations, their characters are equal to the representations matrices.

Now let us take the example of three-dimensional representation Γ_1 for the group of order 2

$$\Gamma_1 = \{\Gamma_1(E) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \Gamma_1(A) = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}\}, \tag{153}$$

which had the following decomposition

$$\Gamma_1 = 2\Gamma_g \oplus \Gamma_u. \tag{154}$$

We can then compute the character of each element

$$\begin{aligned} \chi^1(E) &= \mathrm{tr}(\Gamma_1(E)) = 3 \\ \chi^1(A) &= \mathrm{tr}(\Gamma_1(A)) = 1. \end{aligned} \tag{155}$$

We know that such a representation of dimension 3 is reducible as the irreducible representations of Abelian groups are of dimension one. We write the character table for the reducible and irreducible representations found for the group of order 2

$\chi\backslash G_i$	E	A
χ^g	1	1
χ^u	1	-1
χ^1	3	1

and therefore we see that indeed

$$\begin{aligned} \chi^1(E) &= 3 = 2\times 1 + 1\times 1 = 2\times\chi^g(E) + 1\times\chi^u(E), \\ \chi^1(A) &= 0 = 2\times 1 + 1\times(-1) = 2\times\chi^g(A) + 1\times\chi^u(A). \end{aligned} \tag{156}$$

As we shown earlier, by doing a change of basis we can write the Γ_1 representation in a block diagonal form

$$\Gamma_1 \cong \{ \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \tag{157}$$

where it is clearly apparent that the characters are the same, and the we have indeed two times Γ_g and one time Γ_u.

Examples: the $\mathcal{C}_{3v}$ group

We can now use the characters to know if the two representations of dimension three obtained in Sec. 4.4.2 and 4.4.3 are equivalent or not. As all elements of the same class have the same characters, we only need to compute the characters of one element per class:

$$\chi^1(E) = \mathrm{tr}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = 3, \quad \chi^1(C_3) = \mathrm{tr}\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} = 0, \quad \chi^1(\sigma_1) = \mathrm{tr}\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = 1, \tag{158}$$

and

$$\chi^2(E) = \mathrm{tr}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = 3, \quad \chi^2(C_3) = \mathrm{tr}\begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} = 0, \qquad \chi^2(\sigma_1) = \mathrm{tr}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} = 1. \tag{159}$$

Therefore we immediately see that the two representations are equivalent thanks to their characters.

5 Important theorems about linear representations

In this section, we give the most important theorems about group representations. The proof will not always be given here if they are too lengthy, but some of them can be found in the appendix of this lecture.

5.1 A Fundamental Lemma: Schur's Lemma

Schur's lemma is one of the most fundamental theorem of linear representation of group. In this section, we are going to see two important applications of Schur's lemma in quantum mechanics yielding to

1) the block diagonal structure of the Hamiltonian written on the basis of irreducible representations,

2) the orthogonality of basis functions for different irreducible representations.

This theorem essentially motivates the whole study of group theory in quantum mechanics.

5.1.1 Statement of the theorem

Theorem:*Schur's Lemma*

Consider a group $\mathcal{G} = \{G_i, i = 1, g\}$ of order g, and two *irreducible* representations of the group $\Gamma^\alpha = \{\Gamma^\alpha(G_i), i = 1, g\}$ and $\Gamma^\beta = \{\Gamma^\beta(G_i), i = 1, g\}$ associated with two vector spaces $\mathcal{V}_\alpha$ and $\mathcal{V}_\beta$ of dimension d_α and d_β, respectively.

If a linear map M from $\mathcal{V}_\alpha$ to $\mathcal{V}_\beta$ (*i.e.* an intertwining map) commutes with *all of the representations matrices* of these two irreducible representations, which means that

$$M\Gamma^\alpha(G_i) = \Gamma^\beta(G_i)M \quad \forall G_i \in \mathcal{G}, \tag{160}$$

then such a linear map fulfills the following properties

- if the two irreducible representations Γ^α and Γ^β *are not equivalent*, then M is zero,
- if Γ^α and Γ^β *are equivalent*, then M is a homothetic of the *identity map*, *i.e.* $M = \lambda \mathbb{1}_{d_\alpha}$, $\lambda \in \mathbb{C}$.

5.1.2 Application: the structure of the Hamiltonian

Consider a Hamiltonian H projected on a finite vector space $\mathcal{V}$ of dimension d spanned by basis $\mathcal{B} = \{|\phi_i\rangle, i = 1, d\}$. Such a basis can be for instance an AO basis for some molecular system. Assuming now that the Hamiltonian is invariant with respect to a set of symmetry operations $\mathcal{G} = \{G_i, i = 1, g\}$, it necessarily implies that this set forms a group. We can then obtain a reducible representation of the group $\Gamma^\mathcal{V} = \{\Gamma^\mathcal{V}(G_i), i = 1, g\}$ on the same vector space $\mathcal{V}$ and basis $\mathcal{B}$, and such a representation might not be in a block-diagonal form. By definition of the symmetry group, one knows that the Hamiltonian commutes with all the matrices of $\Gamma^\mathcal{V}$ representing the symmetry elements of the group $\mathcal{G}$, which translates into

$$\Gamma^\mathcal{V}(G)H = H\Gamma^\mathcal{V}(G) \quad \forall G \in \mathcal{G}, \tag{161}$$

where we referred both to the Hamiltonian and its matrix representation as H.

We can then obtain a decomposition of $\Gamma^\mathcal{V}$ into the irreducible representations of the group

$$\Gamma^\mathcal{V} = \Gamma^{\alpha_1} \oplus \Gamma^{\alpha_2} \oplus \ldots, \tag{162}$$

and each irreducible representation Γ^{α_i} is associated with an irreducible vector space labelled $\mathcal{V}_{\alpha_i}$ spanned by a basis $\mathcal{B}^{\alpha_i} = \{|\chi_j^{\alpha_i}\rangle, j = 1, d_{\alpha_i}\}$ where d_{α_i} is the dimension of the irreducible representation Γ^{α_i}. The basis $\mathcal{B}^{\alpha_i}$ for each irreducible representation Γ^{α_i} is obtained as linear combinations of the original basis $\mathcal{B}$ of $\mathcal{V}$

$$|\chi_j^{\alpha_i}\rangle = \sum_{k=1,d} U_{jk}^{\alpha_i} |\phi_k\rangle. \tag{163}$$

For instance, think about the basis for Γ_g and Γ_u that we obtained in H_2^+. One can then obtain a new basis $\mathcal{B}_{\text{SA}}$ which is a *symmetry adapted basis* obtained by the union of each basis $\mathcal{B}^{\alpha_i}$

$$\mathcal{B}_{\text{SA}} = \mathcal{B}^{\alpha_1} \cup \mathcal{B}^{\alpha_2} \cup \ldots, \tag{164}$$

and the whole vector space $\mathcal{V}$ is then obtained as a direct sum of these irreducible vector spaces

$$\mathcal{V} = \mathcal{V}_{\alpha_1} \oplus \mathcal{V}_{\alpha_2} \oplus \dots \tag{165}$$

Notice that in the general case, the same irreducible representation can occur several times in $\Gamma^{\mathcal{V}}$, and therefore one can have Γ^{α_i} and Γ^{α_j} which are equivalent. As an example, if one studies a rotationally invariant system, one might be smart and choose a basis $\mathcal{B}$ which is already symmetry adapted, as for instance the eigenfunctions of the hydrogen atom truncated to a certain n_{max} and l_{max}. For $n_{max} = 3$ and $l_{max} = 1$ for instance, the basis $\mathcal{B}$ contains the $2p$ and $3p$ functions, which generate two equivalent representations Γ^{2p} and Γ^{3p} corresponding to the $l = 1$ irreducible representation of the SO(3) group.

We can then write the Hamiltonian matrix in the symmetry adapted basis $\mathcal{B}_{\text{SA}}$ in terms of blocks

$$H = \begin{pmatrix} H^{\alpha_1,\alpha_1} & H^{\alpha_1,\alpha_2} & \dots \\ H^{\alpha_2,\alpha_1} & H^{\alpha_2,\alpha_2} & \dots \\ \vdots & \vdots & \ddots \end{pmatrix}, \tag{166}$$

where H^{α_i,α_j} is the block of dimension $d_{\alpha_i} \times d_{\alpha_j}$ which connects the irreducible vector spaces $\mathcal{V}_{\alpha_i}$ and $\mathcal{V}_{\alpha_j}$

$$H^{\alpha_i,\alpha_j} = \begin{pmatrix} \left\langle \chi_1^{\alpha_i} \middle| H \middle| \chi_1^{\alpha_j} \right\rangle & \left\langle \chi_1^{\alpha_i} \middle| H \middle| \chi_2^{\alpha_j} \right\rangle & \dots & \left\langle \chi_1^{\alpha_i} \middle| H \middle| \chi_{d_{\alpha_j}}^{\alpha_j} \right\rangle \\ \left\langle \chi_2^{\alpha_i} \middle| H \middle| \chi_1^{\alpha_j} \right\rangle & \left\langle \chi_2^{\alpha_i} \middle| H \middle| \chi_2^{\alpha_j} \right\rangle & \dots & \left\langle \chi_2^{\alpha_i} \middle| H \middle| \chi_{d_{\alpha_j}}^{\alpha_j} \right\rangle \\ \vdots & \vdots & \vdots & \ddots \\ \left\langle \chi_{d_{\alpha_i}}^{\alpha_i} \middle| H \middle| \chi_1^{\alpha_j} \right\rangle & \left\langle \chi_{d_{\alpha_i}}^{\alpha_i} \middle| H \middle| \chi_2^{\alpha_j} \right\rangle & \dots & \left\langle \chi_{d_{\alpha_i}}^{\alpha_i} \middle| H \middle| \chi_{d_{\alpha_j}}^{\alpha_j} \right\rangle \end{pmatrix}. \tag{167}$$

From the mathematical perspective, each H^{α_i,α_j} is an intertwining linear map from $\mathcal{V}_{\alpha_j}$ to $\mathcal{V}_{\alpha_i}$.

Because the matrix representation $\Gamma^{\mathcal{V}}(G_i)$ (for any symmetry elements G_i) is block diagonal when written in the symmetry adapted basis $\mathcal{B}_{\text{SA}}$ (a direct consequence of the notion of stable subspaces defining the irreducible subspaces)

$$\Gamma^{\mathcal{V}}(G_i) = \begin{pmatrix} \Gamma^{\alpha_1}(G_i) & 0 & 0 & \dots \\ 0 & \Gamma^{\alpha_2}(G_i) & 0 & \dots \\ 0 & 0 & \Gamma^{\alpha_3}(G_i) & \dots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \forall G_i \in \mathcal{G}, \tag{168}$$

one can rewrite the commutation relation of Eq. (161) between the Hamiltonian matrix and $\Gamma^{\mathcal{V}}(G_i)$ as

$$\begin{aligned} &\Gamma^{\mathcal{V}}(G)H = H\Gamma^{\mathcal{V}}(G) \quad \forall G \in S \\ \Leftrightarrow &\Gamma^{\alpha_i}(G)H^{\alpha_i,\alpha_j} = H^{\alpha_j,\alpha_i}\Gamma^{\alpha_j}(G) \quad \forall G \in S, \end{aligned} \tag{169}$$

which is precisely the application case of Schur's Lemma.

Therefore, as a consequence of Schur's Lemma, one obtains that

1) the Hamiltonian matrix vanishes between two non equivalent irreducible representations,

$$\boxed{H^{\alpha_i,\alpha_j} = 0 \text{ if } \Gamma^{\alpha_i} \text{ is non equivalent to } \Gamma^{\alpha_j}}, \tag{170}$$

2) the Hamiltonian is *diagonal and degenerate* within the irreducible subspace $\mathcal{V}_{\alpha_i}$ and the degeneracy is equal to the dimension d_{α_i} of the irreducible representation Γ^{α_i}

$$\boxed{H^{\alpha_i,\alpha_i} = \lambda_{\alpha_i} \mathbb{1}_{d_{\alpha_i}}}, \tag{171}$$

3) and last but not least, the *interaction between equivalent irreducible representations is diagonal and degenerate*

$$\boxed{H^{\alpha_i,\alpha_j} = \lambda_{\alpha_i,\alpha_j} \mathbb{1} \text{ if } \Gamma^{\alpha_i} \text{ and } \Gamma^{\alpha_j} \text{ are equivalent}}. \tag{172}$$

Therefore, thanks to Schur's lemma, one only needs to deal with much sparser matrices and it also gives the degeneracy of the eigenvalues.

5.1.3 A pictorial application of Schur's lemma

In order to have a simple illustration of the implication of Schur's lemma in quantum mechanics, let us take the example of a rotationally invariant one-electron system described by the following Hamiltonian

$$H = -\frac{1}{2}\Delta_{\mathbf{r}} + v(|\mathbf{r}|), \tag{173}$$

projected in the basis of hydrogen-like functions with $n_{max} = 3$ and $l_{max} = 1$

$$\mathcal{B} = \{|1s\rangle, |2s\rangle, |3s\rangle\} \cup \{|2p_x\rangle, |2p_y\rangle, |2p_z\rangle\} \cup \{|3p_x\rangle, |3p_y\rangle, |3p_z\rangle\}. \tag{174}$$

One can then obtain a representation Γ of the SO(3) group on the vector space spanned by $\mathcal{B}$, and as each of the basis functions in $\mathcal{B}$ are symmetry adapted, one knows that the representation Γ has the following decomposition into the irreducible representations of the SO(3) group

$$\begin{aligned} \Gamma &= \Gamma^{1s} \oplus \Gamma^{2s} \oplus \Gamma^{3s} \oplus \Gamma^{2p} \oplus \Gamma^{3p} \\ &= 3\,\Gamma^{l=0} \oplus 2\,\Gamma^{l=1}, \end{aligned} \tag{175}$$

where the three one-dimensional equivalent representations $\Gamma^{l=0}$ corresponds to the three s functions, and the two three-dimensional equivalent $l = 1$ irreducible representations correspond to the the $2p$ and $3p$ functions.

Schur's lemma tells us that

1) $H^{s,p} = 0$ as the Hamiltonian vanishes between two non equivalent irreducible representations, and therefore the s and p blocks are completely decoupled,

2) $H^{2p,2p} = \lambda_{2p}\mathbb{1}_3$ and $H^{3p,3p} = \lambda_{3p}\mathbb{1}_3$, which means that the Hamiltonian is diagonal and 3-fold degenerate within each p block,

3) $H^{2p,3p} = \lambda_{2p,3p}\mathbb{1}_3$ which implies that the interaction between the $2p$ and $3p$ blocks is either a single number or zero, and therefore extremely sparse and redundant.

One can then write the Hamiltonian matrix in a pictorial way as

$$H = \begin{pmatrix} H^{s,s} & 0 \\ 0 & H^{p,p} \end{pmatrix}, \tag{176}$$

where $H^{s,s}$ is the Hamiltonian matrix written on the basis of the s functions (and Schur's lemma does not tell much about it), and the p block being explicitly

$$H^{p,p} = \begin{pmatrix} |2p_x\rangle & |2p_y\rangle & |2p_z\rangle & |3p_x\rangle & |3p_y\rangle & |3p_z\rangle \\ \lambda_{2p} & 0 & 0 & \lambda_{2p,3p} & 0 & 0 \\ 0 & \lambda_{2p} & 0 & & \lambda_{2p,3p} & 0 \\ 0 & 0 & \lambda_{2p} & 0 & 0 & \lambda_{2p,3p} \\ \lambda_{2p,3p} & 0 & 0 & \lambda_{3p} & 0 & 0 \\ & \lambda_{2p,3p} & 0 & 0 & \lambda_{3p} & 0 \\ 0 & 0 & \lambda_{2p,3p} & 0 & 0 & \lambda_{3p} \end{pmatrix}, \tag{177}$$

which, by rearranging the basis, can be further rewritten as

$$H^{p,p} = \begin{pmatrix} |2p_x\rangle & |3p_x\rangle & |2p_y\rangle & |3p_y\rangle & |2p_z\rangle & |3p_z\rangle \\ \lambda_{2p} & \lambda_{2p,3p} & 0 & 0 & 0 & 0 \\ \lambda_{2p,3p} & \lambda_{2p} & 0 & 0 & 0 & 0 \\ 0 & 0 & \lambda_{2p} & \lambda_{2p,3p} & 0 & 0 \\ 0 & 0 & \lambda_{2p,3p} & \lambda_{2p} & 0 & 0 \\ 0 & 0 & 0 & 0 & \lambda_{2p} & \lambda_{2p,3p} \\ 0 & 0 & 0 & 0 & \lambda_{2p,3p} & \lambda_{2p} \end{pmatrix}, \tag{178}$$

which is nothing but *3 times the same* 2×2 *matrix*. Therefore, by knowing the irreducible decomposition of the basis we know that we have

- 3 s states not degenerated,
- 2 p states 3 times degenerated.

5.1.4 Application: the structure of the overlap matrix

Another important application concerns the *overlap matrix*

$$S_{ji} = \langle \phi_j | \phi_i \rangle = \langle \phi_j | \mathbb{1} | \phi_i \rangle \,, \tag{179}$$

which also commutes with all matrices representing the elements of the group. Therefore, it has the same structure than that of the Hamiltonian, which implies that

- the basis functions of inequivalent representations are orthogonal
$$\left\langle \chi_k^{\alpha_i} \middle| \chi_l^{\alpha_j} \right\rangle = 0 \text{ if } \Gamma^{\alpha_i} \text{ and } \Gamma^{\alpha_j} \text{ are non equivalent,} \tag{180}$$
- one can obtain orthonormal basis functions spanning the irreducible subspaces of all equivalent representations.

5.2 The great orthogonality theorem for representations

5.2.1 Statement of the theorem

Theorem: *Great orthogonality theorem*
All the *matrices of two irreducible representations* Γ^α and Γ^β satisfy the following orthogonality relations

$$\boxed{\sum_{G\in\mathcal{G}} \Gamma^{\alpha}_{ij}(G)^* \Gamma^{\beta}_{kl}(G) = \frac{g}{d_\alpha} \delta_{ik}\delta_{jl}\delta_{\alpha\beta}} \tag{181}$$

where the summation runs over the group elements, g is the order of the group and d_α is the dimension of the irreducible representation Γ^α, and where $\delta_{\alpha\beta}$ means

$$\delta_{\alpha\beta} = \begin{cases} 1 & \text{if } \Gamma^\alpha \text{ and } \Gamma^\beta \text{ are equivalent,} \\ 0 & \text{if not.} \end{cases} \tag{182}$$

This orthogonality theorem can be understood in a vectorial way by constructing a vector $\left|\gamma_{ij}^{\alpha}\right\rangle$ of length g (*i.e.* the order of the group) which contains the matrix elements $\Gamma^\alpha_{ij}(G)$ for each elements G in the group. More precisely, the m-th component of the vector $\left|\gamma_{ij}^{\alpha}\right\rangle$ is explicitly

$$\gamma^{\alpha}_{ij}(m) = \Gamma^{\alpha}_{ij}(G_m), \quad \forall G_m \in \mathcal{G}. \tag{183}$$

The great orthogonality theorem tells us any two vectors $\left|\gamma_{ij}^{\alpha}\right\rangle$ and $\left|\gamma_{kl}^{\beta}\right\rangle$ are orthogonal

$$\sum_{m=1,g} \left(\gamma^{\alpha}_{ij}(m)\right)^* \gamma^{\beta}_{kl}(m) = \frac{g}{d_\alpha}\delta_{ik}\delta_{jl}\delta_{\alpha\beta}.$$

Therefore we can build a vector space spanned by all these orthonormal vectors. For each irreducible representation Γ^α, the number of orthonormal vectors $\left|\gamma_{ij}^{\alpha}\right\rangle$ is the number of matrix elements, which is $d_\alpha \times d_\alpha$. Therefore one knows that as the vector space is of dimension $\sum_\alpha (d_\alpha)^2$, and therefore one knows that g, which is the length of the vectors $\left|\gamma_{ij}^{\alpha}\right\rangle$, is necessarily greater or equal the dimension of the vector space

$$\sum_\alpha (d_\alpha)^2 \leq g. \tag{184}$$

As we shall see later on, this is not only an inequality but an equality.

5.2.2 Illustrations of the theorem

Let us illustrate the great orthogonality theorem with the examples given above. Regarding the group of order 2, the two reducible representations Γ^g and Γ^u that we found were

$$\begin{aligned}\Gamma^g(E) &= \{\Gamma^g(E) = 1, \Gamma^g(A) = 1\}\\ \Gamma^u &= \{\Gamma^u(E) = 1, \Gamma^u(A) = -1\}\end{aligned} \tag{185}$$

If we take $\Gamma^\alpha = \Gamma^g$ and $\Gamma^\beta = \Gamma^u$, we see that $d_\alpha = d_\beta = 1$, and therefore that $i = j = 1$ and $k = l = 1$. Also, let us run over the elements of the group the product of the matrix elements for Γ^g and Γ^u

$$\Gamma^g(E)^* \times \Gamma^u(E) + \Gamma^g(A)^* \times \Gamma^u(A) = 1 \times 1 + 1 \times -1 = 0 \tag{186}$$

we find here the orthogonality relation. If now run only for Γ^g we obtain

$$\Gamma^g(E)^* \times \Gamma^g(E) + \Gamma^g(A)^* \times \Gamma^g(A) = 1 \times 1 + 1 \times 1 = 2 = g/d_\alpha, \tag{187}$$

and similarly for Γ^u

$$\Gamma^u(E)^* \times \Gamma^u(E) + \Gamma^u(A)^* \times \Gamma^u(A) = 1 \times 1 + -1 \times -1 = 2 = g/d_\alpha. \tag{188}$$

5.3 Orthogonality theorems for characters

5.3.1 First orthogonality theorem for characters

Theorem:*First orthogonality theorem of characters*
For two *irreducible representations* Γ^α and Γ^β, we have the following orthogonality relation

$$\boxed{\sum_{G\in\mathcal{G}} \chi^\alpha(G)^*\chi^\beta(G) = g\delta_{\alpha\beta}.} \tag{189}$$

The proof is quite easy starting from the great orthogonality theorem of Eq. (181) and by setting $i = j$ and $k = l$

$$\sum_{G\in\mathcal{G}} \Gamma^\alpha_{ii}(G)^*\Gamma^\beta_{kk}(G) = \frac{g}{d_\alpha}\delta_{ik}\delta_{\alpha\beta}, \tag{190}$$

then one sums over i and k to make appear the characters

$$\begin{aligned}&\sum_{i=1,d_\alpha}\sum_{k=1,d_\beta}\sum_{G\in\mathcal{G}} \Gamma^\alpha_{ii}(G)^*\Gamma^\beta_{kk}(G) = \frac{g}{d_\alpha}\delta_{\alpha\beta}\sum_{i=1,d_\alpha}\sum_{k=1,d_\beta}\delta_{ik}\\ \Leftrightarrow &\sum_{G\in\mathcal{G}}\big(\sum_{i=1,d_\alpha}\Gamma^\alpha_{ii}(G)^*\big)\big(\sum_{k=1,d_\beta}\Gamma^\beta_{kk}(G)\big) = \frac{g}{d_\alpha}\delta_{\alpha\beta}\sum_{i=1,d_\alpha}1\\ \Leftrightarrow &\sum_{G\in\mathcal{G}}\chi^\alpha(G)^*\chi^\beta(G) = \frac{g}{d_\alpha}\delta_{\alpha\beta}d_\alpha,\end{aligned} \tag{191}$$

and then one obtains Eq. (189).

Since the characters of all elements belonging to the same class $\mathcal{C}$ are identical, we can restrict the summation in Eq. (189) to summations over different classes

$$\boxed{\sum_{k=1}^{n_\mathcal{C}} h_k\chi^\alpha(\mathcal{C}_k)^*\chi^\beta(\mathcal{C}_k) = g\delta_{\alpha\beta},} \tag{192}$$

where $n_\mathcal{C}$ is the number of classes in the group, $\chi^\alpha(\mathcal{C}_k)$ is the character of any element G belonging to the $\mathcal{C}_k$ and h_k is the number of elements in the class $\mathcal{C}_k$.

5.3.2 Second orthogonality theorem for characters

Theorem:*Second orthogonality theorem of characters*
For the set of all irreducible representations of a group we have then the following orthogonality relation

$$\boxed{\sum_{\alpha=1}^{n_r} \chi^{\alpha}(\mathcal{C}_i)^* \chi^{\alpha}(\mathcal{C}_j) = \delta_{ij} \frac{g}{h_i},} \tag{193}$$

where n_r is the number of inequivalent irreducible representations of the group. The proof of this orthogonality relation will not be given here.

An important direct consequence of Eq. (193) can be obtained by looking specifically at the class of the identity. As one knows that there is a single element in that class, we knows that $h_E = 1$, and that $\chi^{\alpha}(E) = d_{\alpha}$. Therefore by application of Eq. (193) one obtains that

$$\boxed{\sum_{\alpha=1} (d_{\alpha})^2 = g.} \tag{194}$$

5.3.3 Illustrations of the theorems of orthogonality for characters

Let us illustrate the theorems of orthogonality in the case of the $\mathcal{C}_{3v}$ group for which we report here the character table.

$\chi \backslash G_i$	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

Let us illustrate the first orthogonality character, which corresponds to make the scalar product between any two lines of Table 5.3.3 Let us begin with A_1 and A_2

$$\begin{aligned} 1 \times (\chi^{A_1}(E)^* \chi^{A_2}(E)) + 2 \times (\chi^{A_1}(C_3)^* \chi^{A_2}(C_3)) + 3 \times (\chi^{A_1}(\sigma_v)^* \chi^{A_2}(\sigma_v)) &= 1(1 \times 1) + 2(1 \times 1) + 3(1 \times -1) \\ &= 3 - 3 = 0. \end{aligned} \tag{195}$$

Then E and A_2

$$\begin{aligned} 1 \times (\chi^{E}(E)^* \chi^{A_2}(E)) + 2 \times (\chi^{E}(C_3)^* \chi^{A_2}(C_3)) + 3 \times (\chi^{E}(\sigma_v)^* \chi^{A_2}(\sigma_v)) &= 1(1 \times 2) + 2(1 \times -1) + 3(1 \times 0) \\ &= 2 - 2 = 0. \end{aligned} \tag{196}$$

And a diagonal one for A_2

$$\begin{aligned} 1 \times (\chi^{A_2}(E)^* \chi^{A_2}(E)) + 2 \times (\chi^{A_2}(C_3)^* \chi^{A_2}(C_3)) + 3 \times (\chi^{A_2}(\sigma_v)^* \chi^{A_2}(\sigma_v)) &= 1(1 \times 1) + 2(1 \times 1) + 3(-1 \times -1) \\ &= 6. \end{aligned} \tag{197}$$

Now we can illustrate the second orthogonality character, which consists into scalar products of the columns. Let us begin by the class E with the class C_3

$$\chi^{A_1}(E)^* \chi^{A_1}(C_3) + \chi^{A_2}(E)^* \chi^{A_2}(C_3) + \chi^{E}(E)^* \chi^{E}(C_3) = 1 \times 1 + 1 \times 1 + 2 \times -1 = 0. \tag{198}$$

And let us do a diagonal term, let us say the σ_v class

$$\chi^{A_1}(\sigma_v)^* \chi^{A_1}(\sigma_v) + \chi^{A_2}(\sigma_v)^* \chi^{A_2}(\sigma_v) + \chi^{E}(\sigma_v)^* \chi^{E}(\sigma_v) = 1 \times 1 + -1 \times -1 + 0 \times 0 = 2 = \frac{6}{3}. \tag{199}$$

5.3.4 Vectorial interpretations of the orthogonality theorems of characters and number of irreducible representations

The orthogonality relation of Eq. (189) can be reformulated as a vectorial orthogonality relation. Indeed, let us build the abstract vector v^α associated with the characters of each irreducible representation Γ^α. As the characters of all elements in a class are equal, v^α is a complex-valued vector in dimension $n_\mathcal{C}$ that we can define as

$$v^\alpha = \begin{pmatrix} \sqrt{h_1}\chi^\alpha(\mathcal{C}_1) \\ \sqrt{h_2}\chi^\alpha(\mathcal{C}_2) \\ \vdots \\ \sqrt{h_n}\chi^\alpha(\mathcal{C}_n) \end{pmatrix}. \tag{200}$$

This vector belongs to a vector space of dimension $n_\mathcal{C}$. Then, one can construct the scalar product of two such vectors corresponding to two irreducible representations

$$\begin{aligned}(v^\alpha, v^\beta) &= \sqrt{h_1}\chi^\alpha(\mathcal{C}_1)^* \times \sqrt{h_1}\chi^\beta(\mathcal{C}_1) + \sqrt{h_2}\chi^\alpha(\mathcal{C}_2)^* \times \sqrt{h_2}\chi^\beta(\mathcal{C}_2) + \dots \\ &= h_1\chi^\alpha(\mathcal{C}_1)^*\chi^\beta(\mathcal{C}_1) + h_2\chi^\alpha(\mathcal{C}_2)^*\chi^\beta(\mathcal{C}_2) + \dots,\end{aligned} \tag{201}$$

which according to the first orthogonality of characters (Eq. (192)) can be rewritten as

$$(v^\alpha, v^\beta) = g\delta_{\alpha\beta}. \tag{202}$$

As a vector space of dimension n has at most n mutually-orthonormal vectors, we deduce that the number of different irreducible representations n_r is at most $n_\mathcal{C}$

$$n_r \leq n_\mathcal{C}. \tag{203}$$

Then, we can also look at Eq. (193) as another form of vectorial orthogonality relation. Indeed, we can associate to a given class $\mathcal{C}_k$ a complex-valued vector $u^{\mathcal{C}_k}$ of dimension n_r composed by the characters of the class $\mathcal{C}_k$ for each non equivalent irreducible representation

$$u^{\mathcal{C}_k} = \begin{pmatrix} \chi^1(\mathcal{C}_k) \\ \chi^2(\mathcal{C}_k) \\ \vdots \\ \chi^{n_r}(\mathcal{C}_k) \end{pmatrix}. \tag{204}$$

Then, the scalar product of two of such vectors reduces in Eq. (193), an we can then form a vector space of dimension n_r. Therefore one deduces that the number of vectors of type $u^{\mathcal{C}_k}$ (which is given by the number of classes $n_\mathcal{C}$) cannot exceed the size of the vector space n_r

$$n_\mathcal{C} \leq n_r. \tag{205}$$

Therefore, in virtue of Eq. (203) and (205), one deduces that

$$\boxed{n_r = n_\mathcal{C},} \tag{206}$$

which means that *the total number of non equivalent irreducible representations of a group equals the number of distinct classes.*

We therefore deduce that for *Abelian groups* (where each element is a distinct class) *the dimension of each irreducible representation is one.*

5.4 Illustration of the two orthogonality theorems of characters: reducing representations

The orthogonality of characters is extremely useful for many reasons as it allows one to know if a representation is reducible or not, and more interestingly, it allows one to know what are the irreducible representations composing the reducible representation. In the case of Abelian groups, as the irreducible representations are of dimension 1, it is easy to know if a representation is reducible or not just by checking the dimension of the representation. In the non Abelian case, it is already more tricky. Let us assume that we have a given representation Γ^α of dimension d. Such a representation is necessarily a direct sum of irreducible representations Γ^{α_i} with $i = 1, n_c$

$$\Gamma^\alpha = c_1\Gamma^{\alpha_1} \oplus c_2\Gamma^{\alpha_2} \oplus \ldots \oplus c_{n_c}\Gamma^{\alpha_{n_c}} \tag{207}$$

where the coefficients $\{c_i\}$ are integers. The theorems of orthogonality of characters allows you to easily find the $\{c_i\}$ provided that the character table of the group is known.

To do so, we can build the character vector of the representation Γ^α

$$v^\alpha = \begin{pmatrix} \sqrt{h_1}\chi^\alpha(\mathcal{C}_1) \\ \sqrt{h_2}\chi^\alpha(\mathcal{C}_2) \\ \vdots \\ \sqrt{h_n}\chi^\alpha(\mathcal{C}_n) \end{pmatrix}. \tag{208}$$

Then one can perform the scalar product with the vector corresponding to a given irreducible representations v^{α_k}

$$(v^{\alpha_k}, v^\alpha) = h_1\chi^{\alpha_k}(\mathcal{C}_1)^* \times \chi^\alpha(\mathcal{C}_1) + h_2\chi^{\alpha_k}(\mathcal{C}_2)^* \times \chi^\alpha(\mathcal{C}_2) + \ldots h_{n_c}\chi^{\alpha_k}(\mathcal{C}_{n_c})^* \times \chi^\alpha(\mathcal{C}_{n_c}). \tag{209}$$

But as the representation Γ^α is decomposed as a direct sum of irreducible representation

$$\Gamma^\alpha(G_i) = c_1\Gamma^{\alpha_1}(G_i) \oplus c_2\Gamma^{\alpha_2}(G_i) \oplus \ldots \oplus c_{n_c}\Gamma^{\alpha_{n_c}}(G_i) \tag{210}$$

and that the character of a sum of representations is directly the sum of the characters

$$\chi^\alpha(\mathcal{C}_i) = c_1\chi^{\alpha_1}(\mathcal{C}_i) + c_2\chi^{\alpha_2}(\mathcal{C}_i) + \ldots c_{n_c}\chi^{\alpha_{n_c}}(\mathcal{C}_i), \tag{211}$$

one obtains for the scalar product

$$\begin{aligned}(v^{\alpha_k}, v^\alpha) &= h_1\chi^{\alpha_k}(\mathcal{C}_1)^* \times (\sum_{m=1,n_c} c_m\chi^{\alpha_m}(\mathcal{C}_1)) + h_2\chi^{\alpha_k}(\mathcal{C}_2)^* \times (\sum_{m=1,n_c} c_m\chi^{\alpha_m}(\mathcal{C}_2)) + \ldots \\ &= \sum_{m=1,n_c} c_m(\sum_{i=1,n_c} h_i\chi^{\alpha_k}(\mathcal{C}_i)))^*\chi^{\alpha_m}(\mathcal{C}_i)))\end{aligned} \tag{212}$$

and in virtue of Eq. (192), one obtains

$$\begin{aligned}(v^{\alpha_k}, v^\alpha) &= \sum_{m=1,n_c} c_m \times g\delta_{km} \\ &= c_k \times g.\end{aligned} \tag{213}$$

It is therefore very easy to obtain the coefficients c_k from a simple scalar product.

Examples: the $\mathcal{C}_{3v}$ group

Let us take the example of one of the representation Γ obtained previously for $\mathcal{C}_{3v}$

$$\begin{aligned}\Gamma = \Bigg\{\Gamma(E) = \begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}, \quad \Gamma(C_3) = \begin{pmatrix}0&0&1\\1&0&0\\0&1&0\end{pmatrix}, \quad \Gamma({C_3}^{-1}) = \begin{pmatrix}0&1&0\\0&0&1\\1&0&0\end{pmatrix}, \\ \Gamma(\sigma_1) = \begin{pmatrix}1&0&0\\0&0&1\\0&1&0\end{pmatrix}, \quad \Gamma(\sigma_2) = \begin{pmatrix}0&0&1\\0&1&0\\1&0&0\end{pmatrix}, \quad \Gamma(\sigma_3) = \begin{pmatrix}0&1&0\\1&0&0\\0&0&1\end{pmatrix}\Bigg\}.\end{aligned} \tag{214}$$

We know the character table of $\mathcal{C}_{3v}$ and the character of Γ

$\chi \backslash G_i$	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
Γ	3	0	1

So we can define a vector for each irreducible representation according to Eq. (208)

$$v^{\mathrm{A}_1} = (1, \sqrt{2}, \sqrt{3}), \quad v^{\mathrm{A}_2} = (1, \sqrt{2}, -\sqrt{3}), \quad v^{\mathrm{E}} = (2, 0, \sqrt{3}), \tag{215}$$

and a vector for the representation Γ

$$v^{\Gamma} = (3, 0, \sqrt{3}). \tag{216}$$

Let us then compute the scalar products between v^{Γ} and the three vectors of Eq. (215)

$$\begin{aligned} \left(v^{\mathrm{A}_1}, v^{\Gamma}\right) &= 1 \times 3 + 0 \times \sqrt{2} + \sqrt{3} \times \sqrt{3} = 6 \times 1, \\ \left(v^{\mathrm{A}_2}, v^{\Gamma}\right) &= 1 \times 3 + 0 \times \sqrt{2} - \sqrt{3} \times \sqrt{3} = 0, \\ \left(v^{\mathrm{E}}, v^{\Gamma}\right) &= 2 \times 3 + 0 \times 0 + \sqrt{3} \times \sqrt{3} = 6 \times 1, \end{aligned} \tag{217}$$

and we deduce then that

$$\Gamma = \Gamma^{\mathrm{A}_1} \oplus \Gamma^{\mathrm{E}}. \tag{218}$$

5.5 Getting directly the good basis: the projection operator

In all the previous sections we have emphasized the existence of the irreducible representations and shown how any representation can be decomposed as a direct sum of these irreducible representations, leaving all matrices in a block diagonal form. This nice decomposition nevertheless relies on a change of basis: we need to find the expression of the basis suited for irreducible representations as a function of the original basis. When matrices are small, it can be found by either following a kind of physical/chemical intuition, or by the diagonalization of some matrices of the group representation.

Nevertheless, one would like to have a *general and systematic procedure* to obtain the basis for irreducible representations that does not rely on diagonalization as it soon becomes impossible to do. Thanks to the great orthogonality theorem, there exists a projection technique to obtain such a change of basis which requires only minimal knowledge of the irreducible representation matrices.

5.5.1 The complete projection operator

Assume that we work on a vector space $\mathcal{V}$ of dimension d spanned by a basis $\mathcal{B} = \{|\phi_i\rangle, i = 1, d\}$ and that we have a representation of the group Γ on such a vector space. Such a representation is necessarily a direct sum of irreducible representations $\{\Gamma^{\alpha}\}$

$$\Gamma = \Gamma^{\alpha_1} \oplus \Gamma^{\alpha_2} \oplus \ldots \tag{219}$$

On the other hand, knowing an irreducible representation Γ^{α} of the group means that we know the specific set of matrices $\{\Gamma^{\alpha}(G_i), i = 1, g\}$ which do not depend on the precise vector space on which we are working on.

If Γ^{α} is contained in Γ, therefore there exists a basis set $\mathcal{B}^{\alpha} = \{|\chi_i^{\alpha}\rangle, i = 1, d_{\alpha}\}$ which can be obtained from a similarity transformation of the initial basis $\mathcal{B}$. This is precisely what we are looking for: the basis for the irreducible representation $\mathcal{B}^{\alpha} = \{|\chi_i^{\alpha}\rangle, i = 1, d_{\alpha}\}$ in the vector space $\mathcal{V}$.

Consider now a vector $|\phi\rangle$ in $\mathcal{V}$ which is decomposed on the known basis $\mathcal{B}$

$$|\phi\rangle = \sum_{i=1,d} c_i |\phi_i\rangle, \tag{220}$$

and such a vector has necessarily a decomposition on the basis of the irreducible representations

$$|\phi\rangle = \sum_{\alpha} \sum_{i=1,d_\alpha} c_i^\alpha \, |\chi_i^\alpha\rangle \, . \tag{221}$$

One would like to obtain a way to go from the known basis $\mathcal{B}$ to the symmetry adapted $\mathcal{B}^\alpha$.

Assume that the representation Γ contains the irreducible representation Γ^α, and let us begin by considering the application of one $\Gamma(G)$ on a given irreducible basis element $|\chi_i^\alpha\rangle$

$$\Gamma(G) \, |\chi_i^\alpha\rangle = \sum_{j=1,d_\alpha} \Gamma_{ji}^\alpha(G) \, |\chi_j^\alpha\rangle \, . \tag{222}$$

One can then multiply Eq. (222) by the complex conjugate of an element of matrix $\left(\Gamma_{mn}^\alpha(G)\right)^*$

$$\left(\Gamma_{mn}^\alpha(G)\right)^* \Gamma(G) \, |\chi_i^\alpha\rangle = \sum_{j=1,d_\alpha} \left(\Gamma_{mn}^\alpha(G)\right)^* \Gamma_{ji}^\alpha(G) \, |\chi_j^\alpha\rangle \, , \tag{223}$$

and then sum Eq. (223) for all $G \in \mathcal{G}$

$$\sum_{G\in\mathcal{G}} \left(\Gamma_{mn}^\alpha(G)\right)^* \Gamma(G) \, |\chi_i^\alpha\rangle = \sum_{G\in\mathcal{G}} \sum_{j=1,d_\alpha} \left(\Gamma_{mn}^\alpha(G)\right)^* \Gamma_{ji}^\alpha(G) \, |\chi_j^\alpha\rangle \, , \tag{224}$$

but because of the great orthogonality theorem (See Eq. (181)), one obtains

$$\sum_{G\in\mathcal{G}} \left(\Gamma_{mn}^\alpha(G)\right)^* \Gamma_{ji}^\alpha(G) = \frac{g}{d_\alpha} \delta_{mj} \delta_{ni}, \tag{225}$$

and therefore inserting Eq. (225) in Eq. (224)

$$\begin{aligned} \sum_{G\in\mathcal{G}} \left(\Gamma_{mn}^\alpha(G)\right)^* \Gamma(G) \, |\chi_i^\alpha\rangle &= \sum_{j=1,d} \frac{g}{d_\alpha} \delta_{mj} \delta_{ni} \, |\chi_j^\alpha\rangle \\ &= \frac{g}{d_\alpha} \, |\chi_m^\alpha\rangle \, \delta_{ni}. \end{aligned} \tag{226}$$

If instead of using just any couples of indices (m, n) in the matrices $\Gamma_{mn}^\alpha(G)$ that we used in the left hand side of Eq. (226) we now impose that $n = m$, one then obtains

$$\begin{aligned} \sum_{G\in\mathcal{G}} \left(\Gamma_{mm}^\alpha(G)\right)^* \Gamma(G) \, |\chi_i^\alpha\rangle &= \sum_{j=1,d} \frac{g}{d_\alpha} \delta_{mj} \delta_{mi} \, |\chi_j^\alpha\rangle \\ &= \frac{g}{d_\alpha} \, |\phi_m^\alpha\rangle \, \delta_{mi}. \end{aligned} \tag{227}$$

As a consequence, one can build a *projection operator* (also referred as the *complete* projection operator)

$$\boxed{P_m^\alpha = \frac{d_\alpha}{g} \sum_{G\in\mathcal{G}} \left(\Gamma_{mm}^\alpha(G)\right)^* \Gamma(G),} \tag{228}$$

such that

$$P_m^\alpha \left|\chi_i^\beta\right\rangle = |\chi_m^\alpha\rangle \, \delta_{mi} \delta_{\alpha\beta}. \tag{229}$$

Let us know apply the projection operator on the genetic vector $|\phi\rangle$

$$\begin{aligned} P_m^\alpha \, |\phi\rangle &= \sum_{\beta} \sum_{i=1,d_\beta} c_i^\beta P_m^\alpha \left|\chi_i^\beta\right\rangle \\ &= \sum_{\beta} \sum_{i=1,d_\beta} c_i^\beta \, |\chi_m^\alpha\rangle \, \delta_{mi} \delta_{\alpha\beta} \\ &= c_i^\alpha \, |\chi_m^\alpha\rangle \, . \end{aligned} \tag{230}$$

Therefore by applying the projection operator P_m^α on any vector $|\phi\rangle$ one obtains directly a vector proportional to $|\chi_m^\alpha\rangle$, if of course it has a non vanishing component on $|\chi_m^\alpha\rangle$. The number of complete projection operators P_m^α corresponding to the irreducible representation α equals the dimension d_α of such an irreducible representation. To build the projection operator P_m^α on needs

- to know the representation matrices $\Gamma(G)$ on $\mathcal{V}$,
- to know the irreducible representation matrices $\Gamma^\alpha(G)$, which usually can be found in the literature.

5.5.2 The incomplete projection operator

As shown in Eq. (228), one can obtain a projector based only from the knowledge diagonal part of the irreducible representations matrices $\Gamma_{mm}^\alpha(G)$ and on the representation matrices $\Gamma_{mm}^{\mathcal{V}}(G)$ on the vector space $\mathcal{V}$ with which we are working on.

Nevertheless, sometimes these matrices $\Gamma_{mm}^\alpha(G)$ are not known but only *their characters*. We can thus obtain an *incomplete projection operator* from the definition of Eq. (228) which is less powerful but allows to project a function not directly on one basis function of a given irreducible representation but *on the vector space spanned by the basis function of that irreducible representation.*

To obtain such an object, one simply has to *sum over all projectors for a given irreducible representation*

$$\begin{aligned} P^\alpha &= \sum_{m=1,d_\alpha} P_m^\alpha \\ &= \sum_{m=1,d_\alpha} \frac{d_\alpha}{g} \sum_{G\in\mathcal{G}} \left(\Gamma_{mm}^\alpha(G)\right)^* \Gamma(G) \\ &= \sum_{G\in\mathcal{G}} \Gamma(G) \frac{d_\alpha}{g} \sum_{m=1,d_\alpha} \left(\Gamma_{mm}^\alpha(G)\right)^* \end{aligned} \tag{231}$$

but as

$$\begin{aligned} \sum_{m=1,d_\alpha} \left(\Gamma_{mm}^\alpha(G)\right)^* &= \Big(\sum_{m=1,d_\alpha} \Gamma_{mm}^\alpha(G)\Big)^* \\ &= \left(\chi^\alpha(G)\right)^*, \end{aligned} \tag{232}$$

when injected in Eq. (231) one obtains

$$\boxed{P^\alpha = \frac{d_\alpha}{g} \sum_{G\in\mathcal{G}} \left(\chi^\alpha(G)\right)^* \Gamma(G).} \tag{233}$$

Such a projector applied on a given $|\phi\rangle$ gives the projection on total vector space α

$$P^\alpha |\phi\rangle = \sum_{i=1,d_\alpha} c_i^\alpha |\chi_i^\alpha\rangle . \tag{234}$$

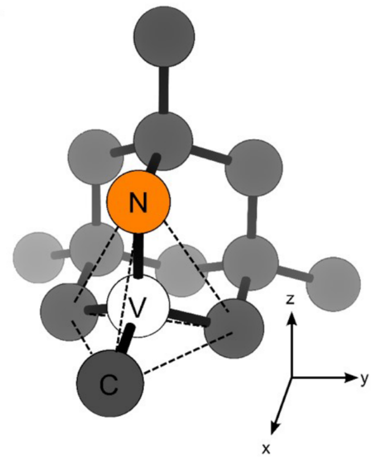
5.6 Application of the projection operators and Schur's lemma: the case of the NV center

5.6.1 Presentation of the problem

In this section, we will give a practical example of how to use the projection operators in the case of a "molecular" system which is the so-called nitrogen-vacancy in diamond (NV center). This system is a defect very often naturally present in diamond (*i.e.* an infinite tetragonal carbon network) and consists in

1) replacing a carbon atom by a nitrogen atom,

Figure 1: Qualitative representation of the NV center in diamond. "N" stands for nitrogen, "V" for vacancy.



2) creating a vacancy in a neighbouring carbon atom (*i.e.* "removing" such carbon atom).

This is illustrated in Fig. 1. We would like to obtain a qualitative representation of the electronic structure at the one-body level. To do so, we will consider here only

1) the closest atoms around the vacancy, which results in the three carbon atoms forming the base of the pyramid in Fig. 1, and the nitrogen atom forming the apex of the pyramid,

2) for each of these atoms, only the valence orbitals which are not already involved in bonding with the surrounding carbon atoms.

In terms of orbitals, this results in

- each carbon atom bears an hybridized sp orbital pointing towards the defect,
- the nitrogen bears a lone pair orbital N_s pointing toward the defect and which is invariant with respect to any rotation around the z axis.

We therefore have a non symmetry adapted basis $\mathcal{B} = \{|N_s\rangle, |sp_1\rangle, |sp_2\rangle, |sp_3\rangle\}$. We will neglect the overlap between the orbitals in the treatment of this problem. By denoting t_1 the interaction between two sp orbitals of carbon atoms, t_2 the interaction between the nitrogen orbital and the sp orbitals of carbon atoms, e_1 and e_2 the diagonal matrix element of the sp and N_s orbitals, respectively, the Hamiltonian matrix can be written as

$$H = \begin{pmatrix} & |N_s\rangle & |sp_1\rangle & |sp_2\rangle & |sp_3\rangle \\ \langle N_s| & e_2 & t_2 & t_2 & t_2 \\ \langle sp_1| & t_2 & e_1 & t_1 & t_1 \\ \langle sp_2| & t_2 & t_1 & e_1 & t_1 \\ \langle sp_3| & t_2 & t_1 & t_1 & e_1 \end{pmatrix}. \tag{235}$$

Here $t_1 < 0$ and $t_2 < 0$, and $e_2 \neq e_1$.

Diagonalizing such a Hamiltonian is not an easy task analytically. Nevertheless, we know that the NV center belongs to the C_{3v} symmetry and therefore we can use the fact that the Hamiltonian is block diagonal on the basis of the irreducible representations. But first we have to obtain a representation of $\mathcal{C}_{3v}$ on the four-dimensional vector space $\mathcal{V} = \text{span}(\mathcal{B})$.

5.6.2 Obtaining a representation of $\mathcal{C}_{3v}$ on $\mathcal{V}$

You can convince yourself that the *sp* functions transform exactly as the *s* functions because they point towards the defect. Therefore, the representation of the group on the vector space $\mathcal{V}_{sp} = \text{span}(|sp_1\rangle, |sp_2\rangle, |sp_3\rangle)$ is simply the same as the one found previously with s functions in Eq. 101

$$\Gamma^{\mathcal{V}_{sp}} = \left\{ \Gamma^{\mathcal{V}_{sp}}(E) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \Gamma^{\mathcal{V}_{sp}}(C_3) = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}, \quad \Gamma^{\mathcal{V}_{sp}}({C_3}^{-1}) = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}, \right.$$
$$\left. \Gamma^{\mathcal{V}_{sp}}(\sigma_1) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad \Gamma^{\mathcal{V}_{sp}}(\sigma_2) = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \quad \Gamma^{\mathcal{V}_{sp}}(\sigma_3) = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \right\}. \tag{236}$$

To obtain a representation on the whole vector space, one just needs to understand how the $|N_s\rangle$ function is changed by the $\mathcal{C}_{3v}$ symmetry operations. As this function is essentially proportional to z, it transforms exactly as the $|e_z\rangle$ vector of $\mathbb{R}^3$, which we found in Sec. 4.4.2 that was unchanged by the $\mathcal{C}_{3v}$ symmetry operations. Therefore, the one-dimensional representation Γ^{N_s} of the group on the vector space spanned by $|N_s\rangle$ is equivalent to the totally symmetrical representation Γ^{A_1}. We deduce then the four-dimensional representation on the whole vector space is

$$\Gamma^{\mathcal{V}} = \Gamma^{N_s} \oplus \Gamma^{\mathcal{V}_{sp}}, \tag{237}$$

where we know that Γ^{N_s} is already an irreducible representation. We therefore have to work on the reducibility of $\Gamma^{\mathcal{V}_{sp}}$.

5.6.3 Reduction and symmetry adapted basis for $\Gamma^{\mathcal{V}_{sp}}$

The first thing that we need to know is what irreducible representations of the $\mathcal{C}_{3v}$ group compose the representation $\Gamma^{\mathcal{V}_{sp}}$. As done before, we compute the character of $\Gamma^{\mathcal{V}_{sp}}$ and use the orthogonality of characters together with the character table of $\mathcal{C}_{3v}$

$\chi \backslash G_i$	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
$\Gamma^{\mathcal{V}_{sp}}$	3	0	1

and as in Eq. (238) we find that

$$\Gamma^{\mathcal{V}_{sp}} = \Gamma^{\text{A}_1} \oplus \Gamma^{\text{E}}. \tag{238}$$

Therefore we know that we have to apply only the projection operator corresponding to Γ^{A_1} and that corresponding to Γ^{E}.

As the A_1 irreducible representation is of dimension 1, the matrix elements of Γ^{A_1} are the characters of Γ^{A_1}. Therefore the complete and incomplete projection operator coincide. Nevertheless, we know that by applying P^{A_1} on any of the three functions $sp_i(\mathbf{r})$ we will obtain a vector proportional to the basis of the A_1 representation

$$P^{A_1} |sp_i\rangle = \langle \chi^{A_1} | sp_i \rangle \, |\chi^{A_1}\rangle \,. \tag{239}$$

Let us first build the projection operator P^{A_1}

$$P^{A_1} = \underbrace{\frac{1}{6}}_{\frac{d_\alpha}{g}} \times \Bigg\{ \underbrace{1^*}_{\chi^{A_1}(E)} \times \underbrace{\begin{pmatrix}1 & 0 & 0\\0 & 1 & 0\\0 & 0 & 1\end{pmatrix}}_{\Gamma^{\mathcal{V}}(E)} + \underbrace{1^*}_{\chi^{A_1}(C_3)} \times \underbrace{\begin{pmatrix}0 & 0 & 1\\1 & 0 & 0\\0 & 1 & 0\end{pmatrix}}_{\Gamma^{\mathcal{V}}(C_3)} + \underbrace{1^*}_{\chi^{A_1}(C_3{}^{-1})} \times \underbrace{\begin{pmatrix}0 & 1 & 0\\0 & 0 & 1\\1 & 0 & 0\end{pmatrix}}_{\Gamma^{\mathcal{V}}(C_3{}^{-1})} + \underbrace{1^*}_{\chi^{A_1}(\sigma_1)} \times \underbrace{\begin{pmatrix}1 & 0 & 0\\0 & 0 & 1\\0 & 1 & 0\end{pmatrix}}_{\Gamma^{\mathcal{V}}(\sigma_1)} + \underbrace{1^*}_{\chi^{A_1}(\sigma_2)} \times \underbrace{\begin{pmatrix}0 & 0 & 1\\0 & 1 & 0\\1 & 0 & 0\end{pmatrix}}_{\Gamma^{\mathcal{V}}(\sigma_2)} + \underbrace{1^*}_{\chi^{A_1}(\sigma_3)} \times \underbrace{\begin{pmatrix}0 & 1 & 0\\1 & 0 & 0\\0 & 0 & 1\end{pmatrix}}_{\Gamma^{\mathcal{V}}(\sigma_3)} \Bigg\} \tag{240}$$

so we can sum the matrices to obtain

$$P^{A_1} = \frac{1}{3}\begin{pmatrix}1 & 1 & 1\\1 & 1 & 1\\1 & 1 & 1\end{pmatrix}. \tag{241}$$

We can then apply the projection operator on the $|sp_1\rangle$ function

$$\begin{aligned} P^{A_1}|sp_1\rangle &= \frac{1}{3}\begin{pmatrix}1 & 1 & 1\\1 & 1 & 1\\1 & 1 & 1\end{pmatrix}\begin{pmatrix}1\\0\\0\end{pmatrix} \\ &= \frac{1}{3}\begin{pmatrix}1\\1\\1\end{pmatrix}. \end{aligned} \tag{242}$$

We can then define the normalized vector $\left|\chi^{A_1}\right\rangle$ which is a basis function of the A_1 irreducible representation

$$\left|\chi^{A_1}\right\rangle = \frac{1}{\sqrt{3}}\big(|sp_1\rangle + |sp_2\rangle + |sp_3\rangle\big). \tag{243}$$

As the irreducible representation A_1 is of dimension 1, we can verify that indeed such a vector $\left|\chi^{A_1}\right\rangle$ is an eigenvector of any matrix of $\Gamma^{\mathcal{V}}$ and that the corresponding eigenvalue is 1. For instance for C_3

$$\Gamma^{\mathcal{V}}(C_3)\left|\chi^{A_1}\right\rangle = \begin{pmatrix}0 & 0 & 1\\1 & 0 & 0\\0 & 1 & 0\end{pmatrix}\frac{1}{\sqrt{3}}\begin{pmatrix}1\\1\\1\end{pmatrix} = \frac{1}{\sqrt{3}}\begin{pmatrix}1\\1\\1\end{pmatrix}, \tag{244}$$

or for σ_2

$$\Gamma^{\mathcal{V}}(\sigma_2)\left|\chi^{A_1}\right\rangle = \begin{pmatrix}0 & 0 & 1\\0 & 1 & 0\\1 & 0 & 0\end{pmatrix}\frac{1}{\sqrt{3}}\begin{pmatrix}1\\1\\1\end{pmatrix} = \frac{1}{\sqrt{3}}\begin{pmatrix}1\\1\\1\end{pmatrix}. \tag{245}$$

The eigenvalue 1 is precisely the matrix representation of the one-dimensional A_1 irreducible representation.

Also, if we define the sub vector space $\mathcal{V}^{A_1}$ associated to the A_1 representation as $\mathcal{V}^{A_1} = \{\left|u^{A_1}\right\rangle = \lambda\left|\chi^{A_1}\right\rangle,\ \lambda \in \mathbb{C}\}$, such a vector space is an *invariant subspace* of $\mathcal{V}$ as

$$\Gamma^{\mathcal{V}}(G)\left|u^{A_1}\right\rangle \in \mathcal{V}^{A_1}\ \forall \left|u^{A_1}\right\rangle \in \mathcal{V}^{A_1} \text{ and } G \in C_{3v}. \tag{246}$$

Let us move now to the E representation. The complete projection operator is very useful to obtain basis functions of irreducible representations of dimension larger than 1. As here the E irreducible representation is of dimension 2, there are two different complete projection operators P_1^E and P_2^E which project on the two basis functions of the E irreducible representation. To build such projection operators, according to Eq. (228), one needs

- The representation Γ on the vector space $\mathcal{V}$ that we are interested in,
- The diagonal elements $\Gamma^{\alpha}_{mm}(S)$ of the irreducible representation we are interested in.

We already built $\Gamma^{\mathcal{V}_{sp}}$, and we shown that $\Gamma^{\mathbb{R}^2}$ of Eq. (88) corresponds indeed to the irreducible representation E, therefore we know the diagonal matrix elements $\Gamma^{E}_{mm}(S)$. We can then build the first projection operator P^E_1 as

$$\begin{aligned} P^E_1 = \underbrace{\frac{2}{6}}_{\frac{d_\alpha}{g}} \Bigg\{ & \underbrace{1^*}_{\left(\Gamma^E_{11}(E)\right)^*} \begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix} + \underbrace{(-\frac{1}{2})^*}_{\left(\Gamma^E_{11}(C_3)\right)^*} \begin{pmatrix}0&0&1\\1&0&0\\0&1&0\end{pmatrix} + \underbrace{(-\frac{1}{2})^*}_{\left(\Gamma^E_{11}(C_3{}^{-1})\right)^*} \begin{pmatrix}0&1&0\\0&0&1\\1&0&0\end{pmatrix} \\ & + \underbrace{(1)^*}_{\left(\Gamma^{\sigma_1}_{11}(\sigma_1)\right)^*} \begin{pmatrix}1&0&0\\0&0&1\\0&1&0\end{pmatrix} + \underbrace{(-\frac{1}{2})^*}_{\left(\Gamma^{\sigma_2}_{11}(\sigma_2)\right)^*} \begin{pmatrix}0&0&1\\0&1&0\\1&0&0\end{pmatrix} + \underbrace{(-\frac{1}{2})^*}_{\left(\Gamma^{\sigma_3}_{11}(\sigma_3)\right)^*} \begin{pmatrix}0&1&0\\1&0&0\\0&0&1\end{pmatrix} \Bigg\}, \end{aligned} \tag{247}$$

which once the matrix are summed yields

$$P^E_1 = \frac{1}{3}\begin{pmatrix}2&-1&-1\\-1&\frac{1}{2}&\frac{1}{2}\\-1&\frac{1}{2}&\frac{1}{2}\end{pmatrix}. \tag{248}$$

Similarly, we can obtain the second projection operator on E as

$$\begin{aligned} P^E_2 = \underbrace{\frac{2}{6}}_{\frac{d_\alpha}{g}} \Bigg\{ & \underbrace{1^*}_{\left(\Gamma^E_{22}(E)\right)^*} \begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix} + \underbrace{(-\frac{1}{2})^*}_{\left(\Gamma^E_{22}(C_3)\right)^*} \begin{pmatrix}0&0&1\\1&0&0\\0&1&0\end{pmatrix} + \underbrace{(-\frac{1}{2})^*}_{\left(\Gamma^E_{22}(C_3{}^{-1})\right)^*} \begin{pmatrix}0&1&0\\0&0&1\\1&0&0\end{pmatrix} \\ & + \underbrace{(-1)^*}_{\left(\Gamma^{\sigma_1}_{22}(\sigma_1)\right)^*} \begin{pmatrix}1&0&0\\0&0&1\\0&1&0\end{pmatrix} + \underbrace{(\frac{1}{2})^*}_{\left(\Gamma^{\sigma_2}_{22}(\sigma_2)\right)^*} \begin{pmatrix}0&0&1\\0&1&0\\1&0&0\end{pmatrix} + \underbrace{(\frac{1}{2})^*}_{\left(\Gamma^{\sigma_3}_{22}(\sigma_3)\right)^*} \begin{pmatrix}0&1&0\\1&0&0\\0&0&1\end{pmatrix} \Bigg\}, \end{aligned} \tag{249}$$

which once the matrix are summed yields

$$P^E_2 = \frac{1}{3}\begin{pmatrix}0&0&0\\0&\frac{3}{2}&-\frac{3}{2}\\0&-\frac{3}{2}&\frac{3}{2}\end{pmatrix}. \tag{250}$$

From these projection operators, we can obtain the basis functions $\left|\chi^E_1\right\rangle$ and $\left|\chi^E_2\right\rangle$ which span the stable vector space $\mathcal{V}_E$.

Let us start with P^E_1. Let us consider the application of P^E_1 on any of the basis function

$$\begin{aligned} P^E_1 \left|sp_1\right\rangle &= \frac{1}{3}\begin{pmatrix}2&-1&-1\\-1&\frac{1}{2}&\frac{1}{2}\\-1&\frac{1}{2}&\frac{1}{2}\end{pmatrix}\begin{pmatrix}1\\0\\0\end{pmatrix} = \frac{1}{3}\begin{pmatrix}2\\-1\\-1\end{pmatrix} \\ &\propto 2\left|sp_1\right\rangle - \left|sp_2\right\rangle - \left|sp_3\right\rangle, \end{aligned} \tag{251}$$

$$\begin{aligned} P^E_1 \left|sp_2\right\rangle &= \frac{1}{3}\begin{pmatrix}2&-1&-1\\-1&\frac{1}{2}&\frac{1}{2}\\-1&\frac{1}{2}&\frac{1}{2}\end{pmatrix}\begin{pmatrix}0\\1\\0\end{pmatrix} = \frac{1}{3}\begin{pmatrix}-1\\\frac{1}{2}\\\frac{1}{2}\end{pmatrix} \\ &\propto 2\left|sp_1\right\rangle - \left|sp_2\right\rangle - \left|sp_3\right\rangle, \end{aligned} \tag{252}$$

$$P_1^E |sp_3\rangle = \frac{1}{3}\begin{pmatrix} 2 & -1 & -1 \\ -1 & \frac{1}{2} & \frac{1}{2} \\ -1 & \frac{1}{2} & \frac{1}{2} \end{pmatrix}\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = \frac{1}{3}\begin{pmatrix} -1 \\ \frac{1}{2} \\ \frac{1}{2} \end{pmatrix} \\ \propto 2|sp_1\rangle - |sp_2\rangle - |sp_3\rangle . \tag{253}$$

Therefore we see here that by applying P_1^E on any of the functions, we obtain a vector which is always proportional to the same vector

$$\left|\chi_1^E\right\rangle = \frac{1}{\sqrt{6}}\big(2|sp_1\rangle - |sp_2\rangle - |sp_3\rangle\big). \tag{254}$$

Let us do the same operation P_2^E on $+|sp_1\rangle$

$$P_2^E |sp_1\rangle = \frac{1}{3}\begin{pmatrix} 0 & 0 & 0 \\ 0 & \frac{3}{2} & -\frac{3}{2} \\ 0 & -\frac{3}{2} & \frac{3}{2} \end{pmatrix}\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = 0. \tag{255}$$

This means that the basis function $|sp_1\rangle$ has no component on $\left|\chi_2^E\right\rangle$ and therefore $P_2^E |sp_1\rangle$ does not give an explicit form $\left|\chi_2^E\right\rangle$. So we have to apply it on the other basis functions

$$P_2^E |sp_2\rangle = \frac{1}{3}\begin{pmatrix} 0 & 0 & 0 \\ 0 & \frac{3}{2} & -\frac{3}{2} \\ 0 & -\frac{3}{2} & \frac{3}{2} \end{pmatrix}\begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} = \frac{1}{3}\begin{pmatrix} 0 \\ \frac{3}{2} \\ -\frac{3}{2} \end{pmatrix} \\ \propto |sp_1\rangle - |sp_2\rangle , \tag{256}$$

$$P_2^E |sp_3\rangle = \frac{1}{3}\begin{pmatrix} 0 & 0 & 0 \\ 0 & \frac{3}{2} & -\frac{3}{2} \\ 0 & -\frac{3}{2} & \frac{3}{2} \end{pmatrix}\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} = \frac{1}{3}\begin{pmatrix} 0 \\ -\frac{3}{2} \\ +\frac{3}{2} \end{pmatrix} \\ \propto |sp_1\rangle - |sp_2\rangle . \tag{257}$$

Then we obtain the second basis vector of the E representation

$$\left|\chi_2^E\right\rangle = \frac{1}{\sqrt{2}}\big(|sp_1\rangle - |sp_2\rangle\big). \tag{258}$$

We can then setup the matrix for the change of the basis $\mathcal{B}_{sp} = \{|sp_1\rangle, |sp_2\rangle, |sp_3\rangle\}$ to that which is symmetry adapted $\mathcal{B}_{sp}^{\mathrm{SA}} = \{\left|\chi^{A_1}\right\rangle, \left|\chi_1^E\right\rangle, \left|\chi_2^E\right\rangle\}$. Such a matrix, referred to as $U^{sp,\mathrm{SA}}$, is defined as

$$U_{ij}^{sp,\mathrm{SA}} = \left\langle sp_i^{\mathcal{B}} \middle| \chi_j^{\mathcal{B}_{\mathrm{SA}}} \right\rangle . \tag{259}$$

To write the matrix $U^{sp,\mathrm{SA}}$ we just have to write in column the vectors of $\mathcal{B}_{\mathrm{SA}}$

$$U^{sp,\mathrm{SA}} = \begin{pmatrix} \frac{1}{\sqrt{3}} & \frac{2}{\sqrt{6}} & 0 \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{2}} \end{pmatrix}. \tag{260}$$

We can notice that such a matrix is *unitary* which means that the vectors of $\mathcal{B}_{\mathrm{SA}}$ are orthonormal. As the matrix is unitary and real, the inverse matrix is simply the transpose matrix

$${U^{sp,\mathrm{SA}}}^{-1} = \begin{pmatrix} \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} \\ \frac{2}{\sqrt{6}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{6}} \\ 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix}. \tag{261}$$

5.6.4 Diagonalization of the Hamiltonian in the symmetry adapted basis

We can now define the symmetry adapted basis for the four-dimensional vector space $\mathcal{V}$ as

$$\mathcal{B}_{\mathrm{SA}} = \{|N_s\rangle, |\chi^{A_1}\rangle, |\chi_1^E\rangle, |\chi_2^E\rangle\}, \tag{262}$$

and this basis block diagonalize the Hamiltonian matrix. As the basis function $|N_s\rangle$ is already a basis for an irreducible representation, the matrix $U^{\mathcal{B}_{\mathrm{SA}}}$ transforming $\mathcal{B}$ to $\mathcal{B}_{\mathrm{SA}}$ is simply

$$\begin{aligned} U^{\mathcal{B}_{\mathrm{SA}}} &= \mathbb{1}_1 \oplus U^{sp,\mathrm{SA}} \\ &= \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{3}} & \frac{2}{\sqrt{6}} & 0 \\ 0 & \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & \frac{1}{\sqrt{2}} \\ 0 & \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{2}} \end{pmatrix}, \end{aligned} \tag{263}$$

and its inverse

$$\begin{aligned} {U^{\mathcal{B}_{\mathrm{SA}}}}^{-1} &= \mathbb{1}_1 \oplus {U^{sp,\mathrm{SA}}}^{-1} \\ &= \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} \\ 0 & \frac{2}{\sqrt{6}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{6}} \\ 0 & 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix}. \end{aligned} \tag{264}$$

The Hamiltonian can now be expressed on the basis of irreducible representations

$$\begin{aligned} H^{\mathrm{SA}} &= {U^{\mathcal{B}_{\mathrm{SA}}}}^{-1} H U^{\mathcal{B}_{\mathrm{SA}}} \\ &= \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} \\ 0 & \frac{2}{\sqrt{6}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{6}} \\ 0 & 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} e_2 & t_2 & t_2 & t_2 \\ t_2 & e_1 & t_1 & t_1 \\ t_2 & t_1 & e_1 & t_1 \\ t_2 & t_1 & t_1 & e_1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{3}} & \frac{2}{\sqrt{6}} & 0 \\ 0 & \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & \frac{1}{\sqrt{2}} \\ 0 & \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{2}} \end{pmatrix}. \end{aligned} \tag{265}$$

By posing $\alpha = (e_1 + 2t_1)$ and $\beta = (e_1 - t_1)$, one obtains

$$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} \\ 0 & \frac{2}{\sqrt{6}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{6}} \\ 0 & 0 & \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{pmatrix} \begin{pmatrix} e_2 & t_2 & t_2 & t_2 \\ t_2 & e_1 & t_1 & t_1 \\ t_2 & t_1 & e_1 & t_1 \\ t_2 & t_1 & t_1 & e_1 \end{pmatrix} = \begin{pmatrix} e_2 & t_2 & t_2 & t_2 \\ \sqrt{3}t_2 & \frac{1}{\sqrt{3}}\alpha & \frac{1}{\sqrt{3}}\alpha & \frac{1}{\sqrt{3}}\alpha \\ 0 & \frac{2}{\sqrt{6}}\beta & -\frac{1}{\sqrt{6}}\beta & -\frac{1}{\sqrt{6}}\beta \\ 0 & 0 & \frac{1}{\sqrt{2}}\beta & -\frac{1}{\sqrt{2}}\beta \end{pmatrix}, \tag{266}$$

and therefore

$$\begin{pmatrix} e_2 & t_2 & t_2 & t_2 \\ \sqrt{3}t_2 & \frac{1}{\sqrt{3}}\alpha & \frac{1}{\sqrt{3}}\alpha & \frac{1}{\sqrt{3}}\alpha \\ 0 & \frac{2}{\sqrt{6}}\beta & -\frac{1}{\sqrt{6}}\beta & -\frac{1}{\sqrt{6}}\beta \\ 0 & 0 & \frac{1}{\sqrt{2}}\beta & -\frac{1}{\sqrt{2}}\beta \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{3}} & \frac{2}{\sqrt{6}} & 0 \\ 0 & \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & \frac{1}{\sqrt{2}} \\ 0 & \frac{1}{\sqrt{3}} & -\frac{1}{\sqrt{6}} & -\frac{1}{\sqrt{2}} \end{pmatrix} = \begin{pmatrix} e_2 & \sqrt{3}t_2 & 0 & 0 \\ \sqrt{3}t_2 & e_1 + 2t_1 & 0 & 0 \\ 0 & 0 & e_1 - t_1 & 0 \\ 0 & 0 & 0 & e_1 - t_1 \end{pmatrix}. \tag{267}$$

Therefore we see that the Hamiltonian has a *much simpler structure*. A few remarks:

- The Hamiltonian is zero between the A_1 and E irreducible representations, which is because they are *non equivalent* irreducible representations,
- The Hamiltonian is $\lambda \times \mathbb{1}_2$ on the E irreducible representation and therefore gives the degeneracy of the two orbitals,

- The Hamiltonian is non zero between basis functions of the same symmetry A_1 but belonging to different vector spaces,
- Because of delocalization, the orbital $\left|\chi^{A_1}\right\rangle$ is stabilized by $2t_1$ as it is totally symmetrical and therefore has no nodes,
- Because of delocalization, the orbitals $\left|\chi_{1/2}^{E}\right\rangle$ are destabilized by $-t_1$ because they have nodes.

6 Appendix

6.1 Proof of Schur's Lemma

Let $\mathcal{V}_1$ and $\mathcal{V}_2$ be two vector spaces, and two irreducible representations $\Gamma^{\mathcal{V}_1}$ and $\Gamma^{\mathcal{V}_2}$. Let $h : \mathcal{V}_1 \to \mathcal{V}_2$ a linear map which commutes with any matrix of the representations $\Gamma^{\mathcal{V}_1}$ and $\Gamma^{\mathcal{V}_2}$, which means that

$$h\Gamma^{\mathcal{V}_1}(G) = \Gamma^{\mathcal{V}_2}(G)h \quad \forall G \in \mathcal{G}. \tag{268}$$

We want to proof that because of the relation of commutation one has the following properties for h:

1) it is zero if the two irreducible representations are non equivalent,

2) it is an homothetic of the identity ($i.e.$ $h = \lambda\mathbb{1}$) if $\mathcal{V}_1 = \mathcal{V}_2$.

In order to demonstrate these relations, it is first important to demonstrate the ***stability of*** $Ker(h)$ and of $\mathrm{Im}(h)$, which are direct consequences of the commuting relation of Eq. (272).

6.1.1 Commutation implies stability of $Ker(h)$ and $\mathrm{Im}(h)$

Let us first show that $Ker(h)$ is stable by the group. Let $x \in Ker(h)$ therefore

$$x \in Ker(h) \Leftrightarrow f(x) = 0, \tag{269}$$

and let us apply the commutation relationship of Eq. (268) at such a vector x

$$\begin{aligned} h\Gamma^{\mathcal{V}_1}(G)x = \Gamma^{\mathcal{V}_2}(G)hx \quad \forall G \in \mathcal{G} \\ h\Gamma^{\mathcal{V}_1}(G)x = 0 \quad \forall G \in \mathcal{G}, \end{aligned} \tag{270}$$

therefore $\Gamma^{\mathcal{V}_1}(G)x \in Ker(h)$ and therefore we have that

$$\boxed{x \in Ker(h) \Rightarrow \Gamma^{\mathcal{V}_1}(G)x \in Ker(h) \quad \forall G \in \mathcal{G},} \tag{271}$$

and therefore $Ker(h)$ is ***stable by*** $\Gamma^{\mathcal{V}_1}$. But, by definition of irreducibility of $\Gamma^{\mathcal{V}_1}$, there are two choices for stable subspaces which are either $\mathcal{V}_1$ or $\{0\}$. Therefore

$$\boxed{Ker(h) = \mathcal{V}_1 \quad \mathrm{or} Ker(h) = \{0\}.} \tag{272}$$

Similarly, we want to show that the commutation relation is equivalent to the stability of $\mathrm{Im}(h)$. Let us apply Eq. (268) to a vector $x \in \mathcal{V}_1$

$$\begin{aligned} h\Gamma^{\mathcal{V}_1}(G)x = \Gamma^{\mathcal{V}_2}(G)hx \quad \forall G \in \mathcal{G} \\ hx' = \Gamma^{\mathcal{V}_2}(G)hx \quad \forall G \in \mathcal{G}, \end{aligned} \tag{273}$$

with $x' = \Gamma^{\mathcal{V}_1}(G)x$. As $\Gamma^{\mathcal{V}_1}$ is a representation in $\mathcal{V}_1$ one necessarily have $x' \in \mathcal{V}_1$, and therefore

$$\Gamma^{\mathcal{V}_2}(G)hx \in \mathrm{Im}(h) \quad \forall G \in \mathcal{G}, \tag{274}$$

which means that $\mathrm{Im}(h)$ is stable by the representation $\Gamma^{\mathcal{V}_2}$. Therefore, as $\Gamma^{\mathcal{V}_2}$ is irreducible, there are no other stable subspaces than $\mathcal{V}_2$ or $\{0\}$. Therefore

$$\boxed{\mathrm{Im}(h) = \mathcal{V}_2 \quad \mathrm{or}\ \mathrm{Im}(h) = \{0\}.} \tag{275}$$

As one cannot have $\{Ker(h) = \{0\}$ and $\text{Im}(h) = \{0\}\}$ nor $\{Ker(h) = \mathcal{V}_1$ and $\text{Im}(h) = \mathcal{V}_2\}$, we can conclude from the relation Eq. (272) and Eq. (275) that there are only two choices for h

$$\boxed{Ker(h) = \{0\} \text{ and } \text{Im}(h) = \mathcal{V}_2} \tag{276}$$

or

$$\boxed{Ker(h) = \{\mathcal{V}_1\} \text{ and } \text{Im}(h) = \{0\}.} \tag{277}$$

6.1.2 Case of two non equivalent irreducible representations

We can now proof that when the two irreducible representations are *non equivalent* we have $h = 0$ or in in a more mathematical writing that

$$\boxed{Ker(h) = \mathcal{V}_1.} \tag{278}$$

From Eq.(272) we know that $Ker(h) = \mathcal{V}_1$ or$Ker(h) = \{0\}$, so we just have to show that it cannot be $Ker(h) = \{0\}$.

Because $\Gamma^{\mathcal{V}_1}$ and $\Gamma^{\mathcal{V}_2}$ are not equivalent, it implies that there are no isomorphism $f : \mathcal{V}_1 \to \mathcal{V}_2$ such that

$$f\Gamma^{\mathcal{V}_1} f^{-1} = \Gamma^{\mathcal{V}_2} \Leftrightarrow f\Gamma^{\mathcal{V}_1} = \Gamma^{\mathcal{V}_2} f. \tag{279}$$

We recall that an isomorphism is a linear map $f : \mathcal{V}_1 \to \mathcal{V}_2$ which is injective

$$Ker(f) = \{0\}, \quad i.e. x \neq y \Rightarrow fx \neq fy, \tag{280}$$

and surjective

$$\text{Im}(f) = \mathcal{V}_2, \quad i.e. \forall y \in \mathcal{V}_2, \ \exists x \in \mathcal{V}_1 | fx = y. \tag{281}$$

Therefore, the *non equivalent representations* $\Gamma^{\mathcal{V}_1}$ and $\Gamma^{\mathcal{V}_2}$ implies that we have two choices for h

$$\boxed{\text{either } Ker(h) \neq \{0\} \quad or \quad \text{Im}(h) \neq \mathcal{V}_2.} \tag{282}$$

Reviewing the two cases one obtains:

1) If $Ker(h) \neq \{0\}$ then we know from Eq. (276) that necessarily $Ker(h) = \mathcal{V}_1$ and $\text{Im}(h) = \mathcal{V}_2$, which means that the application h is zero,

2) If $\text{Im}(h) \neq \mathcal{V}_2$, we know from Eq. (275) that $\text{Im}(h) = \{0\}$ and $Ker(h) = \mathcal{V}_1$, which also means that the application h is zero.

6.1.3 Case when $\mathcal{V}_1 = \mathcal{V}_2$

Let us now analyze the case when $\mathcal{V}_1 = \mathcal{V}_2$. The commuting relation implies that h is an isomorphism, which means that the linear map is invertible and therefore there exists at least one eigenpair (λ_0, x_0)

$$hx_0 = \lambda_0 x_0, \quad \lambda_0 \in \mathbb{C} \quad x_0 \neq 0. \tag{283}$$

As $\lambda\mathbb{1}$ commutes with any linear map, we can build another linear map $f : \mathcal{V}_1 \to \mathcal{V}_1$

$$f = h - \lambda_0 \mathbb{1}, \quad \lambda_0 \in \mathbb{C}, \tag{284}$$

which also fulfills the commuting relation of Eq. (268). Therefore, according to Eq. (272), it implies that $Ker(f) = \{0\}$ or $Ker(f) = \mathcal{V}_1$. But as the non vanishing eigenvector x_0 of h is in $Ker(f)$

$$hx_0 = \lambda_0 x_0 \Leftrightarrow x_0 \in Ker(f), \tag{285}$$

one knows that necessarily $Ker(f) = \mathcal{V}_1$. This means that

$$\begin{aligned} &fx = 0 \quad \forall x \in \mathcal{V}_1 \\ \Leftrightarrow &(h - \lambda_0 \mathbb{1})x = 0 \quad \forall x \in \mathcal{V}_1 \\ \Leftrightarrow &hx = \lambda_0 x \quad \forall x \in \mathcal{V}_1 \end{aligned} \tag{286}$$

and therefore one concludes that $h = \lambda_0 \mathbb{1}$.

6.2 Change of basis: orthonormal and non orthonormal

Here we recall the main results for the change of basis within a vector space. Let us consider a vector space $\mathcal{V}$ of dimension d spanned by an orthonormal basis $\mathcal{B} = \{|e_1\rangle, \dots, |e_d\rangle\}$, and another basis, not necessary orthonormal, $\mathcal{B}' = \{|u_1\rangle, \dots, |u_d\rangle\}$ which is known as a function of the vectors of $\mathcal{B}$

$$\begin{aligned} |u_i\rangle &= \sum_{j=1,d} \langle e_j|u_i\rangle |e_j\rangle \\ &= \sum_{j=1,d} P_{ji}^{\mathcal{B}\mathcal{B}'} |e_j\rangle . \end{aligned} \tag{287}$$

The matrix $P^{\mathcal{B}\mathcal{B}'}$ allows the following change of basis $\mathcal{B}'$ to $\mathcal{B}$. Indeed, if we know a vector $|v\rangle = \sum_{i=1,d} v'_i |u_i\rangle$ in the basis $\mathcal{B}'$, we know its expression in the basis $\mathcal{B}$ by

$$\begin{aligned} |v\rangle &= \sum_{i=1,d} v'_i |u_i\rangle \\ &= \sum_{i=1,d} v'_i \sum_{j=1,d} P_{ji}^{\mathcal{B}\mathcal{B}'} |e_j\rangle \\ &= \sum_{j=1,d} |e_j\rangle \big(\sum_{i=1,d} P_{ji}^{\mathcal{B}\mathcal{B}'} c_i \big) \\ &= \sum_{j=1,d} v_i |e_j\rangle \end{aligned} \tag{288}$$

which can be written as

$$\boldsymbol{v}^{\mathcal{B}} = P^{\mathcal{B}\mathcal{B}'} \boldsymbol{v}^{\mathcal{B}'}, \tag{289}$$

where $\boldsymbol{v}^{\mathcal{B}}$ is the column vector representing the vector $|v\rangle$ in the basis $\mathcal{B}$. Therefore the matrix $P^{\mathcal{B}\mathcal{B}'}$ acts on $\mathcal{B}'$ (the columns) and send to $\mathcal{B}$ (the lines).

The matrix allowing the reverse passage, *i.e.* from $\mathcal{B}$ to $\mathcal{B}'$, is the inverse matrix as we can see that

$$\begin{aligned} & |v\rangle^{\mathcal{B}} = P^{\mathcal{B}\mathcal{B}'} |v\rangle^{\mathcal{B}'} \\ \Leftrightarrow & \big(P^{\mathcal{B}\mathcal{B}'}\big)^{-1} |v\rangle^{\mathcal{B}} = \big(P^{\mathcal{B}\mathcal{B}'}\big)^{-1} P^{\mathcal{B}\mathcal{B}'} |v\rangle^{\mathcal{B}'} \\ \Leftrightarrow & \big(P^{\mathcal{B}\mathcal{B}'}\big)^{-1} |v\rangle^{\mathcal{B}} = |v\rangle^{\mathcal{B}'} . \end{aligned} \tag{290}$$

Therefore, in the general case, we need to invert the matrix to get the inverse transformation.

If we know a matrix $A^{\mathcal{B}\mathcal{B}}$ in the basis $\mathcal{B}$, we can now it in the new basis $\mathcal{B}'$ by

$$\begin{aligned} A^{\mathcal{B}'\mathcal{B}'} &= P^{\mathcal{B}'\mathcal{B}} A^{\mathcal{B}\mathcal{B}} P^{\mathcal{B}\mathcal{B}'} \\ &= (P^{\mathcal{B}\mathcal{B}'})^{-1} A^{\mathcal{B}\mathcal{B}} P^{\mathcal{B}\mathcal{B}'}. \end{aligned} \tag{291}$$

Nevertheless, if the basis $\mathcal{B}'$ is orthonormal, then it means that the corresponding matrix $P^{\mathcal{B}\mathcal{B}'}$ is unitary and therefore that

$$\big(P^{\mathcal{B}\mathcal{B}'}\big)^{-1} = \big(P^{\mathcal{B}\mathcal{B}'}\big)^{\dagger}, \tag{292}$$

and therefore

$$A^{\mathcal{B}'\mathcal{B}'} = (P^{\mathcal{B}\mathcal{B}'})^{\dagger} A^{\mathcal{B}\mathcal{B}} P^{\mathcal{B}\mathcal{B}'}. \tag{293}$$