Localized Spins in solids
M2 ICFP

Gabriel Hétet

April 20, 2024

Contents

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1 The full rotation group – basic notions

In this first part of the course, we will deal with systems with full rotational invariance and thus consider the full rotation group (*i.e.* O(3)) as a start. Since the symmetry elements of the crystalline structure always form a subgroup of O(3), any representations of O(3) is representation of the subgroup. Full rotation groups are also relevant for studying *spinors* – quantum mechanical objects– which, in the absence of spin-orbit coupling, do not "feel" Coulomb interaction with neighboring ions in the crystal.

1.1 Continuous groups

Consider a set of elements $R(a_1, a_2, ..., a_r)$ that depend on r real parameters and that form a group. The elements R all differ by the values a_i.

Definition : The set $R(a_1, a_2, ..., a_r)$ is said to form a *continuous group* if all the elements in the set can be obtained by an infinitesimally small change in the parameters. If the group elements depend on r parameters, it is called an r-parameter continuous group.

Note : For two groups to be isomorphic, the number of parameters must be the same.

1.2 The groups of linear transformations

An important class of groups is the group of linear transformations called GL(E) (general linear group), which in finite dimension d, can be represented by $d \times d$ invertible matrices.

One such transformation in two dimensions is $r' = Mr$ or, in matrix form,

$$\begin{bmatrix} x' \\ y' \end{bmatrix} = \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix} \quad , \text{ where } \det(M) = a_{11}a_{22} - a_{12}a_{21} \neq 0.$$

and where a_{ij} are real. If these four parameters vary continuously, it is a 4-parameter continuous group[1].

1.2.1 1D transformations

The set of 1D transformations f_a in the vector space $\mathbb{R}$ such that $\mathbb{R} \to \mathbb{R} : x \mapsto ax$, $a \in \mathbb{R}^*$ forms a 1-parameter continuous group. They correspond to stretching the real line by a factor a.

$$f_a = \begin{Bmatrix} x_1 & \to ax_1 \\ x_2 & \to ax_2 \\ ... & ... \\ x_n & \to ax_n \end{Bmatrix}$$

The identity is determined from $f_a(x) = x, \forall x \in \mathbb{R}$, which clearly corresponds to the transformation with $a = 1$. Since $1 \in \mathbb{R}^*$, $f_1 = I_d$ is in the set (I_d is the identity of the group).

The composition of two such operations, $f_a(x) = ax$ and $f_b(x) = bx$, $\forall x \in \mathbb{R}$ is

$$f_a o f_b(x) = a f_b(x) = a(bx) = f_{ab}(x) = f_c(x), \qquad \forall x \in \mathbb{R}$$

so that $f_a o f_b = f_c$. The composition of two transformations f_a and f_b is a transformation f_c such that $c = ab$.

The inverse f_a^{-1} of each of these transformations fulfills

$$f_a o f_a^{-1}(x) = x, \ \forall x \in \mathbb{R}$$

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[1]This is true provided the parameters are *essential*. Example : the group of transformations $T : \mathbb{R} \to \mathbb{R} | x \mapsto x + a + b$ is only a 1-parameter continuous group because one could write $a + b = c$ "without losing generality". a and b are not essential parameters. See Ref. [1] for a precise definition.

so

$$f_a o f_a^{-1}(x) = a f_a^{-1}(x) = x$$

which means

$$f_a^{-1}(x) = \frac{1}{a}x = f_{a^{-1}}(x) \qquad \forall x \in \mathbb{R}.$$

The inverse of f_a is then seen to correspond to the transformation $f_{a^{-1}}$, which explains the requirement $a \neq 0$.

Hence, the set of maps $\{f_a, a \in \mathbb{R}^*\}$ form a one-parameter (in fact Abelian) continuous group.

1.2.2 Orthogonal groups

Many transformations in physical applications are required to preserve *length* in the appropriate space. If that space is ordinary Euclidean n-dimensional space, the restriction that the length of a vector $\boldsymbol{r} = (x_1, ...x_n)$ is preserved *via* a transformation M means that its image $\boldsymbol{r}' = (x_1', ...x_n')$ through the transformation fulfills

$$x_1'^2 + x_2'^2 + \ldots + x_n'^2 = x_1^2 + x_2^2 + \ldots + x_n^2. \tag{1}$$

Eq. 1 is equivalent to requiring that the matrix transformation M satisfies ${}^t M M = Id$. Note that this also implies $\det({}^t M M) = (\det(M))^2 = 1$ so that $\det(M) = \pm 1$.

The corresponding groups are subgroups of the general linear group. These groups are called the orthogonal groups, and are denoted by $O(n)$.

Other transformations require preservation of the *orientation between vectors* (i.e., handedness of space). This can be written mathematically by requiring preservation of the vector product between two vectors and is generally quantified by the determinant of the matrix. If $\det(M) = 1$, this corresponds to a proper rotation. Reflection or inversion satisfy $\det(M) = -1$.

$\mathrm{GL}(\mathbb{R}^3)$ (the group of 3 by 3 invertible matrices M with real elements), contains other important subgroups such as

- $\mathrm{SL}_3(\mathbb{R}) = \{M \in \mathrm{GL}(\mathbb{R}^3) | \det(\mathrm{M}) = 1\}$

- $\mathrm{O}_3(\mathbb{R}) = \{M \in \mathrm{GL}(\mathbb{R}^3) | {}^t M M = Id_3\}$

- $\mathrm{SO}(3) = \mathrm{SO}_3(\mathbb{R}) = O_3(\mathbb{R}) \cap \mathrm{SL}_3(\mathbb{R})$

Exercise 1 : Show that these sets are indeed groups.

Proposition : O(3) and SO(3) are three-parameter groups.

Example : SO(2)

Consider the orthogonal group in two-dimensions, *i.e.* O(2), where the coordinates are x and y. Using the transformation matrix we have

$$\begin{aligned} x'^2 + y'^2 &= (a_{11}x + a_{12}y)^2 + (a_{21}x + a_{22}y)^2 & (2) \\ &= (a_{11}^2 + a_{21}^2)x^2 + 2(a_{11}a_{12} + a_{21}a_{22})xy + (a_{12}^2 + a_{22}^2)y^2. & (3) \end{aligned}$$

For the right-hand side of this equation to be equal to $x^2 + y^2$ for all x and y, we must set

$$a_{11}^2 + a_{21}^2 = 1, \quad a_{11}a_{12} + a_{21}a_{22} = 0, \quad a_{12}^2 + a_{22}^2 = 1.$$

Thus, we have three conditions imposed on four parameters, leaving one free parameter. These conditions can be used to establish the following relation:

$$(a_{11}a_{22} - a_{12}a_{21})^2 = 1.$$

(simply by multiplying the first with the third equation). Recognizing the quantity in parentheses as the determinant of the transformation, this condition implies that

$$\det(M) = \pm 1.$$

Consider now SO(2), for which det M =1. The parametrization of the group that we will use is

$$M(\alpha) = \begin{bmatrix} \cos\alpha & -\sin\alpha \\ \sin\alpha & \cos\alpha \end{bmatrix}, \quad \alpha \in [0, 2\pi]$$

where α is the single parameter in this group. As can easily be checked using the trigonometric identities for the sum of two angles,

$$M(\alpha_1)M(\alpha_2) = M(\alpha_1 + \alpha_2).$$

We can in fact use this property to show that SO(2) is a group. Further, this group is clearly Abelian (essentially because $\alpha \in \mathbb{K}$, where $\mathbb{K} = \mathbb{R}$ is a field where the composition law is commutative).

Note : SO(2) is the group that leaves the sphere $S^1 = \{x \in \mathbb{R}^2; ||x|| = 1\}$ invariant. S^1 is called a group manifold.

1.2.3 Special unitary group

Let us now define SU(2): the *special unitary group* in 2D, of importance when dealing with half-integer spins.

Definition : SU(2) =$\{M \in \mathrm{GL}(\mathbb{C}^2)| \ M^\dagger M = Id_2, \det(M) = +1\}$. $M^\dagger \equiv^t \overline{M}$. [2].

Proposition : SU(2) is a 3-parameter group.

Demonstration : We know that $\forall M \in SU(2)$, $M^\dagger M = Id = MM^\dagger$. And $M^{-1} = M^\dagger$ so $M^{-1} \in SU(2)$. To show that SU(2) is a 3-parameter continuous group, consider a general complex transformation in two dimensions

$$\begin{bmatrix} a & b \\ c & d \end{bmatrix}$$

where $\{a, b, c, d\} \in \mathbb{C}$. There are then eight free parameters. $M^\dagger M = Id_2$ implies setting the following conditions on the matrix elements:

$$|a|^2 + |c|^2 = 1, \quad |b|^2 + |d|^2 = 1, \quad ab^* + cd^* = 0$$

These four conditions (the last equation provides two conditions because it involves complex quantities) imply that the original eight free parameters are reduced to four. If, in addition to the conditions above, we require that the determinant of the transformation is unity, the transformation matrix must have the form

$$\begin{bmatrix} a & b \\ -b^* & a^* \end{bmatrix}, \quad |a|^2 + |b|^2 = 1$$

There are indeed 3 free parameters.

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[2]SU(2) is a subset of $\mathrm{GL}(\mathbb{C}^2)$: SU(2) $\subset$ U(2) $\subset \mathrm{GL}(\mathbb{C}^2)$.

Note 1: The columns are now orthogonal in the sense of the hermitian product.

Note 2 : As opposed to the O(3) group, here $M^\dagger M = Id_2$ implies $\det M = e^{i\theta}; \theta \in [0, 2\pi]$. So fixing the determinant to $\det = 1$, fixes the phase parameter θ to 0 and indeed reduces the number of parameters by one unit [3].

1.3 The full rotation group

Definition : A rotation about the origin is a transformation that preserves :

- the origin
- the Euclidean distance (so it is an isometry)
- the orientation i.e., handedness of space.

Proposition 1: Rotations can be defined by a vector $\boldsymbol{n}$, the rotation axis, and by a scalar α, the rotation angle. We will write them $\mathcal{R}(\boldsymbol{n}, \alpha)$. This means that it depends on 3 continuous parameters (in 3D).

Proposition 2 : The set of all rotations in 3D is isomorphic to SO(3).

Demonstration : Rotations $\mathcal{R}$ are linear transformations of $\mathbb{R}^3$. They can thus be represented by matrices with 3 continuous parameters. Let R be a given rotation matrix. With respect to the standard basis e_1, e_2, e_3 of $\mathbb{R}^3$ the columns of R are given by (Re_1, Re_2, Re_3). Since the standard basis is orthonormal, and since R preserves angles and length, the columns of R form another orthonormal basis. This orthonormality condition can be expressed in the form $||R\boldsymbol{r}||^2 = ||\boldsymbol{r}||^2, \forall \boldsymbol{r} \in \mathbb{R}^3$, which is equivalent to

$$^t RR = Id_3.$$

In addition to preserving length, proper rotations must also preserve orientation. The rotation group RG is thus isomorphic to SO(3) (they follow the same multiplication table). RG is therefore often called SO(3).

Here is a now list of important properties of the rotation group:

1. *It is a non-abelian group* : rotations do not commute in 3D when rotation axes $\boldsymbol{u}$ are not co-linear.

$$\forall \boldsymbol{n} \neq \boldsymbol{n}', \quad \mathcal{R}(\boldsymbol{n}, \alpha)\mathcal{R}(\boldsymbol{n}', \alpha) \neq \mathcal{R}(\boldsymbol{n}', \alpha)\mathcal{R}(\boldsymbol{n}, \alpha)$$

   but there may be another rotation $\mathcal{R}(\boldsymbol{n}'', \alpha)$ with $\boldsymbol{n}'' \neq \boldsymbol{n}'$ such that:

$$\mathcal{R}(\boldsymbol{n}, \alpha)\mathcal{R}(\boldsymbol{n}', \alpha) = \mathcal{R}(\boldsymbol{n}'', \alpha)\mathcal{R}(\boldsymbol{n}, \alpha)$$

   In fact it can be shown to be *always* possible, which brings us to the following proposition :

2. *All rotations by the same angle are in the same class*

   Let us define $U = \mathcal{R}(\boldsymbol{n}, \alpha)$. Using the previous relationship, we get to the following proposition:

$$\forall \boldsymbol{n}, \boldsymbol{n}', \alpha, \exists U, \quad \text{such that} \quad \mathcal{R}(\boldsymbol{n}, \alpha) = U^{-1}\mathcal{R}(\boldsymbol{n}', \alpha)U.$$

   i.e., $\mathcal{R}(\boldsymbol{n}, \alpha)$ and $\mathcal{R}(\boldsymbol{n}', \alpha)$ are related by a similarity transformation and, therefore, belong to the same equivalence class. Obviously U are in the group. There are always other rotation elements in the group that connect rotation axes. This can be generalized to any axis $\boldsymbol{n}'''$ etc. so that using the associative property of the similarity transformation, we can conclude that that all rotation elements by the same angle are equivalent and form a class.

   Therefore : *In the rotation group, there is an infinite number of elements in a class (because there is an infinity of rotation axes).*

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[3]Although matrices have the same dimension, as opposed to SO(2), SU(2) is not abelian *a priori*. 1-parameter groups are always abelian.

3. In SO(3) one generally set the angle $\alpha \in [0, \pi]$ and allow $\boldsymbol{n}$ to cover a sphere. One can thus represent graphically the group SO(3) by a vector $\alpha\boldsymbol{n}$ so that SO(3) is a sphere with a radius π. Note that rotations $\mathcal{R}(\boldsymbol{n}, \alpha)$ and $\mathcal{R}(-\boldsymbol{n}, \alpha)$ are equivalent so all diametrically opposite points are identical on the sphere.

4. There is an infinite number of classes in the rotation group (because there is an infinity of angles between 0 and 2π), each are labelled by the rotation angle α only.

1.4 Lie algebra of Lie groups

1.4.1 Définition of a Lie group

A real Lie group is a group that is a finite-dimensional real smooth set (namely what we called a continuous group), in which the group operations of multiplication and inversion are smooth maps.

Smoothness of the group multiplication means that the map is a smooth mapping of the product set $G \times G$ into G. Consider the multiplication of two elements $R(a)$ and $R(b)$ to yield the product $R(c)$:

$$R(c) = R(a)R(b).$$

Then in a continuous group, $f(a, b) = c$ must be a continuous C^∞ real function f of a and b. Obviously, for finite groups, this function is not continuous. f must also satisfy the group multiplication table. It thus also defines the structure of the group in the same way as the multiplication table does for discrete groups.

SO(3), SO(2), SU(2) are Lie groups.

1.4.2 Définition of an algebra

An algebra is a vector space $(g, +, \times, \cdot)$ endowed with an *internal multiplication law ($\times$)*. Algebras allow to multiply elements of groups *together*. Not only can one define a group endowed with the multiplication law (which is not necessarily commutative), but one can find a basis for this group[4].

Example : The ensemble of $n \times n$ matrices, with the usual addition and multiplication laws, is an algebra.

1.4.3 Definition of a Lie Algebra

Let $\mathbb{K}$ a commutative field. A Lie algebra over $\mathbb{K}$ is a vector space g over $\mathbb{K}$ equipped with a bilinear map from $g \times g$ to g, denoted $(x, y) \mapsto [x, y]$, such that

- $\forall x, y \in g, [y, x] = -[x, y]$,

- $\forall x, y, z \in g, [x, [y, z]] + [y, [z, x]] + [z, [x, y]] = 0$.

The map $(x, y) \mapsto [x, y]$ is called the Lie bracket of g, the first property is called anti-commutativity, and the second is called the Jacobi identity for the Lie bracket.

1.4.4 Tangent space in a Lie group

Consider a Lie group G.

Definition : A *one-parameter subgroup g* of G, is a Lie group homomorphism $g : \mathbb{R} \to G$. It thus fulfills $g(t + s) = g(t)g(s)$ for all $s, t \in \mathbb{R}$.

We can use one-parameter subgroups g to define so called *tangent spaces*.

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[4]As we will see the three Pauli matrices are the basis of the algebra of SU(2).

Consider t to take values in a neighborhood of 0, with $g(0) = e$ so that $g(t)$ is a "curve" in G which passes through the identity e. Using $s = \delta t$ we get

$$g(t + \delta t) = g(t)g(\delta t) \quad \text{so that} \quad g^{-1}(t)g(t + \delta t) = g(\delta t)$$

We can now write

$$g(\delta t) = I + \delta t x + \ldots$$

which defines a (tangent) vector x such that

$$x = \frac{d}{dt} g(t) \Big|_{t=0}.$$

Definition : The tangent space $T_e G$ at e to the group G is the vector space generated by the tangent vectors *to all* one-parameter subgroups. It is generally written as $\mathfrak{g}$.

Let ξ_α be coordinates of G in the vicinity of e. A tangent vector is then the differential operator

$$x = x_\alpha \frac{\partial}{\partial \xi_\alpha}.$$

The dimension of this tangent space is thus equal the number of real parameters in the group G.

Proposition : The tangent space $\mathfrak{g}$ of G at e has a Lie algebra structure.

Demonstration : We will give here a demonstration that uses the Lie algebra of matrices (where e is denoted I), because these are the objects that we will use mostly throughout. Consider two one-parameter groups generated by two independent vectors X and Y of $\mathfrak{g}$. Let us write their "lack of commutativity" by constructing the "commutator":

$$g = e^{tX} e^{uY} e^{-tX} e^{-uY}$$

For small t and small u, g is close to the identity and may be written $g = e^Z, Z \in \mathfrak{g}$. To first order:

$$e^{tX} e^{uY} e^{-tX} e^{-uY}$$

$$= (I + tX + \frac{1}{2}t^2 X^2)(I + uY + \frac{1}{2}u^2 Y^2)(I - tX + \frac{1}{2}t^2 X^2)(I - uY + \frac{1}{2}u^2 Y^2)$$

$$= I + (XY - YX)tu + O(t^3).$$

To order 2, one thus sees the Lie bracket of matrices X and Y. In general, for an arbitrary Lie group, the bracket is defined by

$$e^{tX} e^{uY} e^{-tX} e^{-uY} = e^Z, \quad Z = tu[X, Y] + O(t^3)$$

and one proves that this bracket has the properties of a Lie bracket.

1.4.5   Lie algebras of some important groups

Example 1 : the Lie algebra of SO(2)

SO(2) is a one-dimensional Lie group. Its tangent space at Id_2 (its Lie Algebra $\mathfrak{so}(2)$) is spanned by

$$X = \frac{\partial}{\partial \alpha} R_\alpha \Big|_{\alpha=0}$$

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

Noting that $X^2 = -Id_2$ allows us to compute explicitly the series $\exp(\alpha X)$, and we find that $R_\alpha = \exp(\alpha X)$ so that the exponential generates the whole group.

Example 2 : the Lie algebra of SO(3)

An infinitesimal rotation $R(\boldsymbol{n}, \alpha)$ transforms a vector $\boldsymbol{r} = (x_1, x_2, x_3)$ to

$$x_i' = (\delta_{ij} - \alpha \epsilon_{ijk} n_k) x_j$$

so that

$$\Gamma(R(\boldsymbol{n}, \alpha)) = \begin{bmatrix} 1 & -\alpha n_3 & \alpha n_2 \\ \alpha n_3 & 1 & -\alpha n_1 \\ -\alpha n_2 & \alpha n_1 & 1 \end{bmatrix}.$$

The infinitesimal generator X reads :

$$X = \begin{bmatrix} 0 & -n_3 & n_2 \\ n_3 & 0 & -n_1 \\ -n_2 & n_1 & 0 \end{bmatrix}.$$

It can also be expressed as $\boldsymbol{n} \cdot \boldsymbol{L}$ where

$$L_z = \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \qquad L_x = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{bmatrix} \quad \text{and} \quad L_y = \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{bmatrix}.$$

Since

$$\mathcal{R}(\boldsymbol{n}, \alpha') \mathcal{R}(\boldsymbol{n}, \alpha) = \mathcal{R}(\boldsymbol{n}, \alpha) \mathcal{R}(\boldsymbol{n}, \alpha')$$

we find that

$$\mathcal{R}(\boldsymbol{n}, \alpha) = \exp\left(-\alpha \boldsymbol{n} \cdot \boldsymbol{L}\right)$$

is a solution. The set $\{L_x, L_y, L_z\}$ forms a basis for the Lie algebra of SO(3).

Exercise : *Show that the set $L_i, i = x, y, z$ are elements of a Lie algebra.*

Example 3 : the Lie algebra of SU(2)

The matrix elements of the general unitary matrix are expressed in terms of their real and imaginary parts, so we can express it using components of a basis. With $a = a_r + i a_i$ and $b = b_r + i b_i$, a matrix in SU(2) can be written as :

$$U = \begin{bmatrix} a_r + i a_i & b_r + i b_i \\ -b_r + i b_i & a_r - i a_i \end{bmatrix} = a_r \sigma_0 + i(a_i \sigma_z + b_r \sigma_y + b_i \sigma_x),$$

where

$$\sigma_0 = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, \quad \sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}.$$

These three Hermitian matrices (the Pauli matrices) satisfy the following multiplication rules:

$$\sigma_i^2 = I \quad (i = x, y, z), \quad \sigma_i \sigma_j = -\sigma_j \sigma_i = i \epsilon_{ijk} \sigma_k \quad (\{i, j, k\} = x, y, z)$$

where I is the 2×2 unit matrix. They have a trace 0 and fulfill $\sigma_i^\dagger = \sigma_i$.

One can express $SU(2)$ using elements of its Lie algebra $\mathfrak{su}(2)$ as

$$U(\alpha, \boldsymbol{n}) = \exp\left(-\frac{i\alpha}{2}\boldsymbol{n}\cdot\boldsymbol{\sigma}\right)$$

Note that one needs to multiply the Pauli matrices by i so that they are skew-symmetric matrices. The table below is a list of some of the most important Lie algebra.

G		$\mathfrak{g}$	$\dim(\mathfrak{g})$	
$SL_n(\mathbb{R})$	$\{g \in \mathcal{M}_n(\mathbb{R})|\det(g) = 1\}$	$\mathfrak{sl}_n(\mathbb{R})$	$n^2 - 1$	$\{L \in \mathcal{M}_n(\mathbb{R})|\text{Tr}(L) = 0\}$
$SL_n(\mathbb{C})$	$\{g \in \mathcal{M}_n(\mathbb{C})|\det(g) = 1\}$	$\mathfrak{sl}_n(\mathbb{C})$	$4n^2 - 2$	$\{L \in \mathcal{M}_n(\mathbb{C})|\text{Tr}(L) = 0\}$
$SO_n(\mathbb{R})$	$\{g \in \mathcal{M}_n(\mathbb{R})|{}^tg\cdot g = \text{Id}_n\}$	$\mathfrak{so}_n(\mathbb{R})$	$n(n-1)/2$	$\{L \in \mathcal{M}_n(\mathbb{R})|L = -{}^tL\}$
$SO_{pq}(\mathbb{R})$	$\{g \in \mathcal{M}_{p+q}(\mathbb{R})|{}^tg\cdot P_{p,q}\cdot g = P_{p,q}\}$	$\mathfrak{so}_{pq}(\mathbb{R})$	$n(n-1)/2$	$\{L \in \mathcal{M}_n(\mathbb{R})|P_{pq}LP_{pq} = -{}^tL\}$
$U_n(\mathbb{C})$	$\{g \in \mathcal{M}_n(\mathbb{C})|g^\dagger\cdot g = \text{Id}_n\}$	$\mathfrak{u}_n(\mathbb{C})$	n^2	$\{L \in \mathcal{M}_n(\mathbb{C})|L = -L^\dagger\}$
$SU_n(\mathbb{C})$	$U_n(\mathbb{C}) \cap SL_n(\mathbb{C})$	$\mathfrak{su}_n(\mathbb{C})$	$n^2 - 1$	$\{L \in \mathcal{M}_n(\mathbb{C})|L = -L^\dagger \& \text{Tr}(L) = 0\}$

Figure 1: Table of some Lie groups and Lie algebras borrowed from the course of F. Chevy on "Symmetries in Physics" (M1 ICFP).

1.5 Rotating functions using angular momentum operator

1.5.1 Reminder : rotation operators

1. Let us define $\{P_{\mathcal{R}}^{\mathcal{F}}; \mathcal{R} \in RG\}$, as a set of operators $P_{\mathcal{R}}^{\mathcal{F}}$ that act to "rotate functions" via this definition

$$\Psi'(\boldsymbol{r}) = P_{\mathcal{R}}^{\mathcal{F}}\Psi(\boldsymbol{r}) = \Psi(\mathcal{R}^{-1}\boldsymbol{r}).$$

In this course, $\Psi(\boldsymbol{r})$ will be wavefunctions. Thus $P_{\mathcal{R}}^{\mathcal{F}}$ will act on the space of wave functions $\mathcal{F}$ [5].

Proposition : $\{P_{\mathcal{R}}^{\mathcal{F}}; \mathcal{R} \in RG\}$ *and* RG *are isomorphic groups.*

Proof:
1- $\{P_{\mathcal{R}}^{\mathcal{F}}; \mathcal{R} \in RG\}$ is a group (easy).
2- There is one-to-one correspondence between elements of both groups so proving that, for two elements $\mathcal{R}, \mathcal{S} \in RG$, $\mathcal{R}\mathcal{S} = \mathcal{T} \implies P_{\mathcal{R}}P_{\mathcal{S}} = P_{\mathcal{T}}$ establishes an isomorphism.

Let

$$P_{\mathcal{S}}\Psi(\boldsymbol{r}) = \Psi(\mathcal{S}^{-1}\boldsymbol{r}) = \Psi'(\boldsymbol{r}).$$

Then

$$P_{\mathcal{R}}P_{\mathcal{S}}\Psi(\boldsymbol{r}) = P_{\mathcal{R}}\Psi'(\boldsymbol{r}) = \Psi'(\mathcal{R}^{-1}\boldsymbol{r}).$$

So

$$P_{\mathcal{R}}P_{\mathcal{S}}\Psi(\boldsymbol{r}) = \Psi(\mathcal{S}^{-1}\mathcal{R}^{-1}\boldsymbol{r}) = \Psi((\mathcal{R}\mathcal{S})^{-1}\boldsymbol{r}) = \Psi(\mathcal{T}^{-1}\boldsymbol{r}).$$

In the end

$$P_{\mathcal{R}}P_{\mathcal{S}}\Psi(\boldsymbol{r}) = P_{\mathcal{T}}\Psi(\boldsymbol{r}), \forall\Psi(\boldsymbol{r}).$$

CQFD. Both groups have the same multiplication table.

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[5]Note that $\mathcal{F}$, is a sub-space of the space of square integrable functions $\mathcal{L}^2$ because of supplementary conditions on regularity

2. Let us also introduce $\hat{P}_{\mathcal{R}} = P_{\mathcal{R}}^{\mathcal{E}}$, elements of an isomorphic group that acts in the vector states in the Hilbert space $\mathcal{E}$, such that

$$\hat{P}_{\mathcal{R}} \ket{\Psi} = \ket{\mathcal{R}\Psi} = \ket{\Psi'}.$$

where $\hat{P}_{\mathcal{R}}^{\dagger} \hat{P}_{\mathcal{R}} = I_d$. The set $\{\hat{P}_{\mathcal{R}}; \mathcal{R} \in RG\}$ also forms a group that is isomorphic to $\Gamma^{\mathbb{R}^3}$. This representation of SO(3) on $\mathcal{E}$ will be essential when dealing with the spin degree of freedom, for which no spatial wave function $\Psi(\boldsymbol{r})$ exist. Note that whenever $\ket{\Psi}$ is a spatial wavefunction we can always relate $\hat{P}_{\mathcal{R}}$ to $P_{\mathcal{R}}^{\mathcal{F}}$, by writing

$$\bra{\boldsymbol{r}} \hat{P}_{\mathcal{R}} \ket{\Psi} = \braket{\mathcal{R}^{-1}\boldsymbol{r} | \Psi} = \Psi(\mathcal{R}^{-1}\boldsymbol{r}) = \Psi'(\boldsymbol{r}) = P_{\mathcal{R}}^{\mathcal{F}}\Psi(\boldsymbol{r}).$$

1.5.2 Rotations expressed in terms of angular momenta

$\hat{P}_{\mathcal{R}}$ (and $P_{\mathcal{R}}^{\mathcal{F}}$) can be expressed in terms of the angular momentum.

Let us take the spatial part of the state vector $\Psi(\boldsymbol{r})$ and make an infinitesimal geometrical rotation $R(e_z, d\alpha)$ of the vector $\boldsymbol{r}$ by an angle $d\alpha$ about an axis defined as $\boldsymbol{e}_z$. We can then introduce the modified wave-function

$$\Psi'(\boldsymbol{r}) = \Psi(\mathcal{R}^{-1}(e_z, d\alpha)\boldsymbol{r})$$

As we saw, one can associate a rotation operator $\hat{P}_R$ to R, acting on the state vectors instead as on the components, such that

$$\ket{\Psi'} = \hat{P}_{\mathcal{R}} \ket{\Psi}$$

Let us search for an expression for $\hat{P}_{\mathcal{R}}$ in terms of other relevant quantities in atomic physics.
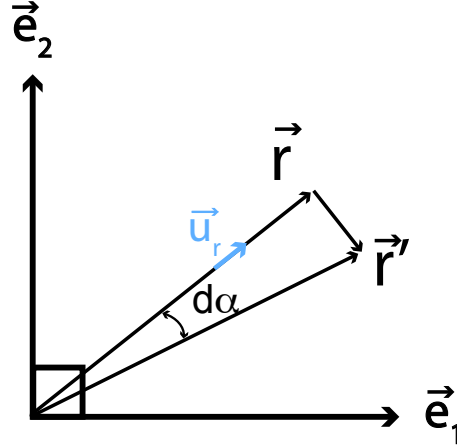
Figure 2: Rotation by an angle α around an axis e_z.

Here comes a central argument in continuous groups. We can always write rotation about any axis into its infinitesimal form. For example, looking at Fig. 2, using a unit vector $\boldsymbol{u}_r = \boldsymbol{r}/|\boldsymbol{r}|$, the infinitesimal rotation $\mathcal{R}_{e_z, d\alpha}^{-1}$ transforms $\boldsymbol{r}$ as

$$\mathcal{R}(e_z, d\alpha)^{-1}\boldsymbol{r} = \boldsymbol{r} - d\alpha \boldsymbol{e}_z \times \boldsymbol{r}$$

Since

$$\Psi(\boldsymbol{r} + \boldsymbol{\epsilon}) \approx \Psi(\boldsymbol{r}) + (\boldsymbol{\nabla}_{\boldsymbol{r}}\Psi(\boldsymbol{r})) \cdot \boldsymbol{\epsilon}$$

we have

$$
\begin{aligned}
\Psi(\mathcal{R}(e_z, d\alpha)^{-1}\boldsymbol{r}) &= \Psi(\boldsymbol{r} - d\alpha \boldsymbol{e}_z \times \boldsymbol{r}) \\
&\approx \Psi(\boldsymbol{r}) - d\alpha(\boldsymbol{\nabla}_{\boldsymbol{r}}\Psi(\boldsymbol{r})) \cdot (\boldsymbol{e}_z \times \boldsymbol{r}) \\
&= \Psi(\boldsymbol{r}) - d\alpha(\boldsymbol{r} \times \nabla_{\boldsymbol{r}}\Psi(\boldsymbol{r})) \cdot \boldsymbol{e}_z
\end{aligned}
$$

12

We can write this expression using the angular momentum operator $\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p}$ [6], where $\boldsymbol{p} = -i\hbar\boldsymbol{\nabla_r}$ as

$$\Psi(\mathcal{R}(e_z, d\alpha)^{-1}\boldsymbol{r}) = (1 - \frac{i}{\hbar}d\alpha L_z)\Psi(\boldsymbol{r})$$

where

$$L_z = -i\hbar(\boldsymbol{r} \times \boldsymbol{\nabla_r}) \cdot \boldsymbol{e_z}$$

We can reexpress in terms of kets as follows :

$$\Psi'(\boldsymbol{r}) \;\; = \;\; \langle \boldsymbol{r} | \hat{P}_\mathcal{R} | \Psi \rangle$$

where

$$\hat{P}_R = 1 - \frac{i}{\hbar}d\alpha \hat{L}_z.$$

It can be generalized to any rotation angle $\boldsymbol{n}$ as

$$\hat{P}_R = 1 - \frac{i}{\hbar}d\alpha \boldsymbol{L} \cdot \boldsymbol{n} \tag{4}$$

For a rotation with arbitrarily large angle α around $\boldsymbol{n}$, we thus get,

$$\hat{P}_R = \exp\left[-\frac{i\boldsymbol{L} \cdot \boldsymbol{n}\alpha}{\hbar}\right]$$

Note that we have not used the commutation properties of angular momenta at this point. The canonical commutation relations for the angular momentum come from the commutation relations of matrix representatives of rotations.

Example : rotation of a p_x orbital by an angle α along the z axis :
Writing $|\boldsymbol{\Omega}\rangle = |\theta, \beta\rangle$, we have

$$\langle \boldsymbol{\Omega} | l = 1, m = 0 \rangle = \sqrt{\frac{3}{4\pi}}\cos\theta \;\; \text{and} \;\; \langle \boldsymbol{\Omega} | l = 1, m = \pm 1 \rangle = \mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\phi}.$$

See Appendix **??**. The kets $|p_i\rangle$, $i = \{x, y, z\}$ are related to the kets $|l = 1, m\rangle$, $m = \{-1, 0, 1\}$ by

$$|p_x\rangle \;\; = \;\; \frac{1}{\sqrt{2}}(|l = 1, m = -1\rangle - |l = 1, m = 1\rangle) \tag{5}$$

$$|p_y\rangle \;\; = \;\; \frac{i}{\sqrt{2}}(|l = 1, m = -1\rangle + |l = 1, m = 1\rangle)) \tag{6}$$

$$|p_z\rangle \;\; = \;\; |m = 0\rangle \tag{7}$$

A rotation of a p_x orbital by an angle α along the z axis is done via the application of $\hat{P}_{R(\boldsymbol{e_z},\alpha)}$ on $|p_x\rangle$. One has

$$\hat{P}_{R(\boldsymbol{e_z},\alpha)}|l = 1, m = \pm 1\rangle = e^{-i\hat{L}_z\alpha/\hbar}|l = 1, m = \pm 1\rangle = e^{\mp i\alpha}|l = 1, m = \pm 1\rangle,$$

so

$$\hat{P}_{R(\boldsymbol{e_z},\alpha)}|p_x\rangle = \frac{1}{\sqrt{2}}(e^{i\alpha}|l = 1, m = -1\rangle - e^{-i\alpha}|l = 1, m = +1\rangle),$$

and

$$\langle \boldsymbol{\Omega} | \hat{P}_{R(\boldsymbol{e_z},\alpha)}|p_x\rangle = P_{R(\boldsymbol{e_z},\alpha)}p_x(\boldsymbol{\Omega}) = p_x(\boldsymbol{\Omega}'),$$

where $|\boldsymbol{\Omega}'\rangle = |\theta, \phi - \alpha\rangle$, as expected.

---

[6]The three projections of the angular momenta are the generators of the rotation group and define its algebra.

1.5.3   Angular momentum operator expressed in the cartesian basis

Let us express angular momentum projections in the cartesian basis, starting from $\hat{L}_z$.

Let $\boldsymbol{r} = \sum_i x_i \boldsymbol{e}_i$.

$$L_z \boldsymbol{r} = (-i\hbar(\boldsymbol{r} \times \boldsymbol{\nabla_r}) \cdot \boldsymbol{e}_z)\boldsymbol{r} = -i\hbar(x\partial_y - y\partial_x)\sum_i x_i \boldsymbol{e}_i = -i\hbar(x\boldsymbol{e}_2 - y\boldsymbol{e}_1),$$

so that evaluated at the point $\boldsymbol{r} = (x, y, z) = (1, 0, 0) = \boldsymbol{e}_1$, normalised by $-i\hbar$ we can write $L_z \boldsymbol{r}|_{\boldsymbol{r}=\boldsymbol{e}_1} = \boldsymbol{e}_2$. In short notations, and doing the same for the two other directions, we get

$$L_z \boldsymbol{e}_1 = \boldsymbol{e}_2 \tag{8}$$
$$L_z \boldsymbol{e}_2 = -\boldsymbol{e}_1 \tag{9}$$
$$L_z \boldsymbol{e}_3 = 0, \tag{10}$$

so that

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

And similarly, we find

$$L_x = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{bmatrix} \quad \text{and} \quad L_y = \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{bmatrix}.$$

This shows that when using functions in $\mathbb{R}^3$ we obtain the same Lie algebra $\mathfrak{so}(3)$ as when using vectors in $\mathbb{R}^3$ (see 1.4.5).

1.6   Relation between SU(2) and SO(3)

Since SU(2) and SO(3) have the same number of parameters, a legitimate question to ask is whether SU(2) is isomorphic to SO(3). To see this we will define the ensemble of hermitian matrices with zero trace ($i\mathfrak{su}(2)$) as :

$$\mathcal{M} = \{M \in GL_2(\mathbb{C}); M^\dagger = M, \text{tr}M = 0\}.$$

Every matrix in $\mathcal{M}$ can be written as

$$h = \begin{bmatrix} z & x - iy \\ x + iy & -z \end{bmatrix}$$

This can be checked simply by noticing that $h^\dagger = h$ and tr $h = 0$. We see that $\det h = -r^2$.

Now, let us write h as $h = \boldsymbol{r} \cdot \boldsymbol{\sigma}$, where $\boldsymbol{r}$ is a vector in $\mathbb{R}^3$ and the components of $\boldsymbol{\sigma}$ are the Pauli matrices. One should see this matrix as another way to represent the vector $\boldsymbol{r}$ instead of using cartesian coordinates.

Let us define a matrix $U \in SU(2)$ that acts to rotate vectors in $\mathcal{M}$ such that

$$\begin{aligned} Q(U) \quad &: \quad \mathcal{M} \to \mathcal{M} \\ &\quad h \mapsto UhU^{-1} \end{aligned} \tag{11}$$

We have defined a map Q acting on elements of $\mathcal{M}$. $h' = UhU^{-1}$ belong to $\mathcal{M}$ because

$$h'^\dagger = (UhU^{-1})^\dagger = (UhU^\dagger)^\dagger = Uh^\dagger U^{-1} = UhU^{-1} = h'; \quad \text{and} \quad \text{tr}h' = \text{tr}(UhU^{-1}) = \text{tr}h = 0$$

Since h' belong to $\mathcal{M}$, one can define a unique vector $\boldsymbol{r}'$ such that

$$h' = \begin{bmatrix} z' & x' - iy' \\ x' + iy' & -z' \end{bmatrix}$$

14

which defines an application $R_U : \mathbb{R}^3 \to \mathbb{R}^3$ such that $\boldsymbol{r}' = R_U \boldsymbol{r}$.

Proposition : R_U is a rotation.

Demonstration : $\boldsymbol{r}'^2 = -\det h = -\det h' = \boldsymbol{r}^2$ so R_U is an isometry. $det > 0$ follows from the continuity with respect to identity.

Another way to see why SU(2) describes rotations is to consider the matrix :

$$U(\alpha, \boldsymbol{n}) = \exp\left(-\frac{i\alpha}{2}\boldsymbol{n} \cdot \boldsymbol{\sigma}\right)$$

where, tentatively, $(\alpha, \boldsymbol{n})$ is the axis-angle representation of a rotation. One could think that because of the $1/2$, the rotation in 3D will be of an angle $\alpha/2$. The Pauli matrices properties nicely accommodate for this apparent problem... To see this, let us decompose this exponential. Since the exponential of a matrix is defined by its Taylor series expansion, we have

$$U(\alpha, \boldsymbol{n}) = \sum_{k=0}^{\infty} \frac{(-i\frac{\alpha}{2}\boldsymbol{n} \cdot \boldsymbol{\sigma})^k}{k!}$$

From $(\boldsymbol{n} \cdot \boldsymbol{\sigma})^2 = I$, we get

$$U(\alpha, \boldsymbol{n}) = \begin{bmatrix} \cos\frac{\alpha}{2} - in_z\sin\frac{\alpha}{2} & -(n_y - in_x)\sin\frac{\alpha}{2} \\ (n_y - in_x)\sin\frac{\alpha}{2} & \cos\frac{\alpha}{2} + in_z\sin\frac{\alpha}{2} \end{bmatrix} \tag{12}$$

The matrix is parametrized in the same way as rotations in $SO(3)$, namely, in terms of a rotation angle α and a rotation axis **n**. Furthermore, it indeed corresponds to a rotation by α. Let us check this using a "rotation" about z. In this case :

$$U(\alpha, z) = \begin{bmatrix} e^{\frac{-i\alpha}{2}} & 0 \\ 0 & e^{\frac{i\alpha}{2}} \end{bmatrix} \tag{13}$$

We find that

$$U(\alpha, z)hU(\alpha, z)^\dagger = \begin{bmatrix} z' & x' - iy' \\ x' + iy' & -z' \end{bmatrix}$$

where $z = z'$, $x' = \cos\alpha x + \sin\alpha y$ and $y' = \sin\alpha x - \cos\alpha y$. So we indeed have a true rotation of the coordinates.

$$U(\alpha, z) = \begin{bmatrix} e^{\frac{-i\alpha}{2}} & 0 \\ 0 & e^{\frac{i\alpha}{2}} \end{bmatrix} \leftrightarrow R(\alpha, z) = \begin{bmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{14}$$

This works nicely ! However, we see here that the relationship is however only a homomorphism, not an isomorphism. The reason for this stems from the periodicity of the two groups: $SO(3)$ has a periodicity of 2π, while $SU(2)$ has a periodicity of 4π. In particular, $U(0, \mathbf{n}) = I$, but $U(2\pi, \mathbf{n}) = -I$, so both of these elements are associated with the identity of $SO(3)$. This can also be seen by noticing that $Q(U) = Q(-U)$.

Another reason lies in the topology of the two groups : SO(3) is doubly-connected while SU(2) is simply connected.

2 Irreducible representations of the rotation group

If we map the rotation group $\mathcal{G}$ homomorphically on a group of operators in a vector space L, we obtain a representation (D) of the group in L. By definition, this means that the mapping D fulfills

$$D(G_i G_j) = D(G_i)D(G_j).$$

If the operators $D(G)$ are linear, D is a linear representation of the group. One can of course have isomorphic representations. One example is SO(3) : faithful representation of the rotation group.

2.1 Representations of a Lie algebra

We call a representation of a Lie algebra $\mathfrak{g}$ in a vector space E a homomorphism from $\mathfrak{g}$ into the Lie algebra of linear operators on the space E, that is, a mapping $X \in \mathfrak{g} \mapsto d(X) \in \mathrm{End}(E)$ which respects linearity and the Lie bracket: for all $X, Y \in \mathfrak{g}$,

$$[X, Y] \mapsto d([X, Y]) = [d(X), d(Y)] \in \mathrm{End}(E).$$

Any differentiable representation Γ of G in a space E provides a mapping d from the Lie algebra $\mathfrak{g}$ into the algebra of operators on E. We obtain it by taking the infinitesimal form of $\Gamma(g)$, for $g(t) = I + tX$ (or $g = e^{tX}$), or for infinitesimal t,

$$d(X) := \left.\frac{d\Gamma(g(t))}{dt}\right|_{t=0}, \quad \Gamma(e^{tX}) = e^{td(X)}.$$

Let's show that this mapping is compatible with the Lie brackets, and therefore it is a representation of the Lie algebra using the results from 1.4.4 and the notations from Ref. 7.

Let $g(t) = e^{tX}$ and $h(u) = e^{uY}$ be two one-parameter subgroups, for infinitesimal t and u of the same order. We have $e^{tX}e^{uY}e^{-tX}e^{-uY} = e^Z$ with $Z = ut[X, Y] + \dots$, and thus

$$\Gamma(e^{tX}e^{uY}e^{-tX}e^{-uY}) = \Gamma(e^{tX})\Gamma(e^{uY})\Gamma(e^{-tX})\Gamma(e^{-uY}) = e^{ut[d(X),d(Y)]} + \dots,$$

$$e^d(Z) = \Gamma(e^Z) = e^t d(X)e^u d(Y)e^{-t}d(X)e^{-u}d(Y),$$

from which by identifying the dominant terms we indeed find $d([X, Y]) = [d(X), d(Y)]$.

Note : The three Lie algebras of 1.4.5 are their own representations.

2.2 Important lemma

Let d be a representation of a Lie algebra, g a one-parameter subgroup of a Lie group G and $\Gamma(g)$ a representation of g.

- If d is irreducible, then $\Gamma(g)$ is irreducible. If the G is connected then the reciprocal is true.

- If the G is connected, d is completely reducible iff $\Gamma(g)$ is completely reducible.

2.3 Reminder : representation of rotations using functions

Rotations can be represented directly using the cartesian basis sets in $\mathbb{R}^3$ as we are accustomed to. One can also use a basis consisting of functions operating in $\mathbb{R}^3$ to do so, or even abstract functions, which are defined only as eigenvectors of the matrix operators. This will be of great help to find the irreps, in the same way as we used basis functions to find representations of finite groups.

Important example : Representation of rotations using p functions

Let us consider a set of functions Ψ_i ($\mathbb{R}^3 \rightarrow \mathbb{R}$) such that

$$\Psi_i(\boldsymbol{r}) = \frac{x_i}{r} = \boldsymbol{e}_i \cdot \boldsymbol{u}_r, \forall i \in \{1, 2, 3\}.$$

Here $\boldsymbol{u}_r = \boldsymbol{r}/r$[7]. We normalized the x_i to $r = \sqrt{x_1^2 + x_2^2 + x_3^2}$ so that Ψ_i are square integrable[8]. This set of functions forms a orthonormal complete basis set for a subspace ν of $\mathcal{F} = \mathrm{span}(\Psi_1, \Psi_2, \Psi_3)$ [9]. Namely, $\forall \Psi \in \nu, \forall \boldsymbol{r} \in \mathbb{R}^3, \exists! \lambda_i \in \mathbb{C}$, such that

$$\Psi(\boldsymbol{r}) = \sum_i \lambda_i \Psi_i(\boldsymbol{r})$$

The goal is to represent the rotation group using the basis $\{\Psi_i, i = 1, 2, 3\}$[10].

To remove the spatial coordinates, we can write Ψ_i as kets $|\Psi_i\rangle = |e_i\rangle$, since $\langle \boldsymbol{r} | \Psi_i\rangle = \boldsymbol{u}_r \cdot \boldsymbol{e}_i$. Using the fact that the wavefunctions Ψ_i are normalized ($\sum_i |\Psi_i|^2 = 1$) and form a complete set, we have the relation

$$\sum_j |e_j\rangle \langle e_j| = \hat{I}_d(3).$$

Let us use $\hat{P}_{\mathcal{R}}$ to rotate the kets $|e_j\rangle$

$$\hat{P}_{\mathcal{R}} |e_i\rangle = \sum_j |e_j\rangle \langle e_j| \hat{P}_{\mathcal{R}} |e_i\rangle$$

We wish to make a connection between the standard representation of RG using cartesian basis and using this basis of functions. For this, let us project the previous expression on the bra $\langle \boldsymbol{r}|$. We obtain

$$\langle \boldsymbol{r}| \hat{P}_{\mathcal{R}} |e_i\rangle = \langle \mathcal{R}^{-1}\boldsymbol{r}| e_i\rangle = \sum_j \frac{x_j}{r} \langle e_j| \hat{P}_{\mathcal{R}} |e_i\rangle .$$

This equation can be written more simply as

$$x_i' = \sum_j x_j \langle e_j| \hat{P}_{\mathcal{R}} |e_i\rangle .$$

We also know that, since here the vectors are turned in the other direction, their components become

$$x_i' = \sum_j x_j [\Gamma^{\mathbb{R}^3}(\mathcal{R}^{-1})]_{ij}.$$

We can now make the identification

$$\langle e_i| \hat{P}_{\mathcal{R}} |e_j\rangle = [\Gamma^{\mathbb{R}^3}(\mathcal{R})]_{ij}$$

This representation is not just equivalent to $\Gamma^{\mathbb{R}^3}$, it is the same. The set Γ^ν of matrices defined as $\Gamma^\nu = \{\Gamma^\epsilon(\mathcal{R}) = \Gamma^{\mathbb{R}^3}(\mathcal{R}); \mathcal{R} \in SO(3)\}$ forms a faithful representation of $SO(3)$, *the basis sets of which spans a subspace of ν of dimension 3.*

---

[7]$\Psi_i(\boldsymbol{r}) \propto \langle \boldsymbol{\Omega}| p_i\rangle$, where $\{|p_i\rangle; i = x, y, z\}$ is the set of 3 p-orbitals. One could in fact have asked the functions to act on normalized vectors $|\boldsymbol{n}\rangle \equiv |\boldsymbol{\Omega}\rangle = |\theta, \phi\rangle$ only since we are dealing with isometries. The functions would then be linear forms.

[8]Note 2 : The square integrability is not essential in principle since we are not dealing with a quantum mechanical problem, so the basis functions can here be discontinuous or not-integrable.

[9]This is a linear form, therefore it forms the basis of the dual : here $\mathcal{F}$. This is also guaranteed by the fact that these functions are eigenfunctions of the hamiltonian of a free ion : they thus necessarily form a complete basis of a vector space.

[10]In fact, since these are eigenfunctions of the hamiltonian of a free ion, we can even say that this will be the basis of an irrep of the full rotation group...

2.4 Irreps of SO(3)

2.4.1 Number of irreps

1. When deriving theorems for finite groups, such as the orthogonality of characters, one make use of sums like $\sum_k \Gamma^\nu(G_k)\Gamma^i(G_k)$. With continuous groups, converting

$$\sum_k \rightarrow \int d\alpha g(\alpha),$$

can be done, but using an appropriate measure of the density g. It was shown that $g(\alpha) = \sin^2(\alpha/2)$, in SO(3) so that, with this choice of g, all theorems that were presented for finite group, such as the great orthogonality theorem, apply. Also, with this choice of g, one can show that the number of irreps equals the number of classes also for continuous groups. See Ref [1] for more discussions.

2. Conclusion that can be drawn from the last property and from the fact that there is an infinite number of classes :

> *There is an infinite number of irreps in the rotation group.*

2.4.2 Representation of rotations using coordinates of vectors in $\mathbb{R}^3$

We saw that the components x_i of vectors $\boldsymbol{r}$ are transformed as

$$x_i' = [\Gamma^{\mathbb{R}^3}(\mathcal{R}))\boldsymbol{r}]_i = \sum_j [\Gamma^{\mathbb{R}^3}(\mathcal{R})]_{ij} x_j. \tag{15}$$

under $\Gamma^{\mathbb{R}^3}(\mathcal{R})$. This transformation has obviously the same analytical form for all rotations $\mathcal{R}(\boldsymbol{u}, \alpha)$ in SO(3). It can be shown that in order to represent *all* 3D rotations using the *same* basis set $\{x_j\}$, a space of dimension 3 is needed and not less. Because of non-collinear rotation axes in the RG in 3D, one cannot find a basis in a smaller vector space that represents all rotations. The group of component transformations $\Gamma^{\mathbb{R}^3} = \{\Gamma^{\mathbb{R}^3}(\mathcal{R}); \mathcal{R} \in RG\}$ forms an irreducible representation of RG.

Since the number of irreps of RG must equal the number of classes, $\Gamma^{\mathbb{R}^3}$ is however not the only irrep of RG.

2.4.3 The complete set of irreps of SO(2)

The irreps of SO(2) are derived in the tutorial on SO(2) using a mixture of handy equations for abelian groups, as well as laws for direct product groups.

We can also find the irreps of SO(2) using the Lie algebra. The equivalent of a direct product for Lie algebras is the direct sum. Given Lie algebras $\mathfrak{g}_1, \mathfrak{g}_2, \ldots, \mathfrak{g}_n$, their direct sum is denoted as $\mathfrak{g}_1 \oplus \mathfrak{g}_2 \oplus \ldots \oplus \mathfrak{g}_n$.

In this case, the Lie bracket operation is defined component-wise. If X_i and Y_i are elements of $\mathfrak{g}_i$ for $i = 1, 2, \ldots, n$, then the Lie bracket of $X = (X_1, X_2, \ldots, X_n)$ and $Y = (Y_1, Y_2, \ldots, Y_n)$ is given by:

$$[X, Y] = ([X_1, Y_1], [X_2, Y_2], \ldots, [X_n, Y_n])$$

where $[X_i, Y_i]$ denotes the Lie bracket of X_i and Y_i in $\mathfrak{g}_i$.

This direct sum of Lie algebras is analogous to the direct product of groups, where the operations are defined component-wise.

Let us start with the tangent space representation in $\mathbb{R}^2$ to see how it works for $\mathfrak{so}(2)$.

$$\begin{aligned} X &= \frac{\partial}{\partial \alpha} R_\alpha \bigg|_{\alpha=0} \\ &= \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}. \end{aligned}$$

The eigenstates are $\pm i$, with eigenvectors $x \mp iy$. We thus get

$$d^{\pm 1} = \{\pm i\}$$

as two irreps of $\mathfrak{so}(2)$. Doing the direct sum of irreps, we obtain recursively that $i(1 + .. + 1)$, m times, is the irrep m so that

$$d^{(m)} = \{im, m \in \mathbb{Z}\}$$

is the irrep m of $\mathfrak{so}(2)$. Note that these are the single valued irreps only (see Tutorial on SO(2)).

2.4.4 Irreps of $\mathfrak{so}(3)$

We know from the q. mechanics courses that the eigenstates of $\hat{L}_z$ and $\hat{L}^2$ are[11].

$$\{|l, m\rangle, m \in [-l, l]\} \quad \text{where} \quad l \in \mathbb{N}/2.$$

The irreps of the Lie algebra $\mathfrak{so}(3)$ are the operators $\hat{L}_i, i = x, y, z$ expressed in the $|l, m\rangle$ basis. Indeed the subspace $\mathcal{E}^{(l)} = \mathrm{span}\{|l, m\rangle, m \in [-l, l]\}$, where $\dim(\mathcal{E}(l)) = 2l + 1$, is stable by $\hat{L}_i$ and

$$d^{(l)} = \{d^{(l)}(L_i) \in \mathfrak{so}(3) | d^{(l)}_{m,m'}(L_i) = \langle l, m | L_i | l, m' \rangle\}$$

has the same multiplication table as the L_i, namely

$$d^{(l)}([L_i, L_j]) = [d^{(l)}(L_i), d^{(l)}(L_j)] \quad \forall L_i, L_j \in \mathfrak{so}(3)$$

The three first irreps $d^{(l)}$ are listed in the table below (the third one after a change of basis)

$\mathfrak{so}(3)$	L_x	L_y	L_z
$d^{(0)}$	1	1	1
$d^{(1/2)}$	$i\sigma_x$	$i\sigma_y$	$i\sigma_z$
$d^{\mathbb{R}^3}$	$\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ -1 & 0 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$

$d^{\mathbb{R}^3}$ is isomorphic to $d^{l=1}$.

2.4.5 The complete set of irreps of SO(3)

To search for irreps of SO(3), we can apply the exponential map on $\mathfrak{so}(3)$ (and then our work is over) or decompose the group of operators $\hat{P}_\mathcal{R}$ in $\mathcal{E}$ into operators that act on smaller supplementary subsets.

We saw that $\hat{P}_\mathcal{R}$ can be expressed in terms of products of projections of angular momenta $\hat{L}_i$ (series expansion of the exponential). We know that operators rotate as :

$$\hat{A}' = \hat{P}_\mathcal{R} \hat{A} \hat{P}_\mathcal{R}^\dagger. \tag{16}$$

An observable $\hat{A}$ is invariant by rotation if $\hat{A}' = \hat{A}, \forall \hat{P}_\mathcal{R}, \mathcal{R} \in SO(3)$. So that $\hat{P}_\mathcal{R} \hat{A} \hat{P}_\mathcal{R}^\dagger = \hat{A}$, which implies that

$$[\hat{P}_\mathcal{R}, \hat{A}] = 0, \forall \hat{P}_\mathcal{R}, \mathcal{R} \in SO(3)$$

so $\hat{P}_\mathcal{R}$ has the same eigenvalues as $\hat{A}$.

---

[11]In the context of group representation theory, the operator $\hat{L}^2$ is called a *Casimir operator*, that is an operator that commutes with all elements of the algebra

If we consider a single free atom, we know that its hamiltonian $\hat{H}$ is proportional to $\hat{L}^2$ and is invariant by rotation. The hamiltonian eigenstates can be labelled by basis of eigenstates of $\{\hat{L}^2, \hat{L}_z\}$. These are $\{|l, m\rangle ; l \in \mathbb{N}/2, m \in [-l, l]\}$. Again, since the subspace $\mathcal{E}(l)$, of $\mathcal{E}$ defined as

$$\mathcal{E}(l) = \text{span}\{|l, m\rangle, m \in [-l, l], l \text{ fixed}\},$$

is globally invariant (stable) under the action of $\boldsymbol{L}$ and $\hat{L}^2$. we have

$$\mathcal{E} = \sum_{\oplus} \mathcal{E}(l), \tag{17}$$

it is then quite possible that all irreps of $SO(3)$ can be found using this basis.

Let us write the set of $\hat{P}_\mathcal{R}$ on the basis of eigenstates of $\hat{L}^2, \hat{L}_z$. The spherical harmonics form a complete basis set, so

$$\hat{P}_\mathcal{R} |l, m\rangle = \sum_{l', m'} |l', m'\rangle \langle l', m'| \hat{P}_\mathcal{R} |l, m\rangle.$$

Since $\hat{P}_\mathcal{R}$ commutes with $\hat{L}^2$, we have

$$\hat{P}_\mathcal{R} |l, m\rangle = \sum_{m'} |l, m'\rangle \langle l, m'| \hat{P}_\mathcal{R} |l, m\rangle \tag{18}$$

$$= \sum_{m'} |l, m'\rangle D^{(l)}_{m', m}(\mathcal{R}) \tag{19}$$

where

$$D^{(l)}_{m', m}(\mathcal{R}) = \langle l, m'| \hat{P}_\mathcal{R} |l, m\rangle.$$

The space $\mathcal{E}(l)$ is thus closed under $\hat{P}_\mathcal{R}$ and all $2l + 1$ functions (must) appear in the decomposition of any rotated function in the subspace $\mathcal{E}(l)$ so the set $D^{(l)}$ of matrices

$$D^{(l)} = \{D^{(l)}(\mathcal{R}), \mathcal{R} \in SO(3)\}$$

of dimension $2l + 1$ is most likely an irrep of $SO(3)$. In fact, it is.

Note 1 : $D^{(l=1)}$ and $\Gamma^{\mathbb{R}^3}$ are equivalent representations.

Note 2 : The proof that $D^{(l)}$ follow the same multiplication as elements of $SO(3)$ can be done using Euler angles (see Ref. [1] for example).

Note 3 : $SO(3)$ is a non-abelian group, so the irreps can be of dimension greater than 1.

Note 4 : The bra $\langle l, m|$ transforms as $D^{*(l)}$.

2.4.6 Characters of SO(3) irreps

All classes have the same character. In each class $\mathcal{C}(\alpha)$ of $SO(3)$, there is a rotation about the axis $\boldsymbol{e}_z$. One therefore has

$$\chi^{(l)}(\mathcal{C}(\alpha)) = \chi(D^{(l)}(\mathcal{R}(\boldsymbol{e}_z, \alpha))).$$

It follows that

$$\begin{aligned}
\chi^{(l)}(\mathcal{C}(\alpha)) &= \sum_{m=-l}^{l} e^{-im\alpha} \\
&= e^{-il\alpha}(1 + e^{i\alpha} + ...e^{i2l\alpha}) \\
&= e^{-il\alpha} \sum_{m=0}^{2l} (e^{i\alpha})^m \\
&= e^{-il\alpha}[\frac{1 - e^{i\alpha(2l+1)}}{1 - e^{i\alpha}}] \\
&= \frac{\sin(l + 1/2)\alpha}{\sin(\alpha/2)}
\end{aligned} \qquad (20)$$

When $\alpha = 0$, the first line gives : $\chi^{(l)}(\mathcal{C}(0)) = 2l + 1$.

This result will be used extensively during this course.

2.4.7 Composition of angular momenta

Consider two basis functions $|l_1, m1\rangle$ et $|l_2, m_2\rangle$ with $l_1 \geq l_2$ and apply a rotation $\hat{P}_R$ to their tensor product such that

$$\hat{P}_R |l_1, l_2; m_1, m_2\rangle = \hat{P}_R^1 \otimes \hat{P}_R^2 |l_1, l_2; m_1, m_2\rangle = \sum_{m_1', m_2'} |l_1, l_2; m_1', m_2'\rangle \, D_{m_1', m_1}^{(l_1)}(R) D_{m_2', m_2}^{(l_2)}(R)$$

$D^{(l_1 \times l_2)} = D^{(l_1)} D^{(l_2)}$ is reducible in general. We thus have

$$\begin{aligned}
\chi^{(l_1 \times l_2)}(\alpha) &= \chi^{(l_1)}(\alpha)\chi^{(l_2)}(\alpha) \\
&= \frac{\sin(l_1 + 1/2)\alpha}{\sin(\alpha/2)} \sum_{m=-l_2}^{l_2} e^{im\alpha} \\
&= \frac{1}{2i \sin \alpha/2} \sum_{m=-l_2}^{l_2} [e^{i(l_1+m+1/2)\alpha} - e^{-i(l_1-m+1/2)\alpha}]
\end{aligned}$$

Since m runs from negative to positive values, we can do $-m \to m$ in the second sum. We then obtain

$$\begin{aligned}
\chi^{(l_1 \times l_2)}(\alpha) &= \sum_{m=-l_2}^{l_2} \frac{\sin(l_1 + m + \frac{1}{2})}{\sin \alpha/2} \\
&= \sum_{L=l_1-l_2}^{l_1+l_2} \chi^{(L)}(\alpha)
\end{aligned}$$

In the last line we did $L \to m+l_1$. This results indicates that the representation $D^{(l_1 \times l_2)}$ was decomposed into a sum of irreps $D^{(L)}$. This is also known as the Clebsch-Gordan decomposition. We recover the well-known result that when two angular momenta $\boldsymbol{L}_1$ and $\boldsymbol{L}_2$ are coupled vectorially, the magnitude L of $\boldsymbol{L} = \boldsymbol{L}_1 + \boldsymbol{L}_2$ runs from $l_1 - l_2$ to $l_1 + l_2$ in integer steps of 1.

Let us now switch to the notation $|j, m\rangle$, for the eigenstates of $\hat{J}^2, \hat{J}_z$.

Example : the composition of two $j = 1/2$ angular momenta

$$\chi^{(j=1/2 \times j=1/2)}(\alpha) = \chi^{(j=0)}(\alpha) + \chi^{(j=1)}(\alpha) \implies D^{(1/2 \times 1/2)} = D^{(j=0)} \oplus D^{(j=1)}.$$

2.5 Half-integer irreps of SO(3)

A major concern is that

$$\chi^{(j)}(\mathcal{C}(0)) \neq \chi^{(j)}(\mathcal{C}(2\pi))$$

when j is half integer. Indeed :

$$\chi^{(1/2)}(\mathcal{C}(2\pi)) = e^{-i\pi} + e^{+i\pi} = -2$$

whereas

$$\chi^{(1/2)}(\mathcal{C}(0)) = 2$$

We would expect that rotations by an angle 0 would yield the same result as rotation by 2π. We conclude that D^j is not a proper representation of SO(3). The solution to this is "go over" SO(3)[12] and use the representations of SU(2) instead.

2.6 Irreps of SU(2)

SU(2) is simply connected, so one could simply use the exponential map from the irreps of $\mathfrak{su}(2)$. Another lengthier way is to find the appropriate basis function. Let us see how it looks like :

2.6.1 2D Irreps of SU(2)

Let us start by considering 2 dimensional vectors in $\mathbb{C}^2$. Similar to in SO(2), we start by considering a pair of basis functions (u, v) where $u, v \in \mathbb{C}$ is transformed by an element U of SU(2) as

$$\begin{align}
u' &= au + bv \tag{21}\\
v' &= -b^*u + a^*v \tag{22}
\end{align}$$

where $|a|^2 + |b|^2 = 1$. These functions are abstract objects now with no spatial dependency, but they do provide a 2D representation of the rotation group. They are called *spinors*. In kets notations $(u, v) \leftrightarrow (|S = 1/2, m_s = -1/2\rangle, |S = 1/2, m_s = 1/2\rangle)$. U can be written as

$$U(\alpha, \boldsymbol{n}) = \exp\left(-\frac{i\alpha}{2}\boldsymbol{n} \cdot \boldsymbol{\sigma}\right)$$

Through an appropriate unitary transformation, U can always be brought to

$$U(\alpha, \boldsymbol{n}) = \exp\left(-\frac{i\alpha}{2}\sigma_z\right)$$

so that the character of this matrix

$$\chi(\alpha) = e^{\frac{i\alpha}{2}} + e^{-\frac{i\alpha}{2}} = \frac{\sin((1/2 + 1/2)\alpha)}{\sin \alpha/2}$$

Let us search for other irreps by considering products of functions, such as the antisymmetric bilinear form $u_1v_2 - u_2v_1$ obtained by combining pairs of pairs of functions.

2.6.2 1D Irreps of SU(2)

We get

$$\begin{align}
u_1'v_2' - u_2'v_1' &= (au_1 + bv_1)(-b^*u_2 + a^*v_2) - (au_2 + bv_2)(-b^*u_1 + a^*v_1) \tag{23}\\
&= (|a|^2 + |b|^2)(u_1v_2 - u_2v_1) \tag{24}
\end{align}$$

and $|a|^2 + |b|^2 = 1$ so that $(u_1v_2 - u_2v_1)$ forms the basis of a fully invariant 1D representation of the rotation group : D^0. It is the antisymmetric part of coupled spinors that can be found through CG rule.

---

[12]In more mathematical terms, this means to find a universal covering group

2.6.3   3D Irreps of SU(2)

One can find the other irreps using the symmetric combinations of the pairs (u_1, v_1) and (u_2, v_2). Since we consider symmetric products, we don't need to write them as two separate functions. Let us take $\{f_{-1}, f_0, f_{+1}\} = \{u^2, uv, v^2\}$ as the 3D symmetric basis.

$$
\begin{align}
f'_{-1} &= a^2 f_{-1} + 2ab f_0 + b^2 f_{+1} \tag{25} \\
f'_0 &= -ab^* f_{-1} + (|a|^2 - |b|^2) f_0 + a^* b f_{+1} \tag{26} \\
f'_{+1} &= b^{*2} f_{-1} - 2a^* b^* f_0 + a^{*2} f_{+1} \tag{27}
\end{align}
$$

It can be shown that the associated matrix is a representation of the rotation group $\Gamma^{\mathbb{R}^3}$ which is isomorphic to $D^{j=1}$. Through a unitary transformation, the matrix representative can be brought to

$$
\begin{bmatrix} e^{i\alpha} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{-i\alpha} \end{bmatrix},
$$

where we see that

$$
\chi(\alpha) = e^{i\alpha} + 1 + e^{-i\alpha} = \frac{\sin((1 + \frac{1}{2})\alpha)}{\sin \alpha/2}.
$$

2.6.4   Full set of Irreps of SU(2)

It can be shown (see Ref. [1] for instance) that the $2j + 1$ dimensional basis set :

$$
\{u^{2j}, u^{2j-1}v, u^{2j-2}v^2, ..., uv^{2j-1}, v^{2j}\}.
$$

is a basis for the the irreps D^j of SU(2), and that

$$
\chi^j(\alpha) = \frac{\sin((j + 1/2)\alpha)}{\sin(\alpha/2)}.
$$

It can be shown that this corresponds to all irreps of SO(3), including the double valued ones, and that the character table can be built in the same way. The table below is the character table for SU(2) where all classes u are labelled by the angle α.

SU(2)	$u(0)$	$u(2\pi)$	..	$u(\alpha)$	$u(\alpha + 2\pi) =$ $-u(\alpha)$	...
D^0	1	1	...	1	1	...
$D^{1/2}$	2	-2	...	$\frac{\sin(\alpha)}{\sin(\alpha/2)}$	$-\frac{\sin(\alpha)}{\sin(\alpha/2)}$	...
...	...	...	...	...	...	...
D^j, j=1/2, 3/2 ...	$2j+1$	$-(2j+1)$	...	$\frac{\sin((j+1/2)\alpha)}{\sin(\alpha/2)}$	$-\frac{\sin((j+1/2)\alpha)}{\sin(\alpha/2)}$	...
D^j, j=0,1,2,...,	$2j+1$	$2j+1$	...	$\frac{\sin((j+1/2)\alpha)}{\sin(\alpha/2)}$	$\frac{\sin((j+1/2)\alpha)}{\sin(\alpha/2)}$	...

These representations are ALWAYS single valued representations *of the unitary group*. When the parameter α (which should not be seen as an angle but rather as a parameter here) runs from 0 to 2π representations are single valued. However each rotation has two matrices associated to it.

Example :
For $j = 1/2$. A rotation about z gives :

$$
D^{1/2}(\alpha) = \begin{bmatrix} e^{i\alpha/2} & 0 \\ 0 & e^{-i\alpha/2} \end{bmatrix},
$$

so

$$D^{1/2}(E) = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}, \quad \text{and} \quad D^{1/2}(C_2^z) = \begin{bmatrix} i & 0 \\ 0 & -i \end{bmatrix} \quad \text{so that} \quad D^{1/2}(C_2^2) = \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}$$

This means that such representations *of the rotations* are double valued. Typical objects come back to their original position after a rotation of 2π so that $D^{1/2}(C_2^2) = D^{1/2}(E)$ so now $D^{1/2}(E) = D^{1/2}(C_2^2)$ is indeed a double valued function, which causes problems when applying the orthogonality theorems. Objects in SU(2) have no such constraint.

Note that : For $j = 1$. A rotation about z gives :

$$D^1(\alpha) = \begin{bmatrix} e^{i\alpha} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{-i\alpha} \end{bmatrix},$$

so

$$D^1(E) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad \text{and} \quad D^1(C_2) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}, \quad \text{so that} \quad D^1(C_2^2) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix},$$

so when $j = 1$, and in fact when it is an integer, no such problem arises.

3   The full orthogonal group

The group $O(3)$ is the group of all 3 by 3 (real) orthogonal matrices whose determinants can be equal to either 1 or -1. So far we have considered SO(3), which consists only of pure (proper) rotations. Atoms are fully rotationally invariant but are also invariant by inversion operations. If we include the operation I, namely, inversion with respect to the origin, we obtain the full rotation group or the rotation-reflection group consisting of all proper and improper rotations. This is the orthogonal group in three dimensions $O(3) = SO(3) \otimes C_j$ with $C_j = \{E, I\}$. I is the inversion operation.

For every $S \in O(3)$ such that $\det S = -1$, the element of the group $I \cdot S$ has determinant $\det I \times \det S = 1$, and thus corresponds to some rotation $R \in O(3)$; thus, by doing $I \cdot S = R$ we can parameterize any improper rotation S as $S = I \cdot R$, where R is an ordinary rotation.

3.1   Parity operator irreps

The two irreps of the C_s group are generally called A^g and A^u for gerade (even) and ungerade (odd) respectively. Let us call $\hat{P}_I$ the operator associated to the inversion element I such that: $\forall \boldsymbol{r} \in \mathbb{R}^3, \langle \boldsymbol{r} | \hat{P}_I = \langle -\boldsymbol{r} |$. It naturally satisfies the property $\hat{P}_I^2 = \hat{I}_d$. We can deduce the action of this operator on wave functions, $\psi(\boldsymbol{r}) \to \langle \boldsymbol{r} | \hat{P}_I | \psi \rangle = \langle -\boldsymbol{r} | \psi \rangle = \psi(-\boldsymbol{r})$. To understand how to obtain wave functions transforming as the irreps of C_s, we recall that any function can be decomposed into even and odd functions:

$$\Psi(\boldsymbol{r}) = \Psi_g(\boldsymbol{r}) + \Psi_u(\boldsymbol{r}),$$

where

$$\Psi_g(\boldsymbol{r}) = \frac{1}{2}(\Psi(\boldsymbol{r}) + \Psi(-\boldsymbol{r})) \quad \text{and} \quad \Psi_u(\boldsymbol{r}) = \frac{1}{2}(\Psi(\boldsymbol{r}) - \Psi(-\boldsymbol{r})).$$

We have $\Psi_g(-\boldsymbol{r}) = \Psi_g(\boldsymbol{r})$ and $\Psi_u(-\boldsymbol{r}) = -\Psi_u(\boldsymbol{r})$ so that

$$P_I \Psi_u(\boldsymbol{r}) = \chi^u(I) \Psi_u(\boldsymbol{r})$$

and

$$P_I \Psi_g(\boldsymbol{r}) = \chi^g(P) \Psi_g(\boldsymbol{r}),$$

where $\chi^g(I) = 1$ and $\chi^u(I) = -1$. For this reason, $\hat{P}_I$ is also called the parity operator because it "checks" which function is even or odd.

Ψ_u and Ψ_g are thus basis functions for the irreps A^u and A^g of C_s.

3.2 Irreps of the full orthogonal group

We call the irreps of O(3), D_p^l. The index p referring to either g or u. Since the group C_j has only two irreducible representations, we can derive all the irreducible representations of $O(3)$ from the D^l of SO(3). This is given in the table below

$\cdot$	R	IR
D_g^l	$D^l(R)$	$D^l(R)$
D_u^l	$D^l(R)$	$-D^l(R)$

where we used $D_g^l(IR) = D_g^l(R)$ and $D_u^l(IR) = -D_u^l(R)$.

4 Crystal field splitting

4.1 Crystal field splitting (without spins)

The set of matrices $D^{(l)} = \{\hat{D}^{(l)}(\mathcal{R}); \mathcal{R} \in O(3)\}$ is an irrep of O(3). In other words the hamiltonian H_0 of the free ion commutes with all of these matrices. Suppose that a perturbation H_{CF} is applied to an original Hamiltonian H_0 of a free ion. If the symmetry of H_{CF} is not lower than that of H_0, the perturbed Hamiltonian has the same symmetry as H_0. In this case, the symmetry group remains unchanged, and the eigenfunctions of the Hamiltonian remain to provide the basis for the same irreducible representation. The perturbation causes only a shift of the energy levels, leaving the degeneracy unchanged.

The situation becomes different when H_{CF} has lower symmetry than H_0. In this case, the symmetry group $\mathcal{S}$ of the perturbed Hamiltonian is a subgroup of the original symmetry group. Such a perturbation of lower symmetry can lift the degeneracy between the degenerate states of the O(3) irreps.

The set of matrices

$$\hat{D}'^{(l)} = \{\hat{D}^{(l)}(\mathcal{R}); \mathcal{R} \in \mathcal{S}\}$$

is a representation of $\mathcal{S}$, but it is not an irrep of $\mathcal{S}$. It can possibly be reduced.

We thus have

$$D'^{(l)} = \sum_\nu a_\nu^l \Gamma_\nu \tag{28}$$

where

$$\Gamma_\nu = \{\hat{\Gamma}_\nu(\mathcal{R}); \mathcal{R} \in \mathcal{S}\}$$

are the irreps of $\mathcal{S}$ and where

$$a_\nu^l = \frac{1}{g} \sum_k N_k (\chi^\nu(C_k))^* \chi^l(C_k)$$

where $C_k \in S$.

Example : crystal field splitting of $l = 1$ states in the D_{2h} group
See TD2.

4.2 OAM quenching

A success of crystal field theory was the explanation of the quenching of the orbital momentum in some compounds such as in iron groups. Through magnetic torque measurements, it has been found that the susceptibilities of many compounds with defects in the iron group could be made to agree with the theoretical formulae if the orbital contribution to the magnetic moment was equated to zero : see Fig. 3.

The physics of the quenching can be formulated as follows :

Ion	Number of unpaired electrons	Spin-only moment /μ_B	observed moment /μ_B
Ti^{3+}	1	1.73	1.73
V^{4+}	1	1.73	1.68–1.78
Cu^{2+}	1	1.73	1.70–2.20
V^{3+}	2	2.83	2.75–2.85
Ni^{2+}	2	2.83	2.8–3.5
V^{2+}	3	3.87	3.80–3.90
Cr^{3+}	3	3.87	3.70–3.90
Co^{2+}	3	3.87	4.3–5.0
Mn^{4+}	3	3.87	3.80–4.0
Cr^{2+}	4	4.90	4.75–4.90
Fe^{2+}	4	4.90	5.1–5.7
Mn^{2+}	5	5.92	5.65–6.10
Fe^{3+}	5	5.92	5.7–6.0

Figure 3: AOM quenching. Comparison between theory and experiment on the iron group. Taken from Solid State Physics : Aschroft and Mermin.

> In the absence of spin-dependent forces, the orbital angular momentum is zero (or quenched) in a non-degenerate eigenstate.

Example : p orbitals in a crystal with D_2 symmetry :

The symmetry group is D_2, which is an abelian group. The three eigenfunctions that appear in the character table are $\{x, y, z\}$ for the three irreps onto which $D^{(l=1)}$ is decomposed. Since $\langle \mathbf{\Omega} | p_{x_i} \rangle = x_i/r$, one can compute the expectation value of $\hat{L}_z$ in one of the non-degenerate eigenstates associated with the irreps B_i, i=1,2,3. We find for example

$$\langle p_x | \hat{L}_z | p_x \rangle = 0$$

whereas

$$\langle 1, \pm 1 | \hat{L}_z | 1, \pm 1 \rangle = \pm \hbar$$

in the eigenstates $|l = 1, m = \pm 1\rangle = |1, \pm 1\rangle$ associated with the irreps of SO(3). This shows orbital momentum quenching.

Note 1 : $\langle p_x | L_{x,y} | p_x \rangle = 0$ also, but this is not a surprise since $\langle m = \pm 1 | L_{x,y} | m = \pm 1 \rangle = 0$. m refers to the projection of $\mathbf{L}$ along z so the angular momentum projection is always zero in the x, y plane in any linear combination of the $|l, m\rangle$ eigenstates.

Note 2: One could also find part of the results using group theory. Matrix elements

$$\langle p_x | \hat{L}_z | p_x \rangle \neq 0 \quad \text{if} \quad B_3 \otimes B_1 \otimes B_3 \supseteq A_1.$$

Since $B_3 \otimes B_1 \otimes B_3 = B_1$, this matrix element is zero. It is clear that the same holds for all diagonal matrix elements.

One can obtain a clear picture for AOM quenching by computing the current density in a given orbital state (See Ref. 5 for a discussion about this effect). Using the current density

$$\boldsymbol{J} \propto -i(\Psi^* \boldsymbol{\nabla} \Psi - \Psi \boldsymbol{\nabla} \Psi^*),$$

shows that wave-function must be of the form $\alpha e^{i\phi}$, where ϕ is a coordinate parameter (and not a constant phase factor) for $\boldsymbol{J}$ to be non-zero. It was shown by J. Van Vleck that AOM quenching is associated to the fact that the wave-functions are real. Since the OAM is a purely imaginary operator, its expectation value (which must be real) is zero if the eigenstates are real. This analysis bears a deep connection with time-reversal symmetry (see Ref. 4) which will not touch upon in the course.

4.3 Spin-orbit coupling

$\rightarrow$ essential ingredient to explain electronic level structures as well as establishing a properly defined temperature in a crystal.

When an electron moves in the electrostatic field created by the proton, special relativity indicates that in the electron frame of reference, a magnetic field

$$\boldsymbol{B}' = -\frac{1}{c^2}\boldsymbol{v} \times \boldsymbol{E}$$

appears.

Since the electron bares an intrinsic magnetic moment $\mu_s = \gamma \boldsymbol{S}$ ($\gamma = g_e q/2m_e$) because it comes from the Dirac theory itself), it interacts with this B field. The corresponding interaction reads :

$$H_{\text{SO}} = -\boldsymbol{\mu}_s \cdot \boldsymbol{B}'$$

Let us write it in a more precise way. The electrostatic field

$$\boldsymbol{E} = \frac{-1}{q}\frac{dV(r)}{dr}\frac{\boldsymbol{r}}{r}$$

where
$V(r) = -\frac{e}{r}$ is the static electrostatic energy of the electron ($e = q/(4\pi\epsilon_0)$). One thus has

$$\boldsymbol{B}' = \frac{1}{qc^2}\frac{1}{r}\frac{dV(r)}{dr}\frac{\boldsymbol{p}}{m_e} \times \boldsymbol{r}$$

so that at a distance R from the nucleus :

$$H_{\text{SO}} = \frac{1}{m_e^2 c^2}\frac{1}{r}\frac{dV(r)}{dr}\boldsymbol{L} \cdot \boldsymbol{S} = \frac{e^2}{m_e^2 c^2 r^3}\boldsymbol{L} \cdot \boldsymbol{S}$$

This is only a factor of $1/2$ away from the Dirac expression for SO coupling (because of Thomas precession about the nucleus that was neglected). Physically, it is the interaction of the magnetic moment of the electron spin in the proton electrostatic field.

Consider $\mathbf{J}^2 = (\mathbf{L}+\mathbf{S})^2 = \mathbf{L}^2 + \mathbf{S}^2 + 2\mathbf{L} \cdot \mathbf{S}$, we can rewrite $\boldsymbol{L} \cdot \boldsymbol{S}$ as $1/2(\boldsymbol{J}^2 - \boldsymbol{S}^2 - \boldsymbol{L}^2)$. This implies that J, S, L are good quantum numbers. Also, one can show that $[J_z, J] = 0$, so m_J is also a quantum number.

Order of magnitude :

$\boldsymbol{L}$ and $\boldsymbol{S}$ are of the order $\hbar$, so

$$H_{\text{SO}} \approx \frac{e^2 \hbar^2}{m_e^2 c^2 R^3}$$

If we compare H_{SO} to $H_0 \approx e^2/R$, we get

$$H_{\text{SO}}/H_0 = \frac{\hbar^2}{m_e^2 c^2 R^2}$$

R is of the order of the Bohr radius, so $\approx \hbar^2/m_e e^2$.
We thus get

$$H_{\text{SO}}/H_0 \approx \frac{e^4}{\hbar^2 c^2} = (\frac{1}{137})^2$$

This is the square of what is then called the fine structure constant. Obviously one can treat the SOC as a perturbation to the general hamiltonian.

We assume that the hamiltonian is such that J is a good quantum number.

4.4 The double group

We saw that D^j representations of SO(3) are double valued. This will be a problem when studying defects in crystals since, we may encounter groups with $D^j(C_2^2) \neq D^j(E)$.

In order to build a character table for symmetry groups S' of crystals that are subgroups of SU(2) and not only of SO(3), H. Bethe proposed to use an extra "symmetry" element called R in the 3D point group S. This elements corresponds to $u(2\pi)$ but it will be treated as a generic element of SO(3) with the defining condition $R^2 = E$. Doing so, the number of elements in the group S' will be twice as large as those of S. We will have E, R as well as all the elements of S multiplied by R.

Note that then the multiplication table of the group is not the same anymore. We will have $C_n^n = R$ instead of E and $C_n^{2n} = E$. Take D_2 for example, $C_{2x}^2 \neq E$ anymore since $D^{1/2}(C_{2x}^2) = U(2\pi, \boldsymbol{e}_x) \neq D^{1/2}(E) = U(0, \boldsymbol{e}_x)$ as we already saw using Eq. 13.

Opechowski rule :
There is a theorem from Opechowski (1940) that states that R and RC_2 are in the same class if there exists a two-fold rotation with an axis perpendicular to that of C_2.
In D_2, this can be seen by noticing that :

$$D^{1/2}(C_2^y)D^{1/2}(C_2^z)D^{1/2}(C_2^y)^{-1} = D^{1/2}(RC_2^z).$$

4.5 Some properties of the irreps of the double group

#1 The new set of irreps of S' will have the "old" ones Γ^α + as much extra irreps $\Gamma^{\alpha'}$ as there extra classes.

Example :
In D_2. 8 elements in the double group $\mathcal{S}'$ but 5 classes only (Opechowsky rule). There must be 5 irreps. 4 Γ^α and one $\Gamma^{\alpha'} = \Gamma'$.

#2 The dimension of the new irreps $\Gamma^{\alpha'}$ can be found through the dimensionality rule.

Example :
In D_2, $l_{A_1}^2 + l_{B_1}^2 + l_{B_2}^2 + l_{B_3}^2 + l_{\Gamma'}^2 = 8$. We obtain : $l_{\Gamma'} = 2$.

4.6 Setting up the character table

We know not much else about the irreps of S' at that stage. Only those of S and the fact that $D^{1/2}$ will be an irrep of S'. The whole character table of S' can however be constructed using the two orthonormality relations on characters, applied to the double group.

4.6.1 Using the first orthonormality theorem for the characters

We first demand that :

$$\sum_{G \in \mathcal{G}} (\chi^\mu(G))^* \chi^\nu(G) = g' \delta_{\mu,\nu}, \quad \text{or} \quad (v^\mu, v^\nu) = g' \delta_{\mu,\nu}$$

where $g' = 2g$ is the order the group, g is the order of the original group. ν, μ are irreps of the whole double group S'.

Decomposing the sum on *all elements* of S plus the ones that depend on R, we get

$$\sum_{k=1}^{g} (\chi^\mu(A_k))^* \chi^\nu(A_k) + \sum_{k=1}^{g} (\chi^\mu(RA_k))^* \chi^\nu(RA_k) = g' \delta_{\mu,\nu}$$

The first $\sum_k$ runs over all elements of the original group $\mathcal{S}$. The second runs over all new elements of the double group. Setting $\mu = \alpha$ and $\nu = \beta$ to be both irreps of S, we get

$$g \delta_{\alpha,\beta} + \sum_{k=1}^{g} (\chi^\alpha(RA_k))^* \chi^\beta(RA_k) = 2g \delta_{\alpha,\beta}$$

where we used the first orthonormality theorem applied to the irreps of S. We obtain :

$$\sum_{k=1}^{g} (\chi^\alpha(RA_k))^* \chi^\beta(RA_k) = g \delta_{\alpha,\beta}, \quad \forall \ \alpha, \beta \text{ irreps of S}$$

This can only be true if

$$\chi^\alpha(RA_k) = \chi^\alpha(A_k), \forall \alpha \in \text{irreps S, and } \forall A_k \in S \tag{29}$$

The first orthogonality theorem therefore helps us finding all characters of the irreps of S in the double group.

4.6.2 Using the second orthonormality theorem for the characters

Again, we will enforce the second orthonormality theorem for the irreps of the double group.

$$\sum_{\nu=1}^{n'_r} (\chi^\nu(C_k))^* \chi^\nu(C'_k) = g' \delta_{k,k'}/N_k, \tag{30}$$

where n'_r are the number of inequivalent irreps in the double group (also equal to the number of distinct classes).

In particular, we demand that :

$$\sum_{\nu=1}^{n'_r} (\chi^\nu(A_k))^* \chi^\nu(A_k) = g'/N_k, \forall \ A_k \in C_k \in S,$$

Let us decompose this sum over the irreps of S + the new ones as

$$\sum_{\alpha=1}^{n_r} (\chi^\alpha(A_k))^* \chi^\alpha(A_k) + \sum_{\alpha'=1}^{n_d} (\chi^{\alpha'}(A_k))^* \chi^{\alpha'}(A_k) = g'/N_k, \forall \ A_k \in S$$

where n_r is the number of irreps of S and n_d of the new irreps in the double group. Using

$$\sum_{\alpha=1}^{n_c}(\chi^\alpha(A_k))^*\chi^\alpha(A_k) = g/N_k$$

we get

$$\sum_{\alpha'=1}^{n_d}(\chi^{\alpha'}(A_k))^*\chi^{\alpha'}(A_k) = g/N_k, \forall \; A_k \in S$$

From Eq. 30, we also have

$$\sum_{\nu=1}^{n_r'}(\chi^\nu(A_k))^*\chi^\nu(RA_k) = 0,$$

if A_k and RA_k are not in the same class.

Let us decompose it also as a sum over the irreps of S + the new ones as

$$\sum_{\alpha=1}^{n_r}(\chi^\alpha(A_k))^*\chi^\alpha(RA_k) + \sum_{\alpha'=1}^{n_d}(\chi^{\alpha'}(A_k))^*\chi^{\alpha'}(RA_k) = 0$$

where n_r is the number of irreps of S and n_d is the number of new irreps in the double group. Using Eq. (29), which tells us that $\chi^\alpha(RA_k) = \chi^\alpha(A_k)$, we obtain

$$\sum_{\alpha=1}^{n_r}(\chi^\alpha(A_k))^*\chi^\alpha(RA_k) = \sum_{\alpha=1}^{n_r}(\chi^\alpha(A_k))^*\chi^\alpha(A_k) = g/N_k$$

where N_k is the number of elements in the class k. We thus demand that

$$\sum_{\alpha'=1}^{n_d}(\chi^{\alpha'}(A_k))^*\chi^{\alpha'}(RA_k) = -g/N_k. \;\; \forall \; A_k \in S$$

Using the previous result, we thus get to the requirement :

$$\chi^{\alpha'}(RA_k) = -\chi^{\alpha'}(A_k) \; \forall A_k \in \mathcal{S} \text{ and } \forall \; \alpha' \in \text{extra (double valued) irreps.}$$

It can be shown that this relationship also holds when A_k and RA_k *are* in the same class. We know that in this case $\chi^{\alpha'}(RA_k) = \chi^{\alpha'}(A_k)$. Together with the previous result, we find that

$$\chi^{\alpha'}(RA_k) = \chi^{\alpha'}(A_k) = 0$$

.

Example :

Using the results in this section, we can derive all character tables of double groups. In D_2, the character table of the double group reads :

D_2'	E	R	$RC_2^z + C_2^z$	$RC_2^y + C_2^y$	$RC_2^x + C_2^x$
x^2, y^2, z^2, A_1	1	1	1	1	1
R_z, z, xy, B_1	1	1	1	-1	-1
R_y, y, xz, B_2	1	1	-1	1	-1
R_x, x, yz, B_3	1	1	-1	-1	1
$D^{1/2}$	2	-2	0	0	0

Note that since $D^{1/2}$ is a representation of SU(2). It is also an irrep of any crystal double group, the only one in D_2', so one could have found the result using the characters of $\chi^{J=1/2}$ directly here.

4.7 Application to term splittings :

Crystal groups are (often) subgroups of SO(3). One can then write :

$$D^J = \sum_\nu a_\nu^J \Gamma_\nu$$

with

$$a_\nu^J = \frac{1}{g'} \sum_k N_k (\chi^\nu(C_k))^* \chi^J(C_k)$$

Decomposing again the sum into elements that contain R or not, we get

$$a_\nu^J = \frac{1}{g'} \sum_k N_k \chi^\nu(A_k) \chi^J(A_k) + \frac{1}{g'} \sum_k \chi^\nu(RA_k) \chi^J(RA_k)$$

We have two situations, depending on whether J is an integer or not :

$\underline{J \text{ is an integer} : \chi^J(RA_k) = \chi^J(A_k).}$

- For $\nu = \alpha'$, $\chi^\nu(RA_k) = -\chi^\nu(A_k)$, so
$$a_\nu^J = 0.$$

- For $\nu = \alpha$, $\chi^\nu(RA_k) = \chi^\nu(A_k)$ so
$$a_\nu^J = \frac{1}{g} \sum_k \chi^\nu(A_k) \chi^J(A_k)$$

This means that the decomposition will be entirely on the single valued representations. It works exactly as it would if the groups had not been doubled.

$\underline{J \text{ is a half integer} : \chi^J(RA_k) = -\chi^J(A_k)}$

- For $\nu = \alpha$, $\chi^\nu(RA_k) = \chi^\nu(A_k)$, so
$$a_\nu^J = 0.$$

- for $\nu = \alpha'$,
$$a_\nu^J = \frac{1}{g} \sum_k \chi^{\alpha'}(RA_k) \chi^J(RA_k)$$

This means that the decomposition will be entirely on the double valued representations. One can sum over RA_k or A_k, it gives the same results.

This result shows that half integer terms are at least two-fold degenerate because all double valued irreps are at least two-dimensional (not trivial to show). This result is a consequence of Kramers's theorem.

Splitting of orbital terms by SO

We will reduce the direct products of single valued irreps Γ^α of the crystal double group $\mathcal{S}'$ and spin representations (the latter must also be expressed/reduced using double valued irreps of $\mathcal{S}'$) as a sum of irreps of the double group $\Gamma^{\nu'}$.

Note :

$$\Gamma^{\alpha\otimes\beta} = \Gamma^\alpha \otimes \Gamma^\beta = \sum_\nu a_\nu^{\alpha\otimes\beta}\Gamma^\nu$$

where

$$a_\nu^{\alpha\otimes\beta} = \frac{1}{g}\sum_k N_k\chi^{\alpha\otimes\beta}(C_k)\chi^\nu(C_k) = \frac{1}{g}\sum_k N_k\chi^\alpha(C_k)\chi^\beta(C_k)\chi^\nu(C_k)$$

Example of the D_2' group and a spin J=L+S=1+1/2.

We saw that $D^{l=1} = B_1 + B_2 + B_3$. The B_i are single valued irreps in the crystal double group. We know that $D^{1/2} = \Gamma_{1/2}$ is still an irrep in the double group representation.

so we find $\Gamma_{1/2} \otimes B_i = \Gamma_{1/2}$ so $D^1 \otimes D1/2 = 3\Gamma^{1/2}$. The 3 orbital levels are two-fold degenerate.

Exercise : *do the same calculation for a term with S=3/2 in the O' group.*
See TD on the O group.

5 Irreducible tensors

To represent SO(3) and finite crystal groups, we have so far been using bases that are either sets of functions. Here, we show that one can also use specific sets of operators to do so : *the irreducible tensors*. Before introducing them, let us first remind us how observables are rotated.

5.1 Rotating observables

We wish to study how an observable $\hat{A}$ is changed upon rotation or any symmetry element. Let us first consider an eigenstate $|\Psi\rangle$ of $\hat{A}$ with eigenvalue a such that

$$\hat{A}|\Psi\rangle = a|\Psi\rangle.$$

If the system is in the eigenstate $|\Psi\rangle$ of $\hat{A}$: the apparatus destined to measure $\hat{A}$ will give the result a for sure. The observable $\hat{A}'$, transformed from $\hat{A}$ by $\hat{P}_\mathcal{R}$, is what is measured when the apparatus has been rotated by $\mathcal{R}$. If we apply the transformation to the *whole* apparatus just before the measurement, the relative positioning of the physical system and the detector remains unchanged so the result of the measurement will be a as well. However, the apparatus will be measuring $\hat{A}'$ and the state will be $|\Psi'\rangle = \hat{P}_\mathcal{R}|\Psi\rangle$. We then have

$$\hat{A}'|\Psi'\rangle = a|\Psi'\rangle.$$

We finally require

$$\hat{A}' = \hat{P}_\mathcal{R}\hat{A}\hat{P}_\mathcal{R}^\dagger. \tag{31}$$

Note that in the case of an infinitesimal rotation, one gets :

$$\hat{A}' = \hat{A} - \frac{i}{\hbar}d\alpha[\hat{\boldsymbol{L}}\cdot\boldsymbol{u}, \hat{A}]. \tag{32}$$

5.2 Invariant and scalar operators

An observable $\hat{A}$ is a *scalar* if $\hat{A}' = \hat{A}, \forall \hat{P}_\mathcal{R}, \mathcal{R} \in G$. G is the group of symmetry. So that $\hat{P}_\mathcal{R} \hat{A} \hat{P}_\mathcal{R}^\dagger = \hat{A}$, which implies that

$$[\hat{P}_\mathcal{R}, \hat{A}] = 0, \forall \hat{P}_\mathcal{R}, \mathcal{R} \in G \tag{33}$$

so $\hat{P}_\mathcal{R}$ has the same eigenvalues as A.

Example in SO(3)
We know the eigenvalues of the hamiltonian of a rotationally invariant system. Using Eq. 32, we see that this also implies

$$[\hat{A}, \hat{L}_i] = 0.$$

A scalar operator (in fact all other operators that fulfill $[\hat{P}_\mathcal{R}, \hat{A}] = 0$) commutes with the three components of $\hat{\boldsymbol{L}}$.

An important scalar operator for systems with centrosymmetry is the hamiltonian. The hamiltonian commutes with P_R, for all $R \in SO(3)$.

Exercice : show that $\hat{\boldsymbol{r}}^2$ and $\hat{\boldsymbol{r}} \cdot \hat{\boldsymbol{p}}$ are scalar operators in SO(3).

5.3 Vector operators

We now introduce another type of operator : namely vectorial, or vector, operators.

In 3D, vector coordinates transforms as $x_i' = \sum_j [\Gamma^{\mathbb{R}^3}(R)]_{ij} x_j$ under the action of the group element R. It is thus reasonable to demand that :

> The expectation value of a vector operators transforms like a classical vector.

This demand can be expressed mathematically as :

$$v_i' = \sum_j [\Gamma^{\mathbb{R}^3}(\mathcal{R})]_{ij} v_j,$$

where $v_i = \langle \Psi | \hat{V}_j | \Psi \rangle$ is the expectation values of $\hat{V}_j$ over any state $|\Psi\rangle$ and $v_i' = \langle \Psi' | \hat{V}_j | \Psi' \rangle$ is the expectation values of $\hat{V}_j$ over the state $|\Psi'\rangle = \hat{P}_\mathcal{R} |\Psi\rangle$. We thus have

$$\langle \Psi' | \hat{V}_j | \Psi' \rangle = \sum_j [\Gamma^{\mathbb{R}^3}(\mathcal{R})]_{ij} \langle \Psi | \hat{V}_j | \Psi \rangle \tag{34}$$

and

$$\langle \Psi' | \hat{V}_j | \Psi' \rangle = \langle \Psi | P_\mathcal{R}^\dagger \hat{V}_j P_\mathcal{R} | \Psi \rangle .$$

Since Eq.34 must hold true for all state vector $|\Psi\rangle$:

$$\hat{P}_R^\dagger \hat{V}_i \hat{P}_R = \sum_j [\Gamma^{\mathbb{R}^3}(\mathcal{R})]_{ij} \hat{V}_j$$

Using Eq. 31, we know that $\hat{P}_R \hat{V}_i \hat{P}_R^\dagger = \hat{V}_i'$, we conclude that

Vector operators transform as

$$\hat{V}_i' = \hat{P}_R \hat{V}_i \hat{P}_R^\dagger = \sum_j [\Gamma^{\mathbb{R}^3}(R^{-1})]_{ij} \hat{V}_j. \tag{35}$$

Note that this transformation differs from the transformation law for components of vectors, but agrees with that of basis vectors.

Example / exercise : $\boldsymbol{J}$ and $\boldsymbol{r}$ are vector operators in SO(3).

The space of "components of vectorial operators" :

Looking at Eq. 35, it is tempting to say that the $\hat{V}_j$ form a basis for $\Gamma^{\mathbb{R}^3}$. Linear operators can be added and multiplied by scalars, so they form a vector space in the mathematical sense. If we rotate any one of these vectorial operators, we obtain a linear combination of the same three operators. Thus, any linear combination of these three operators is mapped into another such linear combination by any rotation, or, equivalently : the space of operators spanned by these three operators is *invariant under rotations*.

We can thus assign a basis set formed by operators that will represent a group. Here the set $\{\hat{V}_i, i = x, y, z\}$ forms a basis for the $\Gamma^{\mathbb{R}^3}$ representation [13].

Spherical vectorial operators

One can define other vectorial operators specific to SO(3) using a spherical basis. Writing the cartesian basis $\boldsymbol{e}_x, \boldsymbol{e}_y, \boldsymbol{e}_z$, we define spherical basis vectors $\boldsymbol{u}_q$ as :

$$\boldsymbol{u}_1 = -\frac{1}{\sqrt{2}}(\boldsymbol{e}_x + i\boldsymbol{e}_y) \tag{36}$$

$$\boldsymbol{u}_{-1} = \frac{1}{\sqrt{2}}(\boldsymbol{e}_x - i\boldsymbol{e}_y) \tag{37}$$

$$\boldsymbol{u}_0 = \boldsymbol{e}_z \tag{38}$$

One can then write

$$\boldsymbol{V} \cdot \boldsymbol{u}_1 = Y_{l=1,m=1}(\hat{V}) = \hat{V}_{+1} = -\frac{1}{\sqrt{2}}(\hat{V}_x + i\hat{V}_y),$$

and $\hat{V}_{-1} = \frac{1}{\sqrt{2}}(\hat{V}_x - i\hat{V}_y)$ and $\hat{V}_0 = \hat{V}_z$ the *standard* components of the vector operator $\hat{\boldsymbol{V}}$. These components do not transform as the cartesian components (can be check by looking at the commutation relation). Since standard components have been set up to have the *same structure* as the $l = 1$ spherical harmonics, it must transform in the same way. Namely :

$$\hat{P}_\mathcal{R} \hat{V}_m \hat{P}_\mathcal{R}^\dagger = \sum_{m'} \hat{V}_{m'} \hat{D}_{m',m}^{(l=1)}(\mathcal{R}).$$

Note : we used $\hat{D}_{m',m}^{(l=1)}(\mathcal{R}) = \hat{D}_{m,m'}^{(l=1)}(\mathcal{R}^{-1})$.

5.4   Irreducible tensor operators

Extending the previous definition of vector operators to larger rank tensors $\{T_p^{(k)}\}$, we can demand

---

[13]Although it is perfectly legitimate, it may seem strange at first to use operators as bases sets since they also act on vectors (that is, kets), which we are accustomed to use as basis sets.

Irreducible tensor operators are operators that transform as

$$\hat{P}_{\mathcal{R}}\hat{T}_p^{(k)}\hat{P}_{\mathcal{R}}^{\dagger} \;=\; \sum_{p'}\hat{T}_{p'}^{(k)}\hat{\Gamma}_{p',p}^{(k)}(\mathcal{R}) \tag{39}$$

5.4.1 Transformation properties and irreducibility

Extending the previous definition of spherical vector operators to larger rank spherical tensors $\{T_m^{(l)}\}$, we have Spherical tensor operators are operators that transform as

$$\hat{P}_{\mathcal{R}}\hat{T}_m^{(l)}\hat{P}_{\mathcal{R}}^{\dagger} \;=\; \sum_{m'=-l}^{m'=l}\hat{T}_{m'}^{(l)}\hat{D}_{m',m}^{(l)}(\mathcal{R}) \tag{40}$$

These tensors have a considerable advantage over cartesian tensors. To see this, let us consider transformation properties of cartesian tensors $T_{ijk...}$. It is customary to define the $T_{ijk...}$ by generalizing the way vectors transform $(V_i \to \sum_j \mathcal{R}_{ij}V_j)$, as follows :

$$T_{ijk...} = \sum_{i'}\sum_{j'}\sum_{k'}....\mathcal{R}_{ii'}\mathcal{R}_{jj'}....T_{i'j'k'}... \tag{41}$$

Note that here $\mathcal{R}_{ii'}$ is a matrix elements of $\Gamma^{\mathbb{R}^3}(\mathcal{R})$.
Let us consider a rank-2 cartesian tensor, defined as

$$T'_{ij} = \sum_{kl}T_{kl}\mathcal{R}_{ki}\mathcal{R}_{lj} \tag{42}$$

Treating the double indices kl as a single index β (and ij as α), we see that T_β forms the basis for a 3×3 representation of the rotation group. Indeed

$$T'_\alpha = \sum_\beta T_\beta[\Gamma(\mathcal{R})]_{\beta,\alpha}$$

where $\Gamma(\mathcal{R})_{kl,ij} = \mathcal{R}_{ki}\mathcal{R}_{lj} = \Gamma^{\mathbb{R}^3}(\mathcal{R})_{ki}\Gamma^{\mathbb{R}^3}(\mathcal{R})_{lj}$ is reducible potentially. The two $\Gamma^{\mathbb{R}^3}$ appearing in the product are 3D irreps of SO(3) and are equivalent to $D^{l=1}$ (see section 2.4.5). One can then write

$$\Gamma = D^{l=1} \otimes D^{l=1} = D^{l=0} \oplus D^{l=1} \oplus D^{l=2}.$$

This is in agreement with the CG decomposition that we saw in section 2.4.7. One basis set for these three irreps are the $\hat{T}_m^l$ where $l = 0, 1, 2$ respectively. The spherical tensors $\hat{T}_m^l$ are thus called "irreducible" tensors, just as the Y_{lm} basis could be called the SO(3) irreducible basis.

5.4.2 Spherical tensors as bases for SO(3) irreps

Spherical tensors being irreducible, they can be used as a basis. One example is the hamiltonian, which can be used as a basis for the completely symmetric representation $l = 0$. We already saw that vectorial operators can form the basis of a 3 dimensional space. This also for any dimensions $2l + 1$. It can be also generalized to any group.

Example : a cartesian dyadic
The simplest form of a cartesian tensor that is often encountered, is a dyadic formed out of two vectors $\boldsymbol{U}$ and $\boldsymbol{V}$ such that

$$\hat{T}_{ij} = \hat{U}_i\hat{V}_j.$$

It is the product of two components of vector operators (which form the basis of a 3 dimensional space) so it is reducible : it can be decomposed into tensors that transform differently under rotations. Indeed :

$$\hat{U}_i \hat{V}_j = \frac{\boldsymbol{U} \cdot \boldsymbol{V}}{3} \delta_{ij} + \frac{1}{2}(\hat{U}_i \hat{V}_j - \hat{U}_j \hat{V}_i) + \frac{1}{2}(\hat{U}_i \hat{V}_j + \hat{U}_j \hat{V}_i) - \frac{\boldsymbol{U} \cdot \boldsymbol{V}}{3} \delta_{ij}$$

The first term is a *scalar* product (invariant under rotation). The second is an *anti-symmetric* second-rank tensor which is the k-th ($k \neq i, j$) component of a vector product. It therefore transforms as a vector, which then altogether has 3 independent components. The last *symmetric traceless tensor* contains 5 independent parameters. The vector space spanned by traceless symmetric matrices has a dimension 5. In the end the dimensions are reduced to

$$3 \otimes 3 = 1 \oplus 3 \oplus 5$$

independent parameters. We have reduced the dyadic as a sum of spherical tensors.

5.5 Expectation values of irreducible tensors : The Wigner Eckart theorem

The expectation values of spherical tensors can be related to the Clebsh-Gordan coefficients using the so-called Wigner Eckart theorem. Using the transformation properties of T_m^l, one can find (see Ref. 1, or the proof in the TD1) that

$$\langle JM | \hat{T}_m^{(l)} | J'M' \rangle = \langle JM | J'l; M'm \rangle \langle J || \hat{T}_l || J' \rangle \tag{43}$$

$\langle J || T_l || J' \rangle$ is a quantity that is constant for a given J, l, J' value. It is often called a reduced matrix elements.

5.5.1 Other form of the Wigner Eckart theorem : equivalent operators

The T_m^l output l-linear combinations of components of vector operators. We already saw three examples of spherical tensors when reducing the cartesian dyadic. Other tensors can be found using spherical harmonics. For example, we get

$$Y_{l=2,m=0}(\boldsymbol{n}) = \sqrt{\frac{5}{16\pi}}(3n_z^2 - \boldsymbol{n}^2) \rightarrow T_{m=0}^{l=2}(\boldsymbol{R}) = \sqrt{\frac{5}{16\pi}}(3\hat{z}^2 - \hat{\boldsymbol{r}}^2).$$

or

$$Y_{l=1,m=0}(\boldsymbol{n}) = \sqrt{\frac{3}{4\pi}}n_z \rightarrow T_{m=0}^{l=1}(\boldsymbol{S}) = \sqrt{\frac{3}{4\pi}}\hat{S}_z$$

where $\boldsymbol{n}$ denote a unitary vector [14].

Importantly, for two vector operators $\boldsymbol{V}$ and $\boldsymbol{W}$ one has :

$$\langle JM | \hat{T}_m^{(l)}(\boldsymbol{V}) | J'M' \rangle = \langle JM | J'l; M'm \rangle \langle J || \hat{T}^l(\boldsymbol{V}) || J' \rangle \tag{44}$$
$$\text{and}$$
$$\langle JM | \hat{T}_m^{(l)}(\boldsymbol{W}) | J'M' \rangle = \langle JM | J'l; M'm \rangle \langle J || \hat{T}^l(\boldsymbol{W}) || J' \rangle$$

One can exploit the fact that the CG coefficients do not depend on the argument of the tensors. In a given J subspace, one has

$$\langle JM | \hat{T}_m^{(l)}(\boldsymbol{V}) | JM' \rangle \propto \langle JM | \hat{T}_m^{(l)}(\boldsymbol{W}) | JM' \rangle$$

which means that two spherical tensors are proportional, irrespective of the operators that are used as arguments.

---

[14]Note that the last tensor can be used as the basis for irreps of S0(3) or subgroups of SO(3) because they do not contain reflexions or inversions. Being axial vectors, angular momentum operators, such as $\boldsymbol{S}$, transform differently under reflexions than real vectors. Other problems arise if there is an odd number of spins as we will see.

6 Effective spin-hamiltonians in solids

Effective spin-hamiltonians for electrons in given orbital state facilitate the analysis of spectral lines in NMR and EPR. The idea behind is to trace out the orbital dependency in the Hamiltonian to leave only the spin dependent parts so that magnetic field dependencies can be understood more simply.

6.1 The g tensor

In purely spherically symmetric systems the $|l, m\rangle$ are eigenstates of L_z where z is arbitrary. In the presence of a B field we are free to set the B field to one of the main cartesian axes (often along z). We will see that this is not possible in crystals where the magnetic response will depend on the angle of the B field with respect to crystal axes.

We will start first by a reminder of two important situations in spherically symmetric system.

6.1.1 Spin-orbit vs magnetic field in atomic physics

We consider first an atom or ion with a negligible crystal field. The hamiltonian reads :

$$\hat{H} = \hat{H}_0 \otimes \hat{I}d_s + \lambda \sum_i \hat{L}_i \otimes \hat{S}_i,$$

where $\hat{H}_0$ is the hamiltonian of the free ion acting on the spatial part of a spinor. $\hat{\boldsymbol{S}}$ is the angular momentum operator, acting on the spin degree of freedom. $\boldsymbol{L}$ is an operator acting on the spatial part only. In the absence of magnetic field, the *total* angular momentum quantum number J and its projection along z are good quantum numbers. They are the eigenstates of $\{J_z, \boldsymbol{J}^2\}$, where the z direction is chosen by convention only because of rotational invariance

In a magnetic field $\boldsymbol{B}$ we add we hamiltonian.

$$\hat{H}_Z = -\boldsymbol{\mu} \cdot \boldsymbol{B},$$

where

$$\boldsymbol{\mu} = -\frac{\mu_B}{\hbar}(g_L \boldsymbol{L} + g_e \boldsymbol{S}).$$

and where $g_L = 1$ and $g_s \approx 2 = 2$. Note : $\boldsymbol{B}$ can still be chosen along $\boldsymbol{z}$ here. More precisely, the basis vectors of $\mathbb{R}^3$ can be rotated so that z coincides with the magnetic field direction.

Spin-orbit stronger than the magnetic field

We cannot know the values of m_l and m_S since the SO has defined new good eigenstates but we can estimate $\langle J, m_J| \boldsymbol{\mu} |J, m'_J\rangle$ knowing that it is proportional to $\langle J, m_J| \boldsymbol{J} |J, m'_J\rangle$ via the WE theorem. The proportionality constant depend on J. Therefore, in the J manifold ,

$$\boldsymbol{\mu}_J = -\mu_B g_J/\hbar \boldsymbol{J}$$

where g_J is a constant that depends on J only. We now have $\hat{H}_Z = -\boldsymbol{\mu}_J \cdot \boldsymbol{B}$ as an effective spin-hamiltonian in the manifold J.

If the B field was strong, the J terms would mix.
Spin-orbit weaker than the magnetic field

Let us rewrite the hamiltonian in the form

$$\hat{H} = \hat{H}_0 \otimes \hat{I}d_s + (-\frac{\mu_B}{\hbar}\boldsymbol{B} \cdot \hat{\boldsymbol{L}}) \otimes \hat{I}d_s + \hat{I}d_r \otimes (-\frac{2\mu_B}{\hbar}\boldsymbol{B} \cdot \hat{\boldsymbol{S}}) + \lambda \sum_i \hat{L}_i \otimes \hat{S}_i,$$

where $\lambda \sum_i \hat{L}_i \otimes \hat{S}_i$ is much smaller than $\hat{H}_u = \hat{H}_0 \otimes \hat{I}d_s + (-\frac{\mu_B}{\hbar}\boldsymbol{B} \cdot \hat{\boldsymbol{L}}) \otimes \hat{I}d_s + \hat{I}d_r \otimes (-\frac{2\mu_B}{\hbar}\boldsymbol{B} \cdot \hat{\boldsymbol{S}})$. Here again z is chosen arbitrarily, so we are free are to choose the B field in the z direction, or rather to rotate the coordinate frame to let it coincide with the B direction and redefine the kets $|l, m_l\rangle$ and $|S, m_S\rangle$ are eigenstates of $\hat{L}_z$ and $\hat{S}_z$ respectively in this new rotated frame.

Note that $|l, m_l\rangle \otimes |s, m_s\rangle$ are eigenstates of the unperturbed hamiltonian $\hat{H}_u$ but not of $\hat{H}$ because terms like $\hat{L}_x \otimes \hat{S}_x$ in the SO hamiltonian do not commute with $\hat{H}_u$ so we will use perturbation theory.

Let us write $|\Psi\rangle = |l, m_l\rangle$ to be a normalized eigenstate of $\hat{H}_0$. The electron "remains" in $|\Psi\rangle$ to leading order in perturbation theory in the limit of weak spin-orbit coupling. Note that it is not true even to zero-th order in the presence of accidental degeneracies. We will thus assume that the magnetic field lifts totally the degeneracy between all $|l, m_l\rangle \otimes |s, m_s\rangle$ states. In this limit, it is possible to define an effective spin hamiltonian $\hat{H}_{\text{eff}}$ as

$$
\begin{aligned}
\hat{H}_{\text{eff}} &= \langle \Psi | H_s | \Psi \rangle && (45) \\
&= (-\frac{2\mu_B}{\hbar}B_z + \lambda \hbar m_l)\hat{S}_z. && (46)
\end{aligned}
$$

$\hat{H}_s = \hat{I}d_r \otimes (-\frac{2\mu_B}{\hbar}\boldsymbol{B} \cdot \hat{\boldsymbol{S}}) + \lambda \sum_i \hat{L}_i \otimes \hat{S}_i$ is to the sum of the hamiltonians that depend only on the spin operators $\hat{S}_i$. The others only add a global shift to all the spin states. We see that here the orbital motion impacts the spin energy through spin-orbit coupling, creating an effective B' field

$$
B' = -\frac{\lambda \hbar^2 m_l}{2\mu_B}.
$$

This is known as the Paschen-Back effect.

Another approach is to express the diagonal values of $-\frac{2\mu_B}{\hbar}\boldsymbol{B} \cdot \hat{\boldsymbol{S}}$ on the eigenstates perturbed by SO.

6.1.2 Strong crystal field compared to Zeeman and SO

Adding the crystal field, the hamiltonian is now of the form

$$
\hat{H} = (\hat{H}_0 + \hat{H}_{CF}) \otimes \hat{I}d_s + (-\frac{\mu_B}{\hbar}\boldsymbol{B} \cdot \hat{\boldsymbol{L}}) \otimes \hat{I}d_s + \hat{I}d_r \otimes (-\frac{2\mu_B}{\hbar}\boldsymbol{B} \cdot \hat{\boldsymbol{S}}) + \sum_i \lambda \hat{L}_i \otimes \hat{S}_i.
$$

We will consider for simplicity that the eigenstates $\{|\Psi_k\rangle, k = 1...n_r\}$, of $\hat{H}_0 + \hat{H}_{CF}$ are *non-degenerate*. In this case the $|\Psi_k\rangle$ all depend on a physical direction defined by the crystalline axes (think about D_2). We can now no longer chose any direction we wish for the magnetic field, unless we rotate the crystal.

Note : if there were two degenerate states, one would have some freedom for $\boldsymbol{B}$ in a plane only.

6.1.3 Magnetic field restores angular momentum

Let us first consider only the orbital angular momentum parts without spin-orbit coupling, namely

$$
\hat{H} = (\hat{H}_0 + \hat{H}_{CF}) \otimes \hat{I}d_s + (-\frac{\mu_B}{\hbar}\boldsymbol{B} \cdot \hat{\boldsymbol{L}}) \otimes \hat{I}d_s.
$$

If the magnetic field dependent term is zero and that the orbital eigenstates $|\Psi_k\rangle$ are all non-degenerate the expectation values of $\boldsymbol{L}$ is zero in all directions due to orbital momentum quenching. This is not the case in a magnetic field, because the orbital singly degenerate states will be mixed, thus restoring some angular momentum. Consider that

$$
|\epsilon_{k'} - \epsilon_k| \gg |\mu_B B|, \quad \text{where} \quad \epsilon_k = \langle \Psi_k | \hat{H}_0 + \hat{H}_{CF} | \Psi_k \rangle.
$$

Using perturbation theory, the new perturbed eigenstates $|\phi_k\rangle$ are found to be

$$
|\phi_k\rangle = |\Psi_k\rangle + \sum_{k'} \xi_{k,k'} |\Psi_{k'}\rangle,
$$

where

$$\xi_{k,k'} = \frac{\langle \Psi_{k'}| \, (-\frac{\mu_B}{\hbar} \boldsymbol{B} \cdot \hat{\boldsymbol{L}}) \, |\Psi_k\rangle}{\epsilon_k - \epsilon_{k'}}.$$

we thus get to leading order

$$\langle \phi_k| \, \boldsymbol{L} \, |\phi_k\rangle = \sum_{k'} \xi_{k,k'} \, \langle \Psi_k| \, \boldsymbol{L} \, |\Psi_{k'}\rangle + c.c$$

Note 1 : $\langle \Psi_k| \, \boldsymbol{L} \, |\Psi_{k'}\rangle$ are purely imaginary terms because $L = -i\hbar \boldsymbol{r} \times \boldsymbol{\nabla}$ is purely imaginary and Ψ_k are real functions here (up to a constant prefactor that cancels out in the product). The complex conjugate is thus the same as the first term. One can thus expect that $\langle \phi_k| \, \boldsymbol{L} \, |\phi_k\rangle$ is now not quenched because $|\phi_k\rangle$ is no longer purely real.

Note 2 : The angular momentum extra diagonal terms are not zero in the unperturbed basis (only the diagonal ones) so $\langle \Psi_k| \, \boldsymbol{L} \, |\Psi_k'\rangle$ can be on the order of $\hbar$. The explains why expectation value of $\boldsymbol{L}$ can thus be significant in a perturbed eigenstate in all 3 directions.

Example : p orbitals in a crystal with D_2 symmetry :

The p_x eigenstate of $H_0 + H_{CF}$ reads

$$|p_x\rangle \quad = \quad \frac{1}{\sqrt{2}}(|l = 1, m = -1\rangle - |l = 1, m = 1\rangle). \tag{47}$$

We thus have

$$L_x |p_x\rangle \quad = \quad \frac{1}{2}(L^+ + L^-)\frac{(|1, -1\rangle - |1, 1\rangle)}{\sqrt{2}} = 0 \tag{48}$$

$$L_y |p_x\rangle \quad = \quad \frac{1}{2i}(L^+ - L^-)\frac{(|1, -1\rangle - |1, 1\rangle)}{\sqrt{2}} = -i\hbar |p_z\rangle \tag{49}$$

$$L_z |p_x\rangle \quad = \quad i\hbar |p_y\rangle \tag{50}$$

where we used

$$L^\pm |1, \mp\rangle = \hbar\sqrt{2} |1, 0\rangle$$

Let us assume that the ground state is $|\phi_x\rangle$, perturbation of the state $|p_x\rangle$ by the magnetic field, and that the electron is in this state. Using the previous results we get

$$\langle \phi_x| \, \hat{L}_x \, |\phi_x\rangle = \sum_{k'} \xi_{x,k'} \, \langle p_x| \, L_x \, |\Psi_{k'}\rangle + c.c. = 0$$

$$\langle \phi_x| \, \hat{L}_y \, |\phi_x\rangle = \sum_{k'} \xi_{x,k'} \, \langle p_x| \, L_y \, |\Psi_k'\rangle + c.c. = i\hbar\xi_{x,z} + c.c.$$

$$\langle \phi_x| \, \hat{L}_z \, |\phi_x\rangle = \sum_{k'} \xi_{x,k'} \, \langle p_x| \, L_z \, |\Psi_k'\rangle + c.c. = -i\hbar\xi_{x,y} + c.c.$$

where

$$\xi_{x,z} = i\frac{\mu_B B_y}{\epsilon_x - \epsilon_z}$$

and

$$\xi_{x,y} = i\frac{\mu_B B_z}{\epsilon_x - \epsilon_y}$$

So that the non-zero contributions for L in the p_x state are

$$\langle \phi_x| \, \hat{L}_{y,z} \, |\phi_x\rangle = \frac{2\hbar\mu_B}{\epsilon_x - \epsilon_{z,y}} B_{y,z}$$

In p_x there is an equal weighting of $|m = \pm 1\rangle$, so no circulation of the electron. Adding a bit of p_y changes their relative weight. The expectation value of L_z is thus non-zero. It is however small if the magnetic field is small and if the crystal field is large.

6.1.4   g-tensor

Chain reaction :

1. The $\boldsymbol{L} \cdot \boldsymbol{B}$ term will act to mix the p states.

2. This will generate some angular momentum.

3. In turn, spin-orbit coupling $\boldsymbol{L} \cdot \boldsymbol{S}$ will split the spin states.

4. This generates an effective B field, potentially stronger in some directions, that can be recast using a g-tensor. defined as

$$H_{\text{eff}} = -\frac{\mu_B}{\hbar} \boldsymbol{B} \cdot \underline{\underline{g}} \boldsymbol{S}.$$

In the orthorhombic case, we get

$$g_{xx} = 2$$
$$g_{yy} = 2(1 - \frac{\hbar^2 \lambda}{\epsilon_z - \epsilon_x})$$
$$g_{zz} = 2(1 - \frac{\hbar^2 \lambda}{\epsilon_y - \epsilon_x})$$

Note 1 : If we apply the magnetic field along the x direction, we then have only a $2S_x B_x$ term. This would look like the typical Zeeman effect of free ions.

Note 2 : If we apply the magnetic field in any other direction, the spin-orbit adds an effective B' field that is proportional to the external B field, similar to in the Pashen-Back effect.

Note 3 : The g tensor reflects the symmetry of the crystal (Rhomboedric here), following the Curie Principle.

Note 4 : λ can be negative. Electrons and holes have an opposite λ for example.

6.2   Spin-spin interaction in solids

Another important mechanism is the direct spin-spin interaction. It reads :

$$\hat{H}_{dd} = \frac{\mu_0}{4\pi \hat{r}^3}[\hat{\boldsymbol{\mu}}_1 \cdot \hat{\boldsymbol{\mu}}_2 - 3(\hat{\boldsymbol{\mu}}_1 \cdot \hat{\boldsymbol{n}})([\hat{\boldsymbol{\mu}}_2 \cdot \hat{\boldsymbol{n}})]$$

where μ_i are the two magnetic moments of each spin dipole. $\hat{\boldsymbol{n}}$ is the unit vector operator that is along the direction formed by the two spins. It can be rewritten in a matrix form as

$$\hat{H}_{dd} = \hat{\boldsymbol{S}}_1 \, \underline{\underline{\hat{D}}} \, \hat{\boldsymbol{S}}_2,$$

where $\underline{\underline{\hat{D}}}$ is the symmetric zero-trace matrix :

$$\underline{\underline{\hat{D}}}_{ij} = \xi(\hat{r})(\delta_{ij} - 3\hat{n}_i \hat{n}_j)$$

and $\xi(\hat{\boldsymbol{r}}) = \frac{\mu_0 \gamma_1 \gamma_2}{4\pi \hat{r}^3}$.

Note 1: this second-rank tensor forms the basis for the irrep $D^{l=2}$.
Note 2: the trace zero character of the tensor indicates conservation of energy when the spins interact.

Finding an effective spin-spin interaction is not trivial here because the Hilbert space (describing orbital motion of the two electrons plus their spins) is more complex than as in the previous section. In principle, one should find a basis for the irrep of the group which satisfies the anti-symmetry of the wavefunction, include Coulomb interaction between electrons (typically stronger than H_{dd}) and trace out the orbital part of $\hat{H}_{dd}$ in this orbital eigenstate state $|\phi\rangle$. Generally, the ground orbital state is antisymmetric because then the Couloumb interaction is weaker. The consequence is that the spin state must be symmetric for the total wave-function to be antisymmetric in the ground state. To find $\xi'(r) = \langle\phi|\,\xi(\hat{r})|\phi\rangle$ quantitatively, one often requires DFT methods.

Example : Axially symmetric crystal :

We will here directly invoke Curie's principle and refer to more advance textbooks (ref [1] for example) for more refined analyses. Let us pick the principal axis along z. Invoking Curie's principle, we get :

$$\hat{H}_{\text{eff}} = \hat{\boldsymbol{S}}_1 \, \underline{\underline{D}} \, \hat{\boldsymbol{S}}_2,$$

where

$$\underline{\underline{D}} = \xi'(r) \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{bmatrix}$$

is now a matrix consisting of scalars, with a trace zero. We can even write $\hat{H}_{\text{eff}}$ using $\boldsymbol{S} = \boldsymbol{S}_1 + \boldsymbol{S}_2$. Since the square of all three Pauli matrices is the identity :

$$\boldsymbol{S}_i \, \underline{\underline{D}} \, \boldsymbol{S}_i = \xi'(r)((\hat{S}_i^x)^2 + (\hat{S}_i^y)^2 - 2(\hat{S}_i^z)^2) = 0.$$

This lead to the more often encountered form:

$$\hat{H}_{\text{eff}} = \frac{1}{2}\hat{\boldsymbol{S}} \, \underline{\underline{D}} \, \hat{\boldsymbol{S}}.$$

Using now $\hat{\boldsymbol{S}}^2 = \hbar^2 S(S+1)\hat{I}d$, we can also write the hamiltonian as

$$\hat{H}_{\text{eff}} = D_{zz}[\hat{S}_z^2 - \frac{1}{3}\hbar^2 S(S+1)\hat{I}d].$$

where $D_{zz} = -3\xi'(r)/2$. It is also customary to normalize spin 1 matrices $\hat{S}_i$ by $\hbar$. We will use this convention in the rest of the course. This means that D_{zz} is homogenous to an energy. The eigenstates energies for a spin S=1 are depicted below, together with a sketch of the Zeeman splitting in the presence of a longitudinal magnetic field (along $\boldsymbol{z}$).

---

7 Spin relaxation

In the context of quantum information and sensing, it is desirable to preserve qubit lifetimes and understand the limits to the spin population decay. Here, we will consider a pure electronic state $|\Psi\rangle$ describing the spinor of a defect inside a crystal at a temperature T and ask ourselves : how long will it stay there ?
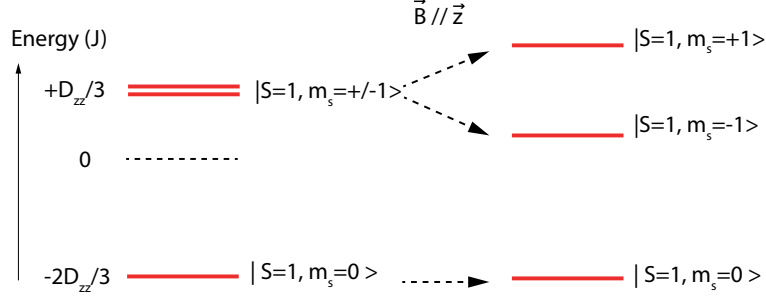
Figure 4: Level structure in the presence of spin-spin interactions in the triplet state $S = 1$.

7.1 Experimental observations

Consider first a two level system with an energy splitting $\hbar\omega_0$. Assuming that equilibrium is well defined, we have

$$\frac{N_+}{N_-} = e^{-\beta\hbar\omega_0},$$

where $N\pm$ are the population in the up and down states. If we displace the spin population from equilibrium (through optical pumping or microwave excitation), the escape rates $\Gamma_\pm$ from $|\pm\rangle$ which allow populations equilibrium will be related to $N\pm$ by the detailed balance condition (see appendix B). At equilibrium, if population is preserved in the two-level manifold, the number of transitions/s from up to down is the same as from down to up : namely $N_+\Gamma_+ = N_-\Gamma_-$.

Note : if there is population inversion (which can be done through optical pumping or apply an RF π pulse), one finds from the Boltzmann formula that the temperature is negative. This seems contradictory with the notion of temperature related to the average kinetic energy of the system's particles. The paradox is resolved by considering the more rigorous definition of thermodynamic temperature as the competition between internal energy and entropy contained in the system. Systems with a positive temperature will increase in entropy as one adds energy to the system, while systems with a negative temperature will decrease in entropy as one adds energy to the system.

A system with a negative temperature is in fact hotter than a system with a positive temperature. If a negative-temperature system and a positive-temperature system come in contact, heat will flow from the negative- to the positive-temperature system (in agreement with the Fourier law).

Experimentalists typically use the T_1 time, also known as longitudinal decay, or decay of the population difference :

$$\frac{1}{T_1} = \Gamma_+ + \Gamma_-$$

At 300K, one typically measures T_1 times ranging from ns to ms for rare earth ions, SiV, NV, GeV centers... At mK temperatures, one measures typical T_1 times ranging from ms to hours.

7.2 Longitudinal relaxation due to photons

Consider first longitudinal relaxation due to photons and assume that we have an isolated two level non-degenerate system for simplicity. The states could be the manifold $|1, 0\rangle \to |1, -1\rangle$ of the spin triplets or a spin $1/2$ in a magnetic field. The two levels $|\pm\rangle$ are split by $\hbar\omega_0$.

Note : For a spin $1/2$, there is no possibility for the motion of the surrounding electrons or nucleus in the crystal to act on the spin states since there is no orbital part. In other words, the change in the electrostatic interaction induced by phonons cannot flip a spin $1/2$. The relaxation of the spin will be due to magnetic

field fluctuations coming from a heat reservoir. Here the crystal. We are thus lead to consider the influence of black body radiation of the two-level system.

The coupling between the spin and the reservoir of magnetic modes is given by $\hat{H}_z = -\hat{\boldsymbol{\mu}} \cdot \boldsymbol{B}$, for a purely magnetic transition, so the formula reads for absorption and emission respectively are:

$$\Gamma_+ = \frac{2\pi}{\hbar^2} \sum_{\boldsymbol{k},\lambda} |\langle -; n_k + 1| \hat{H}_z |+, n_k\rangle|^2 \delta(\omega_0 - \omega_{\boldsymbol{k},\lambda})$$

$$\Gamma_- = \frac{2\pi}{\hbar^2} \sum_{\boldsymbol{k},\lambda} |\langle -; n_k - 1| \hat{H}_z |+, n_k\rangle|^2 \delta(\omega_0 - \omega_{\boldsymbol{k},\lambda})$$

where the sum runs over all possible states in the quasi-continuum of bosonic modes $\boldsymbol{k}$, including the polarisation λ. This is also know as the Fermi golden rule.

From $\boldsymbol{B} = \boldsymbol{\nabla} \times \boldsymbol{A}$, we find:

$$\boldsymbol{B}(\boldsymbol{r}) = i \sum_{\boldsymbol{k},\lambda} \sqrt{\frac{\hbar}{2\epsilon_0 \omega V}} (\boldsymbol{k} \times \boldsymbol{\epsilon}_\lambda)(a_{\boldsymbol{k},\lambda} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} - h.c.) \tag{51}$$

equivalently :

$$\boldsymbol{B}(\boldsymbol{r}) = i \sum_{\boldsymbol{k},\lambda} \sqrt{\frac{\hbar\mu_0\omega}{2V}} (a_{\boldsymbol{k},\lambda} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} - h.c.)\boldsymbol{\nu}_\lambda \tag{52}$$

where $\boldsymbol{\nu}_\lambda$ is the magnetic field direction. In the rotating frame, the coupling between photons and spins can be written as

$$\hat{V} = \frac{1}{2}\hat{\boldsymbol{\mu}} \cdot \hat{\boldsymbol{B}_1}$$

The half comes from the fact that we neglected counter-rotating terms, which do not produce any change in the atomic spin.

$$\hat{V} = \frac{i}{2} \sum_{\boldsymbol{k},\lambda} \sqrt{\frac{\hbar\mu_0\omega}{2V}} (a_{\boldsymbol{k},\lambda} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} - h.c.)(\mu_x \nu_\lambda^x + \mu_y \nu_\lambda^y)$$

. using

$$a |n\rangle = \sqrt{n} |n-1\rangle$$
$$a^\dagger |n\rangle = \sqrt{n+1} |n+1\rangle$$

$$|\langle +; n_k - 1| V |-; n_k\rangle|^2 = \frac{\mu^2}{4} \frac{\hbar\mu_0\omega}{2V} |\nu_\lambda^x + i\nu_\lambda^y|^2 n_{\boldsymbol{k}} \tag{53}$$

We can finally make the substitution in the general formula for Γ

$$\sum_{\boldsymbol{k},\lambda} \rightarrow \frac{1}{(2\pi)^3/L^3} \int 4\pi k^2 dk \sum_\lambda \int \frac{d\boldsymbol{\Omega}}{4\pi} \tag{54}$$

$$= \frac{V}{2\pi^2 c^3} \int \omega^2 d\omega \sum_\lambda \int \frac{d\boldsymbol{\Omega}}{4\pi}$$

$$= \int \rho(\omega)d\omega \sum_\lambda \int d\boldsymbol{\Omega}, \tag{55}$$

where $\rho = \frac{V\omega^2}{8\pi^3 c^3}$ so that

$$\Gamma_- = \frac{2\pi}{4\hbar^2}\mu^2 \frac{V}{2\pi^2 c^3}\int \omega^2 d\omega \frac{\hbar\mu_0\omega_0}{2V}\langle n_\omega\rangle f_{\text{scat}}\delta(\omega - \omega_0), \quad (56)$$

where

$$f_{\text{scat}} = \sum_\lambda \int \frac{d\mathbf{\Omega}}{4\pi}|\nu_\lambda^x + i\nu_\lambda^y|^2 \quad (57)$$

$$= 2 \times \frac{2}{3}. \quad (58)$$

In the end, we obtain

$$\Gamma_+ = \frac{\mu_0\gamma^2\hbar\omega_0^3}{3\pi c^3}(\langle n_{\omega_0}\rangle + 1), \quad (59)$$

where

$$\langle n_{\omega_0}\rangle = \frac{1}{e^{\beta\hbar\omega_0} - 1},$$

so that

$$\frac{1}{T_1} = \frac{\mu_0\gamma^2\hbar\omega_0^3}{3\pi c^3}(2\langle n_{\omega_0}\rangle + 1) \quad (60)$$

$$= \frac{\mu_0\gamma^2\hbar\omega_0^3}{3\pi c^3}\coth(\frac{\hbar\omega}{2kT_0}). \quad (61)$$

For a transition in the GHz range, one finds $10^{-12}s^{-1}$ at 0 K. There are $\approx 10^7$ seconds/year. So one has to wait 10^5 years. $10^{-10}s^{-1}$ at 300K. This is much too long to explain the typical millisecond relaxation times found for spins in solid.

7.3 Longitudinal relaxation due to phonons

In a solid population equilibrium is typical not reached though the interaction with the thermal electromagnetic radiation field, but through the interaction with the lattice vibration. As we will see, these however can viewed as a generating a random magnetic field in the solid, whose energy density is higher at a given frequency than that given by the above equation by a factor of $(c/v)^3 \approx 10^{15}$, where v is the speed of sound.

Apart from the difference arising from the presence of the longitudinal part of the phonon wave, and unless the other factors are lessen by 10^{15} compared to photons, phonons should thus dominate.

Note : in the following, we will assume that the heat capacity of the phonon reservoir is huge, meaning that the crystal is in good contact with some other large reservoir.

7.3.1 Relaxation due to a modulation of the spin-spin interaction

Modulation of the spin-spin interaction is one of the first considered case by Waller for spin relaxation. For simplicity we start to give a toy model inspired by the effective spin-hamiltonian we obtained, where we assume that the two electrons are at two different locations and can move relative to one another under the cristal motion.

Semi-classical toy model

When the nuclei move, the crystal temporally departs from axial symmetry. See Fig.5
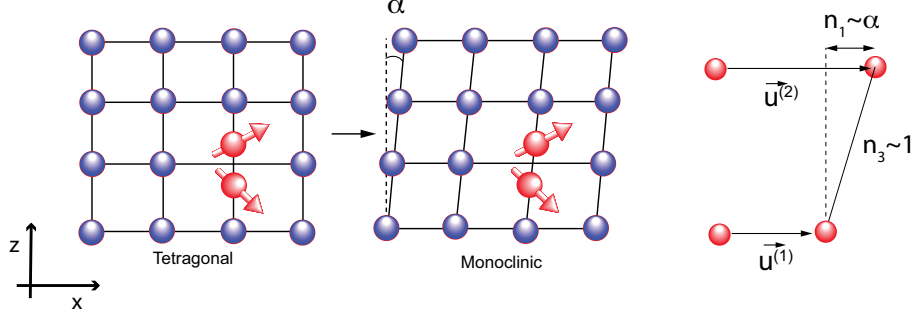
Figure 5: Two spins in a crystal undergoing distortion.

The distance between the electrons varies slightly as compared to at equilibrium, and the dipolar tensor $\underline{\underline{D}}(t)$ becomes

$$\underline{\underline{D}}(t) \approx \xi'(r) \begin{bmatrix} 1 & 0 & -3n_1(t) \\ 0 & 1 & -3n_2(t) \\ -3n_1(t) & -3n_2(t) & -2 \end{bmatrix} \tag{62}$$

where we used $n_3 \gg n_1, n_2$. We write α and β the infinitesimal displacements from equilibrium resulting from a distortion along the x and y directions. We thus have $n_3 \approx z/r = 1$ and $n_1 \approx \beta \ll 1$, $n_2 \approx \alpha \ll 1$. We thus get to a new effective hamiltonian.

Effective spin-lattice Hamiltonian :

$$\begin{aligned} \hat{H}_{sl}/\xi' &\approx \hat{S}_x^2 + \hat{S}_y^2 - 2\hat{S}_z^2 - 3n_1\{\hat{S}_x, \hat{S}_z\} - 3n_2\{\hat{S}_y, \hat{S}_z\} \\ &= S(S+1)\hat{Id} - 3\hat{S}_z^2 - 3n_1(t)\{\hat{S}_x, \hat{S}_z\} - 3n_2(t)\{\hat{S}_y, \hat{S}_z\} \end{aligned} \tag{63}$$

In the triplet state basis $\{-1, 0, +1\}$, one finds

$$\hat{S}_x\hat{S}_z + \hat{S}_z\hat{S}_x = \frac{1}{\sqrt{2}} \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & -1 \\ 0 & -1 & 0 \end{bmatrix}$$

$$\hat{S}_y\hat{S}_z + \hat{S}_z\hat{S}_y = \frac{1}{\sqrt{2}} \begin{bmatrix} 0 & -i & 0 \\ i & 0 & i \\ 0 & -i & 0 \end{bmatrix}$$

We see that the $m_s = \pm 1$ states are only coupled to the $m_s = 0$ state when the crystal is distorted. Assume that the system is prepared in one of the eigenstates $m_s = \pm 1$ and that the crystal modulates n_i. Two situations can occur : If a modulation of n_1 or n_2 is slow, then the system remains in this instantaneous eigenstate over time. If however the modulation of n_1 or n_2 is faster compared to the zero field splitting, it can lead to a spin flip. Let us assume that the system is prepared in the state $m_s = -1$ and estimate the time it takes to reach the ground state $m_s = 0$ under the action of the crystal modulation. We can then rewrite the spin-lattice coupling term $\hat{V}$ in the $m_s = \{0, -1\}$ subspace as

$$\hat{V}/C = \delta x(t)\hat{\sigma}_x + \delta y(t)\hat{\sigma}_y \tag{64}$$

where $C = \xi'(r)/r$. $\delta x(t)$ and $\delta y(t)$ are the result of the motion of both electrons. If they move in the same direction, this does not lead to a change in the dipolar energy so we can write δx in term of the difference between the electronic displacements $u_{x,y}^{(1,2)}$ of spins 1 and 2 from equilibrium, as

$$\delta x = u_x^1 - u_x^2 \approx u_x(z) - u_x(z + dz) = r \frac{\partial u_x}{\partial z}.$$

Here, we took the limit of a quasi-continuous medium with two very close electrons compared to the deformation $\epsilon_{xz} = \frac{\partial u_x}{\partial z}$ of the crystal.

Note : the deformation tensor $\underline{\epsilon}$ elements can also be associated to irreducible representations of the symmetry group. The matrix form must also obey Curie's principle.

Quantizing the strain field

In the same way as normal displacement fields are quantized, giving rise to phonon modes, one can also introduce the strain field operators $\hat{\epsilon}_{ij}$ which characterize atomic displacements from the equilibrium.

We know that in the continuous limit (but in a finite volume V), the displacement and the momentum read :

$$\boldsymbol{u}(\boldsymbol{r}) = \sum_{\boldsymbol{k},\lambda} \hat{Q}_{\boldsymbol{k}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \boldsymbol{\nu}_{\lambda,\boldsymbol{k}} \tag{65}$$

$$\boldsymbol{p}(\boldsymbol{r}) = \sum_{\boldsymbol{k},\lambda} \hat{P}_{\boldsymbol{k}} e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} \boldsymbol{\nu}_{\lambda,\boldsymbol{k}} \tag{66}$$

Imposing canonical commutation relations for $\hat{u}$ and $\hat{p}$, we obtain $[Q_{\boldsymbol{k}}, P_{\boldsymbol{k}'}] = i\hbar\delta_{k,k'}$.

Defining $a^\dagger = \sqrt{\frac{m\omega_q}{2\hbar}} Q_{-k} - i\sqrt{\frac{1}{2m\hbar\omega}} P_k$ we get $[a_k, a_{k'}^\dagger] = \delta_{kk'}$. and the hamiltonian of a quantized harmonics oscillator.

$$\boldsymbol{u}(\boldsymbol{r}) = \sum_{\boldsymbol{k},\lambda} \sqrt{\frac{\hbar}{2m\omega_k}} (\hat{a}_{\boldsymbol{k}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} + h.c.) \boldsymbol{\nu}_{\lambda,\boldsymbol{k}} \tag{67}$$

$$\tag{68}$$

we are interested in the deformation :

$$\hat{\epsilon}_{\alpha,\beta} = \frac{\partial \hat{u}_\alpha}{\partial x_\beta} \tag{69}$$

$$= \sum_{\boldsymbol{k},\lambda} \sqrt{\frac{\hbar}{2m\omega_k}} k_\beta \hat{a}_{\boldsymbol{k}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \nu_{\lambda,\boldsymbol{k}}^\alpha \tag{70}$$

To go further, we assume that all the considered phonons have a low energy and that $\omega \approx |k|v_\lambda$. We also assume an isotropic medium so that the speed of sound is the same for all three modes.

We then get

$$V = i \sum_{\boldsymbol{k},\lambda} \xi \sqrt{\frac{\hbar\omega}{2\rho v_s^2 V}} \hat{k} \cdot \boldsymbol{e}_z (\hat{a}_{\boldsymbol{k}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} - h.c.)(\nu_{\lambda,\boldsymbol{k}}^x \sigma_x + \nu_{\lambda,\boldsymbol{k}}^y \sigma_y) \tag{71}$$

so that

$$|\langle +, n_k - 1| \hat{V} |-, n_k\rangle|^2 = \frac{\hbar\omega\xi^2}{2\rho V v_s^2} (\hat{k} \cdot \boldsymbol{e}_z)^2 |\nu_{\lambda,\boldsymbol{k}}^x + i\nu_{\lambda,\boldsymbol{k}}^y|^2 n_k \tag{72}$$

7.3.2   First order process

$$\sum_{\boldsymbol{k},\lambda} \rightarrow \sum_{\lambda} V \int_0^{k_D} \frac{4\pi k^2 dk}{(2\pi)^3} \delta(\omega_0 - v_\lambda |\boldsymbol{k}|) \int \frac{d\Omega}{4\pi} \tag{73}$$

$$= \frac{3V\omega^2}{2\pi^2 v_s^3} \Theta(\omega_D - \omega) \int \frac{d\Omega}{4\pi} \tag{74}$$

where $3/v_s^3 = 1/v_L^3 + 2/v_t^3$.
We get

$$\Gamma_- \approx \frac{2\pi}{\hbar^2} \frac{3V\omega_0^2}{2\pi^2 v_s^3} \langle n_{\omega_0} \rangle \frac{\hbar}{2m\omega_0} C^2 (\frac{\omega_0}{v_s})^2 \tag{75}$$

$$= \frac{3\omega_0^3 C^2}{2\pi\hbar\rho v_s^5} \langle n_{\omega_0} \rangle \tag{76}$$

if $\omega_0 < \omega_D$
Differences with black body radiation :

- integration up to the Debye freq.

- three modes

- c versus v_s

7.3.3   Raman process

Raman processes correspond to the scenarios shown in the Figure.

There are then two grand kinds of Raman processes. We distinguish between two types of Raman process, which we call 'first order" and 'second order' according to the nature of the perturbation involved:

- A first-order Raman process arises when the crystal potential has matrix elements between the two states a and b of the magnetic ion. One can use the Fermi-golden rule in first order perturbation theory but the hamiltonian can show terms like

$$H = \sum_i E_i F_i$$

  where

$$E_i = \sum_k \lambda_k x_k + \sum_{kk'} \lambda_{k,k'} x_k x_{k'}$$

- a second-order Raman process in which one phonon causes a virtual transition from one of the ground states to an excited state c, followed by another virtual transition induced by the second phonon in which the magnetic ion returns from c to the other ground state. The reason why only Virtual transitions are involved is that the state c has an energy that lies outside the continuum of allowed phonon frequencies.

As before, each of these mechanisms gives transition rates that depend on the product $\epsilon_1\epsilon_2$ where the squares of the strains can be related to the energy densities at the phonon frequencies. Let us consider the Stokes process only assuming non-linear hamiltonian and first order Fermi-golden rule. We have

$$
\begin{aligned}
\Gamma_- &= \frac{2\pi}{\hbar^2} \sum_{\boldsymbol{k},\boldsymbol{k}'} |\langle +, n_k - 1, n_{k'} + 1|V|-, n_k, n_{k'}\rangle|^2 \delta(\omega_0 - (\omega_k - \omega_{k'})) \\
&= \frac{2\pi}{\hbar^2}\xi^2 \iint dk' dk \frac{4\pi k^2}{2\pi^3}\frac{4\pi k'^2}{2\pi^3} \sum_{\lambda,\lambda'} V^2 n_k(n_{k'} + 1) \\
&\times \quad k^2 k'^2 \frac{\hbar}{2\rho V\omega_k}\frac{\hbar}{2\rho V\omega_{k'}}\delta(\omega_0 - (\omega_k - \omega_{k'})) \tag{77}
\end{aligned}
$$

$$\tag{78}$$

We assume that $\omega_k, \omega'_k \gg \omega_0$. We then obtain

$$
\Gamma_- = \frac{2\pi}{\hbar^2}\xi^2 \frac{1}{(2\pi^2)^2}\frac{1}{4\rho^2 v_s^{10}} \int \omega^6 n_\omega(n_\omega + 1)d\omega \tag{79}
$$

Using the fact that

$$
n_\omega(n_\omega + 1) = \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}
$$

and

$$
I_n = \int_0^\infty \frac{x^n e^x}{(e^x - 1)^2} \approx \int_0^\infty x^n e^{-x} = n!
$$

we obtain

$$
\Gamma_- = \frac{\xi^2 6!}{4\pi^3 \rho^2 v_s^{10}}\left(\frac{kT}{\hbar}\right)^7
$$

The T^7 dependency indicates that this process may be more efficient than the single phonon one at room temperature.