Symmetry

University of Cambridge Part II Natural Sciences Tripos

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Preface

This course focuses on the foundational level of group theory and representation theory in the context of chemistry and molecular symmetry. If you want a more mathematical (and hence more abstract) treatment on basic groups and representations, you can look at my notes on Natural Sciences Tripos Part IB *Mathematical Methods*. This level of knowledge is essential (and should be enough) for a good grasp on theoretical chemistry. A slightly more advanced notes on groups (and rings and modules) can be found in Mathematical Tripos Part IB *Groups, Rings and Modules*, but they are largely irrelevant to chemistry.

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1 Symmetry

Definition 1.1. For a system with Hamiltonian $\hat{H}$, a *symmetry operator* is an operator $\hat{R}$ such that the inverse $\hat{R}^{-1}$ exists and commutes with the Hamiltonian

$$\hat{R}\hat{H} = \hat{H}\hat{R}\,. \tag{1.1}$$

The above condition can be trivially rewritten as

$$\hat{H} = \hat{R}\hat{H}\hat{R}^{-1} \quad \text{or} \quad \hat{H} = \hat{R}^{-1}\hat{H}\hat{R}\,. \tag{1.2}$$

Then if we have $|\psi\rangle$ an eigenstate of the Hamiltonian

$$\hat{H}\,|\psi\rangle = E\,|\psi\rangle\ , \tag{1.3}$$

$\hat{R}\,|\psi\rangle$ is also an eigenstate of $|\psi\rangle$ with the same eigenvalue.

$$\hat{H}\hat{R}\,|\psi\rangle = \hat{R}\hat{H}\,|\psi\rangle = \hat{R}E\,|\psi\rangle = E\hat{R}\,|\psi\rangle\ . \tag{1.4}$$

The resulting state $\hat{R}\,|\psi\rangle$ may be equivalent to $|\psi\rangle$, i.e. $\hat{R}\,|\psi\rangle = c\,|\psi\rangle$ for some $c \in \mathbb{C}$, but otherwise $|\psi\rangle$ and $\hat{R}\,|\psi\rangle$ are different states with the same eigenvalue. We see that symmetry leads to degeneracy.

We are going to make a postulate.

Postulate 1.2. If a set of eigenstates are degenerate, then the degeneracy must be a consequence of some symmetry.

This is to say that *accidental degeneracy* does not happen.

Example. For a Hydrogen atom, the three 2p states are degenerate. They are related by spatial rotations 90°. The 2s is also degenerate with the three 2p states. In this case there is no geometric symmetry operations that transforms e.g. $|2\text{s}\rangle$ to $|2p_z\rangle$, but there do exists symmetry operators that transforms $|2\text{s}\rangle$ to $|2p_z\rangle$ — it is only that we cannot find a corresponding geometric representation in our physical space.

1.1 Molecular Symmetry

We will consider molecular systems for which the Hamiltonian looks like

$$\hat{H} = -\sum_i \frac{\hbar^2}{2m_i}\nabla_i^2 + V(\{\mathbf{r}_i\}) \tag{1.5}$$

such that the potential term V only depends on the distances between the particles. Let's see what symmetry such systems can have.

We can divide symmetries in two types: *continuous symmetry* and *discrete symmetry*. Continuous symmetries are those that can be parameterised by continuous parameters (e.g. rotation is parameterised by the degree of rotation, which is a continuous parameter), and discrete symmetries are parameterised by a discrete parameters. We will see a number of examples of them.

1.1.1 Continuous Symmetry

There is a deep and beautiful theorem related to continuous symmetry that we are unable to prove right here.[1]

Theorem 1.3 (Noether's theorem). Every continuous symmetry a physical system has a corresponding conservation law.

This is the best explained with some examples. In this course, we are mainly concerned with two continuous symmetry operations.

(i) *Translation.* Translational symmetry leads to conservation of momentum.

Let's consider a system described by a wavefunction $\psi(\mathbf{x}_i, \mathbf{x}_j, \dots)$ and move all particles by the same amount $\mathbf{a}$. Suppose this action can be represented by an operator $\hat{\mathbf{A}}$, then its is easy to see that the wavefunction after translation $\psi'(\mathbf{x}_i, \mathbf{x}_j, \dots)$ is given by

$$\psi'(\mathbf{x}_i, \mathbf{x}_j, \dots) = \hat{\mathbf{A}}\psi(\mathbf{x}_i, \mathbf{x}_j, \dots) = \psi(\mathbf{x}_i - \mathbf{a}, \mathbf{x}_j - \mathbf{a}, \dots)\,. \tag{1.6}$$

Since the distances between the particles are unchanged after translation of all particles, the potential energy is also unchanged by our assumption. Mathematically, $V(\mathbf{x}_i, \mathbf{x}_j, \dots) = V(\mathbf{x}'_i, \mathbf{x}'_j, \dots)$, where we have defined $\mathbf{x}'_k = \mathbf{x}_k - \mathbf{a}$, so

$$\begin{aligned}
\hat{\mathbf{A}}^{-1} V(\mathbf{x}_i, \dots)\hat{\mathbf{A}}\psi(\mathbf{x}_i, \dots) &= \hat{\mathbf{A}}^{-1} V(\mathbf{x}_i, \dots)\psi(\mathbf{x}_i - \mathbf{a}, \dots) \\
&= \hat{\mathbf{A}}^{-1} V(\mathbf{x}_i - \mathbf{a}, \dots)\psi(\mathbf{x}_i - \mathbf{a}, \dots) \\
&= \hat{\mathbf{A}}^{-1} (V\psi)(\mathbf{x}'_i, \dots) \\
&= V\psi(\mathbf{x})\,,
\end{aligned} \tag{1.7}$$

i.e. the potential energy operator V commutes with the translation operator $\hat{\mathbf{A}}$. Moreover, from chain rule, we have

$$\begin{aligned}
\nabla_i^2 \psi'(\mathbf{x}_i, \mathbf{x}_j, \dots) &= \frac{\partial^2 \psi'(\mathbf{x}_i, \mathbf{x}_j, \dots)}{\partial x_i^2} + \frac{\partial^2 \psi'(\mathbf{x}_i, \mathbf{x}_j, \dots)}{\partial y_i^2} + \frac{\partial^2 \psi'(\mathbf{x}_i, \mathbf{x}_j, \dots)}{\partial z_i^2} \\
&= \frac{\partial^2 \psi'(\mathbf{x}_i, \mathbf{x}_j, \dots)}{\partial (x_i - a_x)^2} + \frac{\partial^2 \psi'(\mathbf{x}_i, \mathbf{x}_j, \dots)}{\partial (y_i - a_y)^2} + \frac{\partial^2 \psi'(\mathbf{x}_i, \mathbf{x}_j, \dots)}{\partial (z_i - a_z)^2} \\
&= \frac{\partial^2 \psi(\mathbf{x}'_i, \mathbf{x}'_j, \dots)}{\partial x_i'^2} + \frac{\partial^2 \psi(\mathbf{x}'_i, \mathbf{x}'_j, \dots)}{\partial y_i'^2} + \frac{\partial^2 \psi(\mathbf{x}'_i, \mathbf{x}'_j, \dots)}{\partial z_i'^2} \\
&= \nabla_i^2 \psi(\mathbf{x}'_i, \mathbf{x}'_j, \dots)\,,
\end{aligned} \tag{1.8}$$

where $\mathbf{x}'_i = \mathbf{x}_i - \mathbf{a}$. By the same argument as above, we can see that the kinetic energy operator (the Laplacian) also commutes with $\hat{\mathbf{A}}$, and hence the whole Hamiltonian commutes with the translation operator $\hat{\mathbf{A}}$ — it is indeed a symmetry operator as we claimed.

[1] A baby version of this Noether's theorem related to the first integral the Euler–Lagrange equation can be seen in the notes on NST Part IB Mathematical Methods, on the chapter of variational principles.

Moving a particle to a new position does not change its energy, so the force that needs to be exerted on the molecule,

$$\mathbf{F} = \frac{\mathrm{d}E}{\mathrm{d}\mathbf{x}}\,, \tag{1.9}$$

is zero. There is no change in momentum.

(ii) *Rotation.* Rotational symmetry leads to conservation of angular momentum.

The proof of rotation operator being a symmetric operator is essentially the same as for the translation operator. Rotation also preserves the distances between the particles so the potential energy does not change. Rotation also commutes with the Laplacian — this is the most easily seen if we identify the rotational axis as the z axis, so that a rotation by degree α results in a transformed wavefunction $\psi'(r,\theta,\varphi) = \psi(r,\theta,\varphi-\alpha)$ in spherical polar coordinates. Therefore, rotating a molecule does not change its energy. Consequently, no torque is needed to perform such operation, and the angular momentum is conserved.

If fact, we will see later that the rotation and angular momentum has a deep connection. For example, if we consider the change in the wavefunction when we act an infinitesimal rotation about the z axis

$$\lim_{\delta\varphi\to 0}\frac{\hat{R}_z(\delta\varphi)-\hat{E}}{\delta\varphi}\psi = \frac{\partial}{\partial\varphi}\psi \propto \hat{J}_z\psi\,.$$

We say angular momentum *generates* spatial rotation.

1.1.2 Discrete Symmetries

We will consider three discrete symmetries of a molecular system.

(i) *Permutation of electrons.*

Since all electrons are equivalent, the Hamiltonian has a kinetic and potential energy terms of the same form for each electron. Therefore, permuting the electrons has no effect on the Hamiltonian, and any permutation is a symmetry operation.

Although permuting electrons does not change the energy, it has some subtle yet important effect to the wavefunction itself. The Pauli principle requires the wavefunction to be antisymmetric with respect to the exchange of identical Fermions, and symmetric with respect to the exchange of identical Bosons. Electrons are Fermions, so

$$\hat{P}_{ij}\psi(\mathbf{x}_i,\mathbf{x}_j,\dots) = \psi(\mathbf{x}_j,\mathbf{x}_i,\dots) = -\psi(\mathbf{x}_i,\mathbf{x}_j,\dots)\,. \tag{1.10}$$

(ii) *Permutation of identical nuclei.*

Just as for electrons, the Hamiltonian is unchanged if we permute the labels of a set of identical nuclei. But as an important aside, the Pauli principle still applies. Nuclei with even masses are Bosons, and those of odd masses are Fermions.

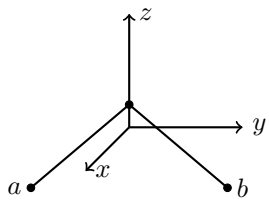
(iii) *Parity inversion.*

Parity operator inverts the coordinates of the particles though the origin. Again, this leaves particle-particle distances and the kinetic Laplacian terms unchanged, so it commutes with the Hamiltonian. The parity operator is denoted $\hat{E}^*$. Note that this is different to the inversion operator $\hat{\imath}$, which only exists for molecules with a centre of symmetry.

1.2 Internal Frame of Reference

We will investigate what operations like inversion and nuclear permutation do on the geometries of our molecules. We are mainly interested on the internal degrees of freedom of the molecules, including electronic and vibrational degrees of freedom of the molecules. To do this, apart from the *global frame* of the system, (X, Y, Z), which measures the location of some point relative to an origin in the space, it is often convenient to construct a *local frame* within the molecule, denoted (x, y, z).

For example, let's consider a water molecule. The origin is chosen to be the centre of mass of the molecule. It is conventional to define the z axis to be along the principal axis (the axis of the highest rotational symmetry), so in our case, we let the z axis to bisect the $\mathrm{H}-\mathrm{O}-\mathrm{H}$ reflex angle. We further define y axis to be in the molecular plane, perpendicular to the z axis and pointing from proton a to proton b, and we let the x axis to be the one completing the right-handed coordinate system. You can check that this well defines a unique internal coordinate system in our H_2O molecule.



Let's associate some orbitals and vectors to track what everything is going on. Consider a nuclear permutation operator (ab) that permutes the labels of the hydrogen nuclei a and b only, leaving everything else unchanged. The action of this operator is shown in figure 1.1. Notice that since the internal frame is defined using the nuclear labels, when we permute the labels, the internal frame also changes its orientation. We can switch our perspective to reorient our system — then we see that the effect of (ab) operation on internal coordinates is the same as that of C_z^2, a two-fold rotation along the z axis that rotates the functions and coordinates only but not the nuclear labels.

Similarly, the action of the parity inversion operator E^* is the same as acting a σ_v^{yz} to the associated objects (vectors, functions etc.), as shown in figure 1.2, and the action of $(ab)E^*$ is the same as σ_v^{xz} to the associated objects as shown in figure 1.3.

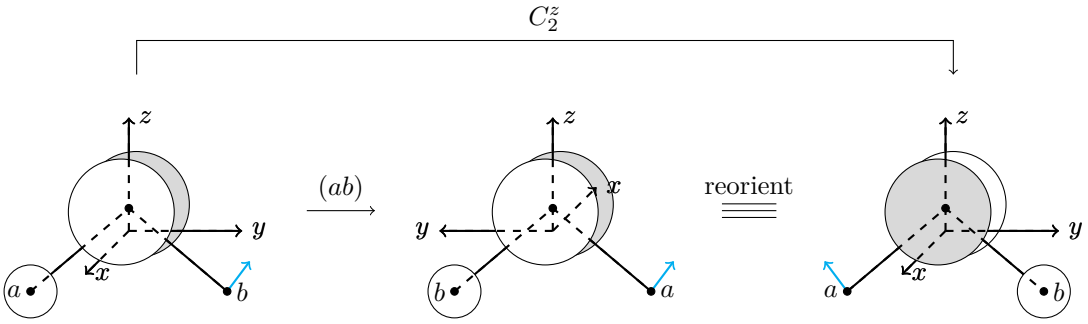


Figure 1.1: The action of a nuclear permutation operator (ab) on H_2O is equivalent to C_2^z on associated objects.

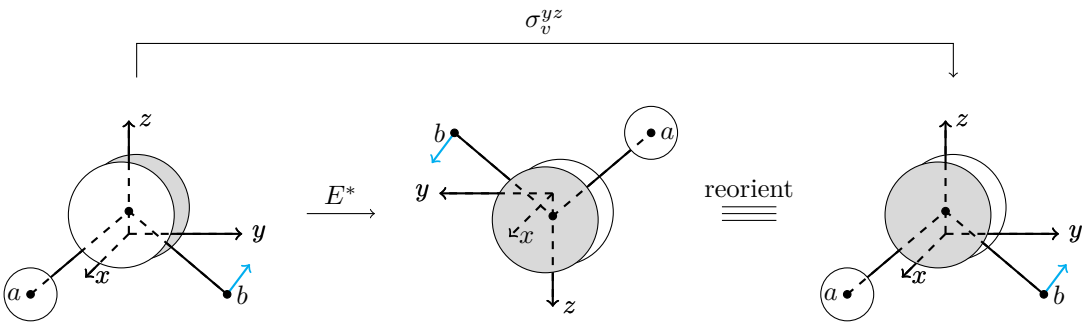


Figure 1.2: The action of a parity inversion operator E^* on H_2O is equivalent to σ_v^{yz} on associated objects.

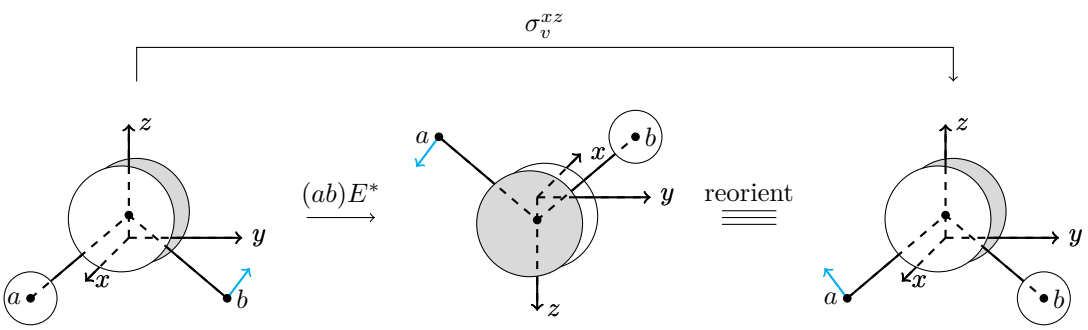


Figure 1.3: The action of a parity inversion operator $(ab)E^*$ on H_2O is equivalent to σ_v^{xz} on associated objects.

1.2.1 Allowed Rotational States of Molecules

We can expand the total wavefunction of a molecule into a product of electronic, vibrational, rotational, translational and nuclear spin factors

$$\Psi = \psi_{\text{elec}}\psi_{\text{vib}}\psi_{\text{rot}}\psi_{\text{trans}}\psi_{\text{ns}}\,. \tag{1.11}$$

However, recall that Pauli principle requires the wavefunction to be symmetric with respect to the exchange of identical Bosons (integer-spin nuclei) and antisymmetric with respect to the exchange of identical Fermions (electrons and half-integer-spin nuclei). This means that we cannot combine any components of the wavefunction

with each other — we must maintain the overall symmetry/antisymmetry.

Ortho and Para Hydrogen

Let's consider a ground electronic and vibrational state H_2 molecule with the two nuclei labelled by a and b. What happens if we perform the symmetry operator (ab) which exchanges the proton labels?

The ground state electronic state of H_2 is ${}^1\Sigma_g^+$, i.e. totally symmetric, so it is unchanged by (ab). The vibrational wavefunction only depends on the bond length $|\mathbf{r}_a - \mathbf{r}_b|$, which is unchanged by the exchange of the labels a and b. The translational wavefunction only depends on the overall (centre of mass) position of the molecule. It is also unchanged by (ab).

However, ψ_{rot} is a spherical harmonic $Y_{JM}(\theta, \varphi)$, where θ and φ are defined with respect to the z (principal) axis. This axis is reversed when a and b are interchanged (e.g. if we define z axis to be from a to b, then if we exchange a and b, the axis is naturally reversed), and the rotational wavefunction changes sign if J is odd, and is unchanged if J is even.[2]

Finally, the spin of hydrogen is $I = 1/2$, so the nuclear spin function of H_2 is either a singlet

$$\psi_{\text{singlet}} = \sqrt{\frac{1}{2}}(\alpha_a\beta_b - \beta_a\alpha_b) \tag{1.15}$$

that is antisymmetric with respect to (ab), or one of the triplet functions

$$\psi_{\text{triplet}} = \begin{cases} \alpha_a\alpha_b \\ \sqrt{\frac{1}{2}}(\alpha_a\beta_b + \beta_a\alpha_b) \\ \beta_a\beta_b \end{cases} \tag{1.16}$$

that are symmetric with respect to (ab). Because the nuclear spins interacts only very weakly with the environment, the spin states does not change easily. We can speak of *ortho hydrogen* for the ones with triplet nuclear spin, and *para hydrogen* for those with singlet nuclear spin.

[2]The easiest way to confirm this without using mathematics is to check the angular parts of the atomic orbitals. $J = 0$ is the s orbitals, $J = 1$ is the p orbitals and $J = 2$ is the d orbitals etc. If you are not convinced by this, you can check that the spherical harmonics have the general expression

$$Y_{\ell m} = \sqrt{\frac{2\ell+1}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}}P_\ell^{|m|}(\cos\theta)e^{im\varphi}\,, \tag{1.12}$$

where P_ℓ^m is the associated Legendre polynomial, defined by

$$P_\ell^{|m|}(x) = (-1)^{|m|}(1-x^2)^{|m|/2}\frac{\mathrm{d}^{|m|}}{\mathrm{d}x^{|m|}}(P_\ell(x))\,, \tag{1.13}$$

$$P_\ell(x) = \frac{1}{2^\ell \ell!}\frac{\mathrm{d}^\ell}{\mathrm{d}x^\ell}(x^2-1)^\ell \tag{1.14}$$

When the nuclei are interchanged, θ becomes $\pi - \theta$ and φ is changed to $-\varphi$ (check this). One can straightforwardly confirm that $P_\ell(-x) = (-1)^\ell P_\ell(x)$, $P_\ell^{|m|}(-x) = (-1)^{\ell-|m|}P_\ell^{|m|}(x)$. Hydrogen can only rotate in an axis perpendicular to the z axis, so $m = 0$, and so we get the claimed result $Y_{\ell,m}(\pi-\theta, -\varphi) = (-1)^\ell Y_{\ell,m}(\theta,\varphi)$.

Therefore, to maintain the overall antisymmetry of the total wavefunction when we perform the permutation of the two Fermion nuclei a and b, the ortho hydrogen with symmetric spins must combine with odd J rotational states, while the para hydrogen with antisymmetric spins must have even rotational states. This can be confirmed in Raman spectrum. Since there are three times as much ortho hydrogen as para at equilibrium at high temperatures due to nuclear spin degeneracy, the rotational Raman spectra of H_2 shows alternating intensities of $3:1$ between odd and even J.

Carbon Dioxide

In CO_2, O has $I = 0$, so the nuclear spin function is trivially $\psi_{\text{ns}} = 1$. The wavefunction is symmetric with respect to the exchanged of the labels of the two Bosonic oxygens, so only even J rotational functions are allowed — odd-J peaks are absent in the rotational and vibration-rotational Raman spectra of CO_2.

Oxygen

The oxygen molecule has a more interesting ground electronic state of ${}^3\Sigma_g^-$. The minus sign means that the electronic wavefunction has a dependence $\sin(\varphi_1 - \varphi_2)$ on the coordinates of the two unpaired electrons in O_2. When we exchange a and b, we inverted the direction of the z axis, and to maintain the right-handedness, the φ must also be inverted. Hence, the electronic wavefunction changes its sign under (ab). The nuclear wavefunction is symmetric under (ab). As a result, to obey Pauli principle, the rotational wavefunction of O_2 must have odd J.

2 Groups

Definition 2.1. A *group* is a triple $(G, \cdot, E)$ of a set G, a binary operation $\cdot : G \times G \to G$ often known as the *group product*, and an element $E \in G$ such that the following axioms are satisfied:[3]

1. *Associativity*: $(R \cdot S) \cdot T = R \cdot (S \cdot T)\ \forall R, S, T \in G$. This allows us to write both as $R \cdot S \cdot T$ directly without ambiguity.
2. *Identity*: There is an element $E \in G$ such that $R \cdot E = E \cdot R = R$ for all $R \in G$.
3. *Inverse*: For every $R \in G$, there is an $R^{-1} \in G$ such that $R \cdot R^{-1} = R^{-1} \cdot R = E$.

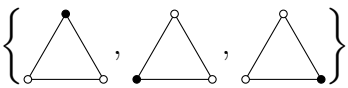
Groups naturally arise when studying symmetries, because the symmetry operations of a certain system naturally form a group. If you perform a symmetry operation, then perform another, then the combined action is another symmetry operation. This defines the group product. Doing nothing is a symmetry operation — this is the identity. Whatever symmetry operation you perform, you can always undo it. This reverse operation is the inverse.

To better investigate the symmetry of objects using group theory. We need to let the group elements (the symmetry operations) to act on some object (the object that we wish to describe the symmetry of). This leads to the definition of a group action.

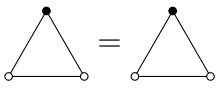
Definition 2.2. Let $(G, \cdot, E)$ be a group and X be a set. A *group action* $*$ of G on X is a map $* : G \times X \to X$ that satisfies the following axioms

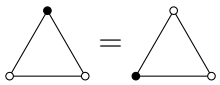
1. *Identity.* $E * x = x\ \forall x \in X$.
2. *Compatibility.* $R * (S * x) = (R \cdot S) * x\ \forall R, S \in G, x \in X$.

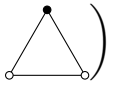
Example. Consider the rotational symmetry of a triangle. The group of the symmetry operations is $G = \{E, C_3, C_3^2\}$, and the set that group G is acting on is

$X =$  . (2.1)

Then we have, for example,

$E *$  . (2.2)

$C_3 *$  . (2.3)

$C_3 * \Big(C_3 *$  $\Big) = C_3 *$ $=$ (2.4)

$= C_3^2 *$ $=$ (2.5)

In the last equation, the first line computed the two actions separately, while in the second line we take the group product first. This shows the compatibility axiom.

[3]Some author may include *closure* as one of the group axioms — this is stupid. Closure is naturally guaranteed by the definition of a binary operation.

From now on, we use the notation $*$ for group action exclusively to avoid confusion. We will also some times omit $\cdot$ or $*$ when what we are doing is clear from the context. However, note that $RS\psi$ means $R * (S * \psi)$. We act S on ψ first, and then act R on the result of $S * \psi$.

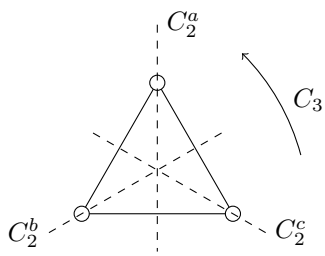
Definition 2.3. A group G is *finite* if G consists of a finite number of elements. The *order* of a finite group is the number of elements in it.

Definition 2.4. A group G is *Abelian* if $\forall R, S \in G$, $RS = SR$, i.e. the group product is commutative.

If a group is finite, then we can clearly list all possible results of the product of any two elements. If we construct a table by putting the first argument of the group product in rows, and the second argument of a group product in columns, then we obtain a *multiplication table.*

Example. The multiplication table of D_3.

We define the symmetry operations on a dihedral triangle as shown in the diagram below.



Then the symmetries form a D_3 group, whose group table can be obtained as following.

	E	C_3	C_3^2	C_2^a	C_2^b	C_2^c
E	E	C_3	C_3^2	C_2^a	C_2^b	C_2^c
C_3	C_3	C_3^2	E	C_2^c	C_2^a	C_2^b
C_3^2	C_3^2	E	C_3	C_2^b	C_2^c	C_2^a
C_2^a	C_2^a	C_2^b	C_2^c	E	C_3	C_3^2
C_2^b	C_2^b	C_2^c	C_2^a	C_3^2	E	C_3
C_2^c	C_2^c	C_2^a	C_2^b	C_3	C_3^2	E

For example, the entry marked in blue means that

$$C_3 C_2^a = C_2^c \,, \tag{2.6}$$

i.e. if you flip the triangle along the axis a, then rotate 120° along the principal axis anticlockwise, then the overall effect is equivalent to flipping the triangle along the axis c. However, if you do the to operation in a reverse order, then what you get is the entry marked in red

$$C_2^a C_3 = C_2^b \,. \tag{2.7}$$

This clearly shows that the D_3 group is not Abelian — the order of operations matters.

Definition 2.5. A group is said to be *generated* by a subset of its elements if all the group elements can be produced by performing group products within this subset of elements.

Example. The cyclic group C_n.

Consider the rotational symmetry on a regular n-gon. The cyclic group of order n, denoted C_n, contains all the rotational symmetry operations, i.e. rotations by $360°k/n$ for $k = 1, \ldots n$. We denote the rotation of $360°/n$ as R, then we see that the group C_n is generated by R, since all the group elements can be written as R^k, and in particular, the identity element $E = R^n$.

A lot of groups are generated by more than one elements. For example, you can check that D_3 is generated by $\{C_3, C_2^a\}$.

Definition 2.6. If $(G, \cdot, E)$ is a group, then $(H, \cdot, E)$ is a *subgroup* of G, denoted $H \leq G$, if H is a non-empty subset of G, and H is a group on its own under the same group product $\cdot$.

Example. $C_3 \leq D_3$. This can be seen from the group multiplication table.

	E	C_3	C_3^2	C_2^a	C_2^b	C_2^c
E	E	C_3	C_3^2	C_2^a	C_2^b	C_2^c
C_3	C_3	C_3^2	E	C_2^c	C_2^a	C_2^b
C_3^2	C_3^2	E	C_3	C_2^b	C_2^c	C_2^a
C_2^a	C_2^a	C_2^b	C_2^c	E	C_3	C_3^2
C_2^b	C_2^b	C_2^c	C_2^a	C_3^2	E	C_3
C_2^c	C_2^c	C_2^a	C_2^b	C_3	C_3^2	E

Definition 2.7. Let $(G, \cdot, E)$ and $(H, *, I)$ be groups. Then the *direct product group* P, denoted $P = G \times H$, is a group whose elements are $P = \{(g, h) \mid g \in G, h \in H\}$, and the group product $\circ$ is defined by

$$(g_1, h_1) \circ (g_2, h_2) = (g_1 \cdot g_2, h_1 * h_2)\,. \tag{2.8}$$

We can prove some properties of the direct product group.

Proposition 2.8. Let $(G, \cdot, E)$ be a group of order n_G and $(H, *, I)$ be a group of order n_H. Let $P = G \times H$. Consider the following subsets of P:

$$G' = \{(g, I) \mid g \in G\} \quad \text{and} \quad H' = \{(E, h) \mid h \in H\}\,. \tag{2.9}$$

We have

(i) The order of P is $n_G n_H$.

(ii) G', H' are subgroups of P.

(iii) G' is the same group as G, and H' is the same group as H.

(iv) $G' \cap H' = (E, I)$.

(v) Every element of P can be expressed as the product of an element in G' and an element in H'.

(vi) Every element in G' commutes with every element in H'.

Proof.

(i) By definition, $P = \{(g, h) \mid g \in G, h \in H\}$. There are n_G elements in G and n_H elements in H, so we can construct $n_G n_H$ distinct pairs.

(ii) G', H' are clearly subsets of P. G' is closed because $(g_1, I) \circ (g_2, I) = (g_1 \cdot g_2, I)$, which is by definition in P because $g_1 \cdot g_2 \in G$. The inverse of $(g_1, I) \in G$ is $(g_1^{-1}, I) \in G$. G' is indeed a group, so it is a subgroup. The same for H'.

(iii) There is a one-to-one correspondence between elements in G and the elements in G'. If we identify $(g, I) \in G'$ as $g \in G$, then clearly G' and G are the same. Mathematically, we say G and G' are *isomorphic*, meaning that they are essentially the same group. Same for H'.

(iv) $(g, h) = (g, I) \circ (E, h)$.

(v) $(g, I) \circ (E, h) = (g, h) = (E, h) \circ (g, I)$. □

We can see that the direct product is the simplest possible way to build up large groups from smaller groups. But more importantly, some times we may find that some larger groups are in fact the direct product of some smaller groups. In that case, we may treat the symmetry of its component groups individually.

Moreover, we can see that the conditions (iv), (v) and (vi) above uniquely determine the algebraic structure of the direct product P. That is, if P is any group, and we have found two subgroups G and H that satisfy the properties above, then P is necessarily the direct product of G and H. In this situation, P is sometimes referred to as the *internal direct product* of its subgroups G and H.

Example. $D_{3h} = D_3 \times C_s$, via

	E	C_3	C_3^2	C_2^a	C_2^b	C_2^c
E	E	C_3	C_3^2	C_2^a	C_2^b	C_2^c
σ_h	σ_h	S_3	S_3^2	σ_v^a	σ_v^b	σ_v^c

Definition 2.9. Two elements $R, S \in G$ are *equivalent*, denoted $R \sim S$, if there exists $Q \in G$ such that

$$S = QRQ^{-1}\,. \tag{2.10}$$

The operator QRQ^{-1} can be thought of the operator obtained by applying Q to the operator R itself. For example, in D_3 group,

$$C_3 C_2^a C_3^{-1} = C_2^b\,. \tag{2.11}$$

The rotational axis of C_2^b that of C_2^a, rotated by C_3.

However, not all operations "of the same type" are equivalent. For example, in C_{2v}, there is no symmetry operation that transforms the σ_v^{xz} plane to the σ_v^{yz} plane.

Proposition 2.10. Let G be a group.

(i) *Reflexive.* $S \sim S$.

(ii) *Symmetry.* If $S \sim R$, then $R \sim S$.

(iii) *Transitivity.* If $S \sim R$ and $R \sim T$, then $S \sim T$.

Proof.

(i) $S = ESE^{-1}$.

(ii) If $S = QRQ^{-1}$, then $R = Q^{-1}SQ$.

(iii) If $R = PSP^{-1}$ and $S = QTQ^{-1}$, then $R = (PQ)T(PQ)^{-1}$. $\square$

This allows us to partition the group elements into *equivalent classes*, so that all elements in each class are equivalent to each other, and to no other element of the group.

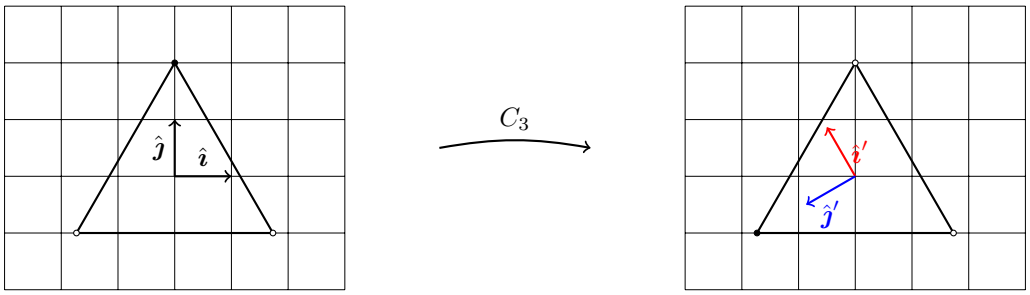
Note that in any group, the identity always forms a group by itself, because for any Q, $QEQ^{-1} = E$. Note also that in Abelian group, every element forms a class by itself, since for any Q, R, $QRQ^{-1} = QQ^{-1}R = R$.

3 Representations

3.1 Matrix Representations

When we think of a group, we think of it as a collection of symmetry operations that we can act on a physical object. But naturally, the operations we can do to an object, such as rotations and inversions, can also be described by linear transformations if we consider the object to be embedded in a vector space.

Let's consider the rotational symmetries of a triangle, which forms the C_3 group. To consider the action of the C_3 group operations on the square, we put it into a two dimensional vector space, with the centre of mass at the origin and the one of the unit vector parallel to one of the sides.



Then to act a C_3 operation to the triangle, we can rotate the underlying vector space by 120°. This operation sends the unit vector $\hat{\boldsymbol{\imath}}$ to $\hat{\boldsymbol{\imath}}' = -\frac{1}{2}\hat{\boldsymbol{\imath}} + \frac{\sqrt{3}}{2}\hat{\boldsymbol{\jmath}}$, and sends $\hat{\boldsymbol{\jmath}}$ to $\hat{\boldsymbol{\jmath}}' = -\frac{\sqrt{3}}{2}\hat{\boldsymbol{\imath}} - \frac{1}{2}\hat{\boldsymbol{\jmath}}$. Mathematically, this means that we can describe this by a transformation matrix

$$\mathsf{D}(C_3) = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \tag{3.1}$$

since this operation transform the basis by

$$\begin{pmatrix} \hat{\boldsymbol{\imath}}' & \hat{\boldsymbol{\jmath}}' \end{pmatrix} = \begin{pmatrix} \hat{\boldsymbol{\imath}} & \hat{\boldsymbol{\jmath}} \end{pmatrix} \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} . \tag{3.2}$$

Then for any vector

$$\mathbf{v} = v_x\hat{\boldsymbol{\imath}} + v_y\hat{\boldsymbol{\jmath}} = \begin{pmatrix} \hat{\boldsymbol{\imath}} & \hat{\boldsymbol{\jmath}} \end{pmatrix} \begin{pmatrix} v_x \\ v_y \end{pmatrix} , \tag{3.3}$$

we have

$$\begin{aligned} C_3 * \mathbf{v} &= C_3 * \begin{pmatrix} \hat{\boldsymbol{\imath}} & \hat{\boldsymbol{\jmath}} \end{pmatrix} \begin{pmatrix} v_x \\ v_y \end{pmatrix} \\ &= \begin{pmatrix} \hat{\boldsymbol{\imath}} & \hat{\boldsymbol{\jmath}} \end{pmatrix} \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} v_x \\ v_y \end{pmatrix} . \end{aligned} \tag{3.4}$$

Similarly, to act the operation C_3^2 to the triangle, one can rotate the underlying

vector space by 240°. This corresponds to a basis transformation matrix

$$\mathsf{D}(C_3^2) = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}, \tag{3.5}$$

since the transformed basis is

$$\begin{pmatrix} \hat{\boldsymbol{\imath}}'' & \hat{\boldsymbol{\jmath}}'' \end{pmatrix} = \begin{pmatrix} \hat{\boldsymbol{\imath}} & \hat{\boldsymbol{\jmath}} \end{pmatrix} \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}. \tag{3.6}$$

Moreover, the identity operation does nothing to the vector space, and so it corresponds to the identity matrix

$$\mathsf{D}(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \tag{3.7}$$

We have obtained a set of matrices, each corresponds to an operation in the group C_3. A natural consequence is that doing two group operations to the triangle is equivalent to doing two corresponding actions on the underlying vector space. For example, since $C_3 \cdot C_3^2 = E$, transforming the underlying vector space by 240°, then 120° is equivalent to doing nothing, so we naturally have the corresponding relationship for the transformation matrices

$$\mathsf{D}(C_3)\mathsf{D}(C_3^2) = \mathsf{D}(E). \tag{3.8}$$

What we have done above is to use a set of matrices to *represent* the elements in the C_3 group, such that the for any relationship of group elements under group product $R \cdot S = T$, we have the corresponding relationship for the representation matrices under matrix multiplication

$$\mathsf{D}(R)\mathsf{D}(S) = \mathsf{D}(T). \tag{3.9}$$

This is because for any vector $\mathbf{v} = v_x\hat{\boldsymbol{\imath}} + v_y\hat{\boldsymbol{\jmath}}$, we have

$$R * (S * \mathbf{v}) = R * \begin{pmatrix} \hat{\boldsymbol{\imath}} & \hat{\boldsymbol{\jmath}} \end{pmatrix} \mathsf{D}(S) \begin{pmatrix} v_x \\ v_y \end{pmatrix} \tag{3.10}$$

$$= \begin{pmatrix} \hat{\boldsymbol{\imath}} & \hat{\boldsymbol{\jmath}} \end{pmatrix} \mathsf{D}(R)\mathsf{D}(S) \begin{pmatrix} v_x \\ v_y \end{pmatrix}, \tag{3.11}$$

while by the compatibility of group actions, we also have

$$R * (S * \mathbf{v}) = (R \cdot S) * \mathbf{v} = \begin{pmatrix} \hat{\boldsymbol{\imath}} & \hat{\boldsymbol{\jmath}} \end{pmatrix} \mathsf{D}(R \cdot S) \begin{pmatrix} v_x \\ v_y \end{pmatrix}. \tag{3.12}$$

Mathematically, what we are constructing here is called a *homomorphism*.

Definition 3.1. Let $(G, \cdot, E)$ and $(H, \circ, I)$ be groups. A function $\phi : G \to H$ is a *homomorphism* if for all $R, S \in G$,

$$\phi(R) \circ \phi(S) = \phi(R \cdot S). \tag{3.13}$$

You can check that the set of all $n \times n$ invertible matrices with real entries form a group under matrix multiplication, which is often called the *general linear group*, denoted

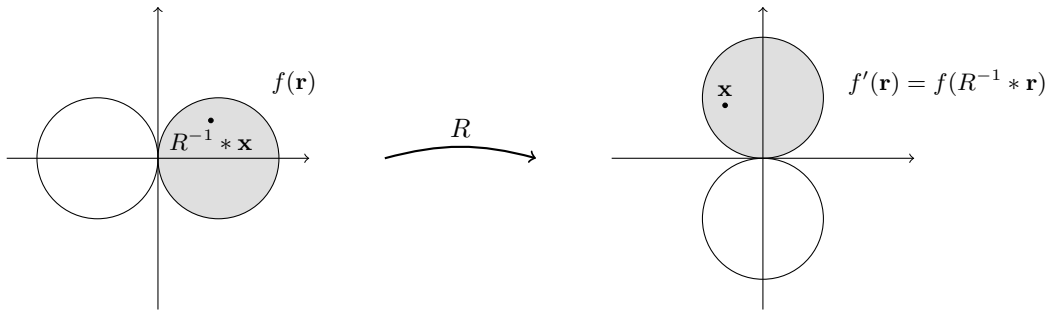


Figure 3.1: Acting a group element on a function.

$\mathrm{GL}(n, \mathrm{R})$ (or $\mathrm{GL}(n, \mathbb{C})$ if the entries are complex). Therefore, what we have done in the above example is to construct a homomorphism from the group C_3 to $GL(2, \mathbb{R})$, i.e. a map from the elements in C_3 to 2×2 invertible matrices that preserves the group product. In mathematics, this is called a *representation*.

Definition 3.2. A *representation* of a group G a homomorphism from G to a general linear group. The *dimension* of a representation is the dimension of the representation matrix. A representation is *unitary* if the representation matrices are unitary matrices.

Conventionally, we denote a representation by Γ, and denote the representation matrix of a element R by $\mathsf{D}(R)$. It can be shown that all representations of a finite group are unitary, and all representations in this course (even for the infinite groups) are unitary.

Given this generalised definition of representations, we find that the representation of a group is not unique. For example, for any group, we can always construct the *trivial* or *symmetric* by mapping all the elements to the one dimensional matrix (1), so that

$$\mathsf{D}(R)\mathsf{D}(S) = (1)(1) = (1) = \mathsf{D}(RS) \tag{3.14}$$

for all R, S in the group. For representations like this that maps different group elements to the same matrix, we say the representation is *unfaithful*; if the representation matrix of all group elements are different, then the representation is *faithful*.

To construct a different representation of a group, we can choose a different basis. We can choose any basis we want as long as we ensure that the group action of any group element on any basis falls in the span of the basis. You will find that a convenient and useful basis set is a set of functions. From our previous discussion, we know how group elements can act on vectors in a vector space. We need to consider what it means by acting a group element on a function.

3.1.1 Functions as a Basis

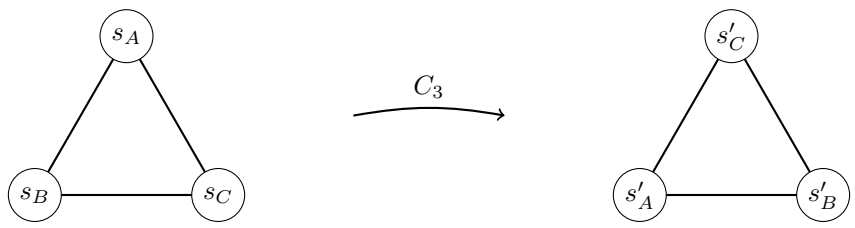
When talking about a function, what we do is to associate a value to each point in the space. When we act the group element to the function, what we do is the change the associated value to a different place. For example, if the value of a function f is $f(\mathbf{r})$ at some position $\mathbf{r}$. Then if we act a group element R on the function, the value $f(\mathbf{r})$

will now be associated to a new position $R * \mathbf{r}$. Therefore, if we call the function after the group action $f'(\mathbf{r}) \coloneqq R * f(\mathbf{r})$, then we have $f'(R * \mathbf{r}) = f(\mathbf{r})$. We can rewrite this as

$$R * f(\mathbf{r}) = f'(\mathbf{r}) = f(R^{-1} * \mathbf{r}) \,. \tag{3.15}$$

For example, to construct another representation of the C_3 group, we can attach one s orbitals to each of the vertex of a equilateral triangle. Then under the symmetry operations of the triangle, the three s orbitals transform to each other, so we can use the three s orbitals as a basis

$$\begin{pmatrix} s_A & s_B & s_C \end{pmatrix} \,. \tag{3.16}$$



Then, for example, since we have

$$C_3 * s_A = s_B \,,\; C_3 * s_B = s_C \,,\; C_3 * s_C = s_A \,, \tag{3.17}$$

the representation of C_3 in this basis will be

$$\mathsf{D}(C_3) = \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \,. \tag{3.18}$$

In general, the n-dimensional representation matrix $D(R)$ of a symmetry operator R in a properly chosen basis $(\varphi_1, \varphi_2, \ldots, \varphi_n)$ is defined by the equation

$$R * \varphi_1 = \sum_j \varphi_j D_{ji}(R) \,. \tag{3.19}$$

A representation constructed this way is guaranteed to be a homomorphism since

$$\begin{aligned} R * (S * \varphi_i) &= R * \varphi_j D_{ji}(S) \\ &= \varphi_k D_{kj}(R) D_{ji}(S) \end{aligned} \tag{3.20}$$

(summation convention applies), and by compatibility,

$$\begin{aligned} R * (S * \varphi_i) &= (R \cdot S) * \varphi_i \\ &= \varphi_k D_{ki}(RS) \,, \end{aligned} \tag{3.21}$$

and therefore we have a homomorphism

$$\mathsf{D}(R)\mathsf{D}(S) = \mathsf{D}(RS) \,. \tag{3.22}$$

From the homomorphism condition, we can see that for any representation D of the group G,

$$\mathsf{D}(R) = \mathsf{D}(ER) = \mathsf{D}(E)\mathsf{D}(R) = \mathsf{I}\mathsf{D}(R)\,, \tag{3.23}$$

so the representation of the identity element is always the identity matrix, and

$$\mathsf{D}(E) = \mathsf{D}(R)\mathsf{D}(R^{-1}) = \mathsf{I}\,, \tag{3.24}$$

so $\mathsf{D}(R^{-1}) = (\mathsf{D}(R))^{-1}$ for all $R \in G$.

3.2 Equivalence

Let $(\hat{\boldsymbol{\imath}}, \hat{\boldsymbol{\jmath}}, \hat{\mathbf{k}})$ be a basis of a three dimensional vector space, and $\mathbf{v}$ be some vector with coordinates (x, y, z) in this basis. Then

$$\mathbf{v} = \begin{pmatrix} \hat{\boldsymbol{\imath}} & \hat{\boldsymbol{\jmath}} & \hat{\mathbf{k}} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} . \tag{3.25}$$

Let T be any invertible matrix, then we have $\mathsf{T}\mathsf{T}^{-1} = \mathsf{I}$, and so we also have

$$\mathbf{v} = \begin{pmatrix} \hat{\boldsymbol{\imath}} & \hat{\boldsymbol{\jmath}} & \hat{\mathbf{k}} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} \hat{\boldsymbol{\imath}} & \hat{\boldsymbol{\jmath}} & \hat{\mathbf{k}} \end{pmatrix} \mathsf{T}\mathsf{T}^{-1} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} \hat{\boldsymbol{\imath}}' & \hat{\boldsymbol{\jmath}}' & \hat{\mathbf{k}}' \end{pmatrix} \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} , \tag{3.26}$$

where

$$\begin{pmatrix} \hat{\boldsymbol{\imath}}' & \hat{\boldsymbol{\jmath}}' & \hat{\mathbf{k}}' \end{pmatrix} = \begin{pmatrix} \hat{\boldsymbol{\imath}} & \hat{\boldsymbol{\jmath}} & \hat{\mathbf{k}} \end{pmatrix} \mathsf{T}\,, \quad \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \mathsf{T}^{-1} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \tag{3.27}$$

are a transformed basis and transformed representation of exactly the same vector in this transformed basis.

We can do the same thing to transform a basis we used to construct a representation, and see what happens to the representation matrix. Let the action of R on a vector $\mathbf{v}$ give

$$R * \mathbf{v} = \begin{pmatrix} \hat{\boldsymbol{\imath}} & \hat{\boldsymbol{\jmath}} & \hat{\mathbf{k}} \end{pmatrix} \mathsf{D}(R) \begin{pmatrix} x \\ y \\ z \end{pmatrix} , \tag{3.28}$$

then we can also write

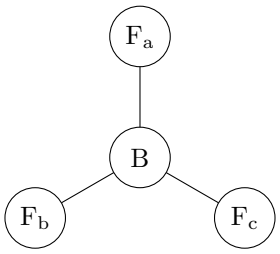
$$\begin{aligned} R * \mathbf{v} &= \begin{pmatrix} \hat{\boldsymbol{\imath}} & \hat{\boldsymbol{\jmath}} & \hat{\mathbf{k}} \end{pmatrix} \mathsf{T}\mathsf{T}^{-1}\mathsf{D}(R)\mathsf{T}\mathsf{T}^{-1} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \\ &= \begin{pmatrix} \hat{\boldsymbol{\imath}}' & \hat{\boldsymbol{\jmath}}' & \hat{\mathbf{k}}' \end{pmatrix} \mathsf{D}(R)' \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} . \end{aligned} \tag{3.29}$$

This time, in the transformed basis, the representation of R is given by

$$\mathsf{D}(R)' = \mathsf{T}^{-1}\mathsf{D}(R)\mathsf{T}\,. \tag{3.30}$$

We call this type of transformations on a representation matrix *similarity* or *equivalence* transformation, and the two representation D and D' are said to be *equivalent*. Crucially, there is nothing fundamentally different between two equivalent representations — they have just used two different set of basis vectors that represents the same vector space.

Example. Let's consider a BF_3 molecule, whose symmetry is given by the D_{3h} group. We will use a number of basis to construct some different representation of D_{3h}.



	E	C_3	C_3^2	C_3^a	C_3^b	C_3^c
(s)	(1)	(1)	(1)	(1)	(1)	(1)
(p_z)	(1)	(1)	(1)	(-1)	(-1)	(-1)
(p_x, p_y)	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$
(p_1, p_{-1})	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \omega^* & 0 \\ 0 & \omega \end{pmatrix}$	$\begin{pmatrix} \omega & 0 \\ 0 & \omega^* \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -\omega \\ -\omega^* & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -\omega^* \\ -\omega & 0 \end{pmatrix}$
(s_a, s_b, s_c)	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$

The basis functions are all atomic orbitals for BF_3. s_a, s_b and s_c are the fluorine $2s$ orbitals and the rest are boron orbitals. The functions p_1 and p_{-1} are the complex p orbitals (that are eigenfunctions of $\hat{L}_z$ operators) defined by

$$p_1 = -\frac{1}{\sqrt{2}}(p_x + ip_y) \qquad p_{-1} = \frac{1}{\sqrt{2}}(p_x - ip_y)\,. \tag{3.31}$$

ω is the third root of unity

$$\omega = \exp\left(\frac{2\pi i}{3}\right) = -\frac{1}{2} + \frac{\sqrt{3}}{2}i\,. \tag{3.32}$$

From the definition of the complex $p_{\pm 1}$ orbitals, we can see that they span the same vector space as the (p_x, p_y) basis functions, and so these two representations should be equivalent. We have

$$\begin{pmatrix} p_1 & p_{-1} \end{pmatrix} = \begin{pmatrix} p_x & p_y \end{pmatrix} \mathsf{T} = \begin{pmatrix} p_x & p_y \end{pmatrix} \begin{pmatrix} -\frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ -\frac{i}{\sqrt{2}} & -\frac{i}{\sqrt{2}} \end{pmatrix}\,. \tag{3.33}$$

You can check that these two rows of representation matrices are related by

$$\mathsf{D}^{\pm 1}(R) = \mathsf{T}^{-1}\mathsf{D}^{xy}(R)\mathsf{T}\,. \tag{3.34}$$

3.3 Reducibility

In the example above, we formed a one-dimensional representation of D_3 using the basis set (p_z) and a two-dimensional representation using (p_x, p_y). There is nothing stopping us to construct a three-dimensional representation using the combined basis set (p_x, p_y, p_z). However, all the operations in D_3 will leave the p_x, p_y orbitals into a linear combination of themselves, and leave p_z either unchanged or merely change its sign. The two vector subspaces spanned by (p_x, p_y) and (p_z) does not mix — that's why we are able to form representations using these two basis sets at the beginning. We call these two space, $\mathrm{span}(p_x, p_y)$ and $\mathrm{span}(p_z)$, the *invariant subspaces* of the whole vector space $\mathrm{span}(p_x, p_y, p_z)$. Then if we use this three dimensional basis set to form a representation, it will look like this.

$$
\begin{aligned}
\mathsf{D}^{xyz}(E) &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \mathsf{D}^{xyz}(C_3) &= \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \\
\mathsf{D}^{xyz}(C_3^2) &= \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} & \mathsf{D}^{xyz}(C_2^a) &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \\
\mathsf{D}^{xyz}(C_3) &= \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & -1 \end{pmatrix} & \mathsf{D}^{xyz}(C_3^2) &= \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & -1 \end{pmatrix} .
\end{aligned}
\tag{3.35}
$$

All these representations are in the block diagonal form, where the two blocks are the two smaller representations formed by (p_x, p_y) and (p_z).

$$
\mathsf{D}^{xyz} = \begin{pmatrix} \mathsf{D}^{xy} & \\ & \mathsf{D}^{z} \end{pmatrix} . \tag{3.36}
$$

There are no off-block-diagonal elements since as we just claimed before, the two vector subspaces do not mix. For the representations that can be written in the block diagonal form, we say it is a *direct sum* of its diagonal-block representations, written

$$
\mathsf{D}^{xyz} = \mathsf{D}^{xy} \oplus \mathsf{D}^{z} . \tag{3.37}
$$

This definition can be extended to direct sums of multiple representations.

Some representations themselves are not in the block diagonal form, but they are equivalent to the direct sum of the direct sum of smaller representations. Let's consider the example above again. This time, we define a new basis set

$$
\begin{aligned}
\varphi_1 &= \sqrt{\frac{1}{3}}(s_a + s_b + s_c) \\
\varphi_2 &= \sqrt{\frac{1}{6}}(2s_a - s_b - s_c) \\
\varphi_3 &= \sqrt{\frac{1}{2}}(s_b - s_c) .
\end{aligned}
\tag{3.38}
$$

This is a similarity transform of the (s_a, s_b, s_c) basis

$$\begin{pmatrix}\varphi_1 & \varphi_2 & \varphi_3\end{pmatrix} = \begin{pmatrix}s_a & s_b & s_c\end{pmatrix} \begin{pmatrix} \sqrt{\frac{1}{3}} & \sqrt{\frac{2}{3}} & 0 \\ \sqrt{\frac{1}{3}} & -\sqrt{\frac{1}{6}} & \sqrt{\frac{1}{2}} \\ \sqrt{\frac{1}{3}} & -\sqrt{\frac{1}{6}} & -\sqrt{\frac{1}{2}} \end{pmatrix}, \tag{3.39}$$

and so in this new basis, the representation matrices are

$$\mathsf{D}^{3\mathrm{F},s}(E) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \mathsf{D}^{3\mathrm{F},s}(C_3) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$$

$$\mathsf{D}^{3\mathrm{F},s}(C_3^2) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \qquad \mathsf{D}^{3\mathrm{F},s}(C_2^a) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

$$\mathsf{D}^{3\mathrm{F},s}(C_3) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix} \qquad \mathsf{D}^{3\mathrm{F},s}(C_3^2) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}. \tag{3.40}$$

This time the representation is again is a direct sum form, with

$$\mathsf{D}^{\varphi} = \mathsf{D}^{\mathrm{B},s} \oplus \mathsf{D}^{xy}, \tag{3.41}$$

and hence the representation formed by fluorine s orbitals is equivalent to the direct sum of $\mathsf{D}^{B,s}$ and D^{xy}, written

$$\mathsf{D}^{\mathrm{F},s} \sim \mathsf{D}^{\mathrm{B},s} \oplus \mathsf{D}^{xy}. \tag{3.42}$$

If a representation is equivalent to a direct sum of some lower-dimensional representation, then we say this representation is *reducible*. On the other hand, there are some representation that cannot be reduced in this way (the one dimensional trivial representation is clearly an example). These representations are *irreducible*. The irreducible representations of a group have their canonical names, which you can find in the character table of the group (although we have not introduced what is a character table yet).

Any representation of a group can be reduced in into a number of irreducible representations of the group (by finding a suitable basis in which this matrix is block diagonal) so we can always write

$$\Gamma \sim \bigoplus_{i=1}^{N} m_i \Gamma^i, \tag{3.43}$$

where $\{\Gamma^i\}_{i=1}^N$ are the inequivalent irreducible representations of the group, and the multiplicity m_i is the time a certain irreducible representation Γ^i appear on the diagonal blocks. However, in practice, we often just write it as

$$\Gamma = \bigoplus_{i=1}^{N} m_i \Gamma^i \tag{3.44}$$

since we don't usually distinguish between equivalent matrices.

However, it is not straight forward at all to figure out under what basis is our representation block diagonal, making it seems very difficult to reduce a representation. Next, we will introduce a powerful concept called *character*, which is, as its name suggests, characteristic of a representation and allows us to reduce a representation easily.

4 Characters

4.1 Characters

Representations are nice and intuitive, but they are just not the nicest thing to work with. Matrices are too large and it is a tedious job to manipulate them. More crucially, two equivalent representations, which are fundamentally the same thing, may look completely different after similarity transform. Is there a nicer thing that is invariant under the transformation of a basis?

The answer is the trace.

Definition 4.1. The *character* of a representation Γ is the traces of the representation matrices, denoted χ^Γ.

Proposition 4.2. Let D, T be $n \times n$ matrices with T invertible. Then

$$\mathrm{tr}(\mathsf{D}) = \mathrm{tr}(\mathsf{T}^{-1}\mathsf{D}\mathsf{T})\,. \tag{4.1}$$

Proof.

$$\begin{aligned}\mathrm{tr}(\mathsf{T}^{-1}\mathsf{D}\mathsf{T}) &= \mathsf{T}_{ij}\mathsf{D}_{jk}(\mathsf{T}^{-1})_{ki} \\ &= (\mathsf{T}^{-1})_{ki}\mathsf{T}_{ij}\mathsf{D}_{jk} \\ &= \delta_{kj}\mathsf{D}_{jk} \\ &= \mathsf{D}_{jj} = \mathrm{tr}(\mathsf{D})\,. \end{aligned} \tag{4.2}$$

□

This has two immediate consequences. First, if two representations are equivalent, then their characters are the same. This is obvious. Second, if $R, S \in G$ are in the same conjugacy class (say, $R = QSQ^{-1}$), then their characters under the same representation are the same. This is because by the homomorphism requirement,

$$\begin{aligned}\mathsf{D}(R) &= \mathsf{D}(QSQ^{-1}) \\ &= \mathsf{D}(Q)\mathsf{D}(S)\mathsf{D}(Q^{-1}) \\ &= \mathsf{D}(Q)\mathsf{D}(S)\mathsf{D}(Q)^{-1}\,, \end{aligned} \tag{4.3}$$

so their traces are equal.

This allows us to construct a so called *character table* to list the characters of all the inequivalent irreducible representations of a group[4], in which the rows are the different inequivalent irreducible representations and the columns are the character classes (Remember the characters of the elements in the same class are equal, so we can list them in the same column). For example, for the D_3 group, we will get something like this.

[4]For a finite group, there is necessarily a finite number of irreducible representations this table can be listed to a completion — we will show this later.

	E	$2C_3^z$	$3C_2$
A_1	1	1	1
A_2	1	1	1
E	2	-1	0

Moreover, since the trace is a sum of the diagonal elements, it is clear that the character of a reducible matrix is the character of its components. That is, if

$$\Gamma = \bigoplus_{i=1}^{N} m_i \Gamma^i \,, \tag{4.4}$$

then

$$\chi^\Gamma = \sum_{i=1}^{N} m_i \chi^{\Gamma^i} \,. \tag{4.5}$$

Then, to figure out the component of a reducible representation Γ, we only need to work out the characters of what irreducible representations (which are listed in the character table) sum to it. This still seems to be a difficult task to do if we have a large number of irreducible representations. But luckily, we have the orthogonality theorems!

4.2 Orthogonality Theorems

Now we will introduce one of the most powerful theorems in representation theory, upon which many useful results are derived.

Theorem 4.3. Let $\{\Gamma^a\}$ be the set of inequivalent irreducible unitary representations of a finite group G, then

$$\sum_{R\in G} \mathsf{D}^a_{ip}(R)^* \mathsf{D}^b_{jq}(R) = \frac{|G|}{n_a} \delta_{ab}\delta_{ij}\delta_{pq} \,. \tag{4.6}$$

where n_a is the dimension of Γ^a.[5]

This is an extremely powerful result, as can be seen by the three Kronecker deltas — you need to sum over the same element of the same irreducible representation, otherwise you will get a zero. This great orthogonality theorems allows us to show some useful properties of the characters.

Theorem 4.4 (First orthogonality theorem). Let $\{\chi^a\}$ be the characters of the inequivalent irreducible representations $\{\Gamma^a\}$ of a finite group G.

$$\sum_{R\in G} \chi^a(R)\chi^b(R) = |G|\, \delta_{ab} \,. \tag{4.7}$$

[5] We requested the irreducible representations in $\{\Gamma^a\}$ to be inequivalent to avoid the case that $\Gamma^a \sim \Gamma^b$ but $\Gamma^a \neq \Gamma^b$ — a formula do exists for such case, but it is more complicated. We are not proving it here. A proof of this, along with a more expanded and rigorous treatment in groups and representations can be found in my notes on NST Part IB Mathematical Methods. It spends half a chapter to arrive at this result, so it is too large to fit in the margin.

Proof.

$$\begin{aligned}\sum_R \chi^a(R)\chi^b(R) &= \sum_R \sum_{i,k} \mathsf{D}^a_{ii}(R)\mathsf{D}^b_{kk}(R) \\ &= \sum_{i,k} \frac{|G|}{n_a}\delta_{ab}\delta_{ik}\delta_{ik} \\ &= |G|\,\delta_{ab}\,. \end{aligned} \tag{4.8}$$

□

This is also known as the row orthogonality, because what it says is that the rows of a character table are orthogonal. To see this, we need to rewrite it a little bit. In a character table, we group the group elements in the same conjugacy class together into the same column since their characters are the same. We can use this to simplify our sum. Instead of summing over all the elements in the group, we can also sum over the conjugacy classes, provided that we remember to multiply the number of elements in the conjugacy class.

Corollary (Row orthogonality).

$$\frac{1}{|G|}\sum_c h_c \chi^a(c)^* \chi^b(c) = \delta_{ab}\,, \tag{4.9}$$

where h_c is the size of the conjugacy class c.

If we view each row of a character table the entries of a vector, what this means is that these vectors are orthonormal under some slightly modified version of the dot product where we have an additional factor:[6]

$$\mathbf{a}\cdot\mathbf{b} = \sum_i \frac{h_i}{|G|} a_i b_i\,. \tag{4.10}$$

This then allows us to conveniently reduce a reducible representation! Suppose we have a vector space spanned by orthonormal basis $(\mathbf{e}_1, \mathbf{e}_2, \ldots, \mathbf{e}_n)$, and we want to find out the components of a vector $\mathbf{v}$, i.e. to find out the coefficients $c_1, c_2, \ldots, c_n$ such that

$$\mathbf{v} = \sum_{i=1}^n c_i \mathbf{e}_i\,. \tag{4.11}$$

What we can do is to take the dot product of $\mathbf{v}$ with each of the basis vector $\mathbf{e}_j$ and we would obtain the coefficient c_j.

$$\mathbf{e}_j\cdot\mathbf{v} = \sum_{i=1}^n c_i \mathbf{e}_j\cdot\mathbf{e}_i \tag{4.12}$$

$$= \sum_{i=1}^n c_i \delta_{ij} = c_j\,. \tag{4.13}$$

[6] If you have learned some linear algebra before, you should discover that this is the metric of the scalar product.

We can do exactly the same thing here, as long as we remember to use our slightly modified version of the dot product.

Theorem 4.5 (Reduction formula). Let $\{\chi^a\}_{a=1}^m$ be the characters of the inequivalent irreducible representations $\{\Gamma^a\}_{a=1}^m$ of a finite group G, and Γ is a reducible representation with character χ, then Γ is reduced to

$$\Gamma = \bigoplus_{a=1}^{m} m_a \Gamma^a \tag{4.14}$$

with

$$m_a = \frac{1}{|G|} \sum_c h_c \chi^a(c)^* \chi(c)\,, \tag{4.15}$$

where h_c is the number of elements of equivalent class c.

Proof. We use the row orthogonality.

$$\begin{aligned} \frac{1}{|G|} \sum_c h_c \chi^a(c)^* \chi(c) &= \frac{1}{h} \sum_c h_c \chi^a(c)^* \sum_i m_i \chi^i(c) \\ &= \sum_i m_i \delta_{ia} \\ &= m_a\,. \end{aligned} \tag{4.16}$$

□

What's even nicer about the character table is that the columns of it are also orthogonal! This is the second orthogonality theorem, also known as column orthogonality.

Theorem 4.6. Let $\{\chi^a\}$ be the characters of the inequivalent irreducible representations $\{\Gamma^a\}$ of a finite group G.

$$\sum_a \chi^a(c)\chi^a(c') = \frac{|G|}{h_c} \delta_{cc'}\,. \tag{4.17}$$

This is, however, much harder to prove and we will not prove it. The row orthogonality and column orthogonality combined leads to a very nice result.

Corollary (Character table is square). Let G be a finite group, then the number of inequivalent irreducible representations of G and the number of conjugacy classes of G are equal.

Proof. Let $\{c_i\}_{i=1}^p$ be the equivalent classes and $\{\Gamma^a\}_{a=1}^m$ be the inequivalent irreducible representations, i.e. there are p equivalent classes and m inequivalent irreducible representations.

Each row has p entries, so we can view each row as a vector in $\mathbb{C}^p$, and by row orthogonality these vectors are orthonormal. These m linear independent vectors in $\mathbb{C}^p$ must span a subspace $\mathbb{C}^m \leq \mathbb{C}^p$, so $m \leq p$. Similarly, column orthogonality means that viewing each column as a vector in $\mathbb{C}^m$, these vectors are also orthonormal. These are p linear independent vectors in $\mathbb{C}^m$, so they must span a subspace $\mathbb{C}^p \leq \mathbb{C}^m$, so $p \leq m$. $m = p$. □

Corollary. Let $\{\Gamma^a\}$ be the inequivalent irreducible representations of a finite group G, then

$$\sum_a n_a^2 = |G| \ , \tag{4.18}$$

where n_a is the dimension of Γ^a.

Proof. Put $c = c' = \{E\}$, the class of the identity element in the column orthogonality theorem (4.17). □

Example. Consider again the representation of D_3 group spanned by the three fluorine s orbital in BF_3. Last time we have shown that under the basis transformation

$$\begin{aligned} \varphi_1 &= \sqrt{\frac{1}{3}}(s_a + s_b + s_c) \\ \varphi_2 &= \sqrt{\frac{1}{6}}(2s_a - s_b - s_c) \\ \varphi_3 &= \sqrt{\frac{1}{2}}(s_b - s_c) \, , \end{aligned} \tag{4.19}$$

this reducible representation becomes a direct sum

$$\Gamma = A_1 \oplus E \, . \tag{4.20}$$

But finding the suitable basis transformation matrix out of nowhere to block-diagonalise the representation matrix seems like a difficult thing to do. Now, using the reduction formula, we can directly reduce a representation without doing so. To use the reduction formula, we only need to find the character of our representation spanned by (s_a, s_b, s_c). This is simple — the character is the sum of the diagonal element of a representation matrix, and a diagonal element of a representation matrix means how much has a basis transformed into itself after the group action. For example, to work out the character of C_2^a, we need to find

$$\chi(C_2^a) = \mathsf{D}_{11}(C_2^a) + \mathsf{D}_{22}(C_2^a) + \mathsf{D}_{33}(C_2^a) \, . \tag{4.21}$$

$\mathsf{D}_{11}(C_2^a)$ is the s_a component of s_a after the action of C_2^a; s_a is not moved by C_2^a so this is one. $\mathsf{D}_{22}(C_2^a)$ is the s_b component of s_b after the action of C_2^a, while s_b is not moved to s_c after C_2^a so this is zero, meaning $s_b' = C_2^a * s_b$ has no component of s_b. Similarly, $s_c' = C_2^a * s_c$ has no component of s_c, so $\mathsf{D}_{33}(C_2^a) = 0$. Summing these up, we get $\chi(C_2^a) = 1 + 0 + 0 = 1$. Now since the three C_2 elements are in the same equivalent class, their characters are 1 as well. Doing this for all other character classes, we find that the characters of our representation is

	E	$2C_3$	$3C_2$
χ	3	0	1

Now to reduce this representation, we need the character table.

	E	$2C_3$	$3C_2$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

Now we can use the reduction formula to compute the multiplicities.

$$m_{A_1} = \frac{1}{|G|}\sum_c h_c \chi^{A_1}(c)^* \chi(c) = \frac{1}{6}(1\times 1\times 3 + 2\times 1\times 0 + 3\times 1\times 1) = 1 \tag{4.22}$$

$$m_{A_2} = \frac{1}{|G|}\sum_c h_c \chi^{A_2}(c)^* \chi(c) = \frac{1}{6}(1\times 1\times 3 + 2\times 1\times 0 + 3\times (-1)\times 1) = 0 \tag{4.23}$$

$$m_{E} = \frac{1}{|G|}\sum_c h_c \chi^{E}(c)^* \chi(c) = \frac{1}{6}(1\times 2\times 3 + 2\times (-1)\times 0 + 3\times 0\times 1) = 1\,, \tag{4.24}$$

and hence we have successfully reduced out representation:

$$\Gamma = A_1 \oplus E\,. \tag{4.25}$$

4.3 Projection Formula and Schmidt Orthogonalisation

Now we can successfully reduce a representation without finding the basis transformation matrix that block-diagonalises the representation matrix! But it actually turns out that this transformation matrix is a rather useful thing, and we want to know it in the most cases. For example, if we know that after the transformation

$$\begin{aligned}
\varphi_1 &= \sqrt{\frac{1}{3}}(s_a + s_b + s_c) \\
\varphi_2 &= \sqrt{\frac{1}{6}}(2s_a - s_b - s_c) \\
\varphi_3 &= \sqrt{\frac{1}{2}}(s_b - s_c)\,,
\end{aligned} \tag{4.26}$$

the representation becomes block diagonalised to

$$\Gamma^{\varphi} = \begin{pmatrix} \boxed{A_1} & \\ & \boxed{E} \end{pmatrix}, \tag{4.27}$$

then this means that (φ_1) itself spans A_1, and (φ_2, φ_3) together transforms as E. This is known as the *symmetry orbitals* — the linear combination of atomic orbitals that transform as a specific irreducible representation. They are extremely useful in molecular orbital theories since, as you have seen in Part IB *Symmetry and Bonding* course, only orbitals that transforms as the same irreducible representations have non-zero interactions. Therefore, knowing how to construct these orbitals would greatly reduce our workload when constructing molecular orbitals!

Luckily, this is not difficult to do as long as we know to what irreducible representations our representation reduces to. Let's consider the following operator

$$\hat{P}_i^a := \frac{n_a}{|G|} \sum_{R \in G} \mathsf{D}_{ii}^a(R)^* R\,, \tag{4.28}$$

which is a particular linear combination of group elements, and see how it acts to a vector $\mathbf{v}_j^b = \sum_k (v_j^b)_k \mathbf{e}_k$, represented in the basis $(\mathbf{e}_1, \mathbf{e}_2, \dots)$, that transforms as the jth component of the irreducible representation Γ^b. We have

$$\begin{aligned}
\hat{P}_i^a * \mathbf{v}_j^b &= \frac{n_a}{|G|} \sum_R \mathsf{D}_{ii}^a(R)^* R * \mathbf{v}_j^b && (4.29)\\
&= \frac{n_a}{|G|} \sum_R \mathsf{D}_{ii}^a(R)^* \sum_k (v_j^b)_k \mathbf{e}_k \mathsf{D}_{kj}^b(R) && (4.30)\\
&= \sum_k \delta_{ab}\delta_{ik}\delta_{ij}(v_j^b)_k \mathbf{e}_k && (4.31)\\
&= \begin{cases} \sum_k (v_i^a)_k \mathbf{e}_k = \mathbf{v}_i^a & \text{if } a = b, i = j \\ 0 & \text{otherwise,} \end{cases} && (4.32)
\end{aligned}$$

This is exactly what defines a *projection operator*! If you act $\hat{P}_i^a$ on any vector, you will only get the component of it that transform as the i component of the irreducible representation Γ^a, and anything else will be annihilated, i.e. the projects a vector onto $\mathbf{v}_i^a$.

Theoretically, we can use this to obtain each component of a irreducible representation by acting the projection operators on arbitrary vectors, but this would require us to know the irreducible representations. What we usually have is only the character of the irreducible representations. What we can do is to sum up the components of the projection operators of the same irreducible representations, and define

$$\hat{P}^a := \sum_{i=1}^{n_a} \hat{P}_i^a = \frac{n_a}{|G|} \sum_R \chi^a(R)^* R\,. \tag{4.33}$$

Now when you act this on an arbitrary vector, you will obtain the sum of its projection on all the components of a irreducible representation

$$\hat{P}^a * \mathbf{v} = \sum_{i=1}^{n_a} \hat{P}_i^a * \mathbf{v} = \sum_i \mathbf{v}_i^a\,. \tag{4.34}$$

This could be troublesome for a irreducible representation that is not one-dimensional. For example, in the BF_3 example, if you act $\hat{P}^E = \hat{P}_1^E + \hat{P}_2^E$ on an arbitrary vector, you will get a linear combination of φ_2 and φ_3, the two components that together transform as E.

Of course, we can directly use this mixture as one of the components of E, since this is only a basis transformation of E and you will still get something equivalent to E, which is still an E — but we still need to get the other orthogonal components of the basis transforming as E. This is done by a process called *Schmidt orthogonalisation*. Let $\mathbf{v}_1$ be the vector that we obtained from the projection operator, which we use as the

vector that transforms as the first component of an irreducible representation Γ with dimension greater than 1. Γ is clearly not the totally symmetric representation (since its dimension is not 1), so there must be an operator R that acts on $\mathbf{v}_1$ to generate some vector $\mathbf{v}' = R * \mathbf{v}_1$ that is not completely aligned with $\mathbf{v}_1$. Since $\mathbf{v}_1$ in the basis set that generates Γ, it will only be transformed into a sum of different components that transforms as Γ. Therefore, if $\mathbf{v}' = R * \mathbf{v}_1$ has some component orthogonal to $\mathbf{v}_1$, then this can be seen as a vector that transforms as the second component of Γ. To extract this, we first normalise $\mathbf{v}_1$ and $\mathbf{v}'$, and then let

$$\mathbf{v}_2 = \mathbf{v}' - (\mathbf{v}' \cdot \mathbf{v}_1)\mathbf{v}_1 \tag{4.35}$$

to get rid of any component of $\mathbf{v}'$ that is aligned with $\mathbf{v}_1$. This $\mathbf{v}_2$ might be unnormalised, so we can normalise it, and we then get a $\mathbf{v}_2$ that is orthonormal with $\mathbf{v}_1$. We can repeat this process until we have generated all components of the basis that transforms as Γ.

Example. Back to the example of using the fluorine F orbitals in BF_3 to represent D_3 group. We know that the representation is $\Gamma = A_1 + E$, and let's find out the symmetry orbitals.

First the A_1 orbitals. This should be easy. We just pick any vector and act the projection operator of A_1,

$$\begin{aligned} \hat{P}^{A_1} &= \frac{n_{A_1}}{|D_3|} \sum_{R \in D_3} \chi^{A_1}(R)^* R \\ &= \frac{1}{6}(E + C_3 + C_3^2 + C_2^a + C_2^b + C_2^c)\,, \end{aligned} \tag{4.36}$$

onto it. The simplest choice of vector is one of the basis vectors. We would use s_a and we get

$$\hat{P}^{A_1} * s_a = \frac{1}{6}(s_a + s_b + s_c + s_a + s_c + s_b) = \frac{1}{3}(s_a + s_b + s_c)\,. \tag{4.37}$$

This can be normalised to get the A_1 symmetry orbital

$$\phi_{A_1} = \frac{1}{\sqrt{3}}(s_a + s_b + s_c)\,. \tag{4.38}$$

Next, let's calculate the E symmetry orbitals. This should be a little more difficult. Let's first construct the projection operator.

$$\begin{aligned} \hat{P}^{E} &= \frac{n_{E}}{|D_3|} \sum_{R \in D_3} \chi^{E}(R)^* R \\ &= \frac{1}{3}(2E - C_3 - C_3^2)\,. \end{aligned} \tag{4.39}$$

We act this on s_a to get

$$\hat{P}^{E} * s_a = \frac{1}{3}(2s_a - s_b - s_c)\,. \tag{4.40}$$

We can normalise this to get the first E symmetry orbital

$$\phi_{E,1} = \frac{1}{\sqrt{6}}(2s_a - s_b - s_c)\,. \tag{4.41}$$

Next, let's construct the second E symmetry orbital by Schmidt orthogonalisation. We act some arbitrary group element onto our first symmetry orbital that does not leave it unchanged. C_3 seems to be a good choice.

$$\phi' = C_3 * \phi_{E,1} = \frac{1}{\sqrt{6}}(2s_b - s_c - s_a)\,. \tag{4.42}$$

We subtract the $\phi_{E,1}$ component from it and get

$$\phi' - (\phi' \cdot \phi_{E,1})\phi_{E,1} = \frac{1}{\sqrt{6}}(2s_b - s_c - s_a) - \frac{1}{6}(-2-2+1)\frac{1}{\sqrt{6}}(2s_a - s_b - s_c) \tag{4.43}$$

$$= \frac{3}{2\sqrt{6}}(s_b - s_c)\,. \tag{4.44}$$

This can be normalised to get the second symmetry orbital of E:

$$\phi_{E,2} = \frac{1}{\sqrt{2}}(s_b - s_c)\,. \tag{4.45}$$

You can check that these are identical to what we asserted in (4.26).

5 Rotation Group and Spherical Harmonics

In the first chapter, we have shown that for a molecular system, rotation is a symmetry operation. We can therefore consider the group of all 3D rotations about any axis that leaves an origin unchanged (that is the centre of mass for a molecular system), known as the *full rotation group*. We can denote its elements by $R(\mathbf{u})$, where $\mathbf{u} = \alpha\hat{\mathbf{u}}$, $\alpha = \|\mathbf{u}\|$ is the angle of rotation, and $\hat{\mathbf{u}}$ is the unit vector along the rotation axis. Mathematically, the full rotation group is exactly the *special orthogonal group of order 3*, the group of 3×3 orthogonal matrices with determinant $+1$, denoted SO(3). There is a one-to-one correspondence between rotation operations R and matrices $\mathsf{R} \in \mathrm{SO}(3)$ — they are isomorphic, so we see them as the same group.

We have claimed before that the theory of the SO(3) group is deeply linked to the theory of angular momentum. This can be seen from Noether's theorem, which says the rotational symmetry leads to the conservation of momentum. Also, if we consider the rotation $\mathsf{R} \in \mathrm{SO}(3)$ of a function $\psi(\mathbf{r})$ in 3D space (for example the wavefunction), then the function after rotation, denoted $\psi'(\mathbf{r})$, satisfies

$$\psi'(\mathbf{r}) = \psi(\mathsf{R}^{-1}\mathbf{r})\,. \tag{5.1}$$

More explicitly, if we identify the axis of rotation as the z axis, and we rotated by a degree of α, then the value of the rotated function now at (r, θ, φ) would be the value of the function originally at $(r, \theta, \varphi - \alpha)$. We can construct a operator

$$\hat{J}_z = i\hbar \lim_{\alpha \to 0} \frac{R(\alpha\hat{\mathbf{z}}) - E}{\alpha} \tag{5.2}$$

which captures the effect of an infinitesimal rotation about z axis (the $i\hbar$ here is just a matter of convention). This is known as the *generator* of the rotation. Then its effect on some function ψ is

$$\hat{J}_z\psi(r, \theta, \varphi) = i\hbar \lim_{\alpha \to 0} \frac{\psi(r, \theta, \varphi - \alpha) - \psi(r, \theta, \varphi)}{\alpha} = -i\hbar\frac{\partial\psi}{\partial\varphi}\,. \tag{5.3}$$

This is exactly the z component of the angular momentum operator! We say angular momentum *generates* the rotation.

The properties of rotations give hints on the properties of angular momentum operators. For systems governed by Hamiltonians with rotational symmetries, since rotation is a symmetry action, the angular momentum operator commutes with the Hamiltonian operator: $[\hat{H}, \hat{\mathbf{J}}] = 0$. However, since rotations along different axes does note commute. You can try it! Find an object, rotate it 90° along the x direction, then 90° along z direction, and you will find that it is different if you first rotate it 90° along z axis then along x axis — the order of rotations matters. Hence the different components of the angular momentum operators does not commute. However, the rotation along the same axis commute. Therefore we have $[\hat{J}_i, \hat{J}_j] \neq 0$ for $i \neq j$, while $[\hat{J}_i, \hat{J}_i] = 0$.

A quick aside, if you run the same process above for spatial translation, you will find that the momentum operator is the generator of spatial translation. Rotating an object followed by a translation is not the same as translating the object followed by a

rotation (because the object is now off the origin), unless the direction of translation and the axis of rotation is the same (then the object is still on the rotation axis), so we have $[\hat{J}_i, \hat{P}_j] \neq 0$ for $i \neq j$, while $[\hat{J}_i, \hat{P}_i] = 0$. More specifically, since momentum is a vector, it *transforms as a vector* under rotation, so

$$[\hat{J}_i, \hat{P}_j] = i\hbar \sum_k \epsilon_{ijk} \hat{P}_k \,. \tag{5.4}$$

The position operator $\hat{X}$ is also a vector, so it also transforms as a vector under rotation

$$[\hat{J}_i, \hat{X}_j] = i\hbar \sum_k \epsilon_{ijk} \hat{X}_k \,. \tag{5.5}$$

However, translations in different directions commute: translation along x by 1 m then along y by 2 m is the same as first translating along y by 2 m then along x by 1 m — the order does not matter. Therefore, all components of translation commute with each other

$$[\hat{P}_i, \hat{P}_j] = 0 \,. \tag{5.6}$$

Reporting your coordinate does not affect anything, so components of the position operator commutes

$$[\hat{X}_i, \hat{X}_j] = 0 \,. \tag{5.7}$$

Finally, asking where you are and then move away is not the same as first move away then ask where you are, unless the component of the position coordinate you are asking is orthogonal to the direction you are moving, so

$$[\hat{X}_i, \hat{P}_j] = i\hbar\delta_{ij} \,. \tag{5.8}$$

The idea of generators allows us to understand the commutation relations of operators in a simple and intuitive way.

Next, we will quote, without proof, some properties of the SO(3) group and its representations. The theory detail is far beyond the scope of our course.

(i) The rotation $R(\alpha\hat{\mathbf{u}})$ through an angle α about an axis $\hat{\mathbf{u}}$ is in the same class as a rotation $R(\alpha'\hat{\mathbf{u}}')$ if and only if $\alpha = \alpha'$. The class of SO(3) contains all rotations through the same angle α about any axis.

(ii) The irreducible representations of SO(3) are labelled by the quantum number J of angular momentum. Representation Γ^J has dimension $2J + 1$.

(iii) The spherical harmonics Y_{JM} are the basis functions for the representation Γ^J.[7]

[7] We will not prove this. This is exactly the last result in the Mathematical Tripos Part II *Representation Theory* course so it is impossible to cover this in a 6-lecture chemistry course. However, we can briefly justify this. The angular momentum operator generates a rotation, so an infinitesimal rotation $R(\delta\alpha\hat{\mathbf{z}})$ is represented by

$$E - \frac{i}{\hbar}\delta\alpha\hat{J}_z \tag{5.9}$$

by reverting the expression (5.2). Then a rotation of non-infinitesimal degree α can be obtained by repeatedly acting the infinitesimal rotations by α/N for $N \to \infty$ times:

$$R(\alpha\hat{\mathbf{z}}) = \lim_{N\to\infty}\left(1 - \frac{i\alpha}{\hbar N}\hat{J}_z\right)^N = e^{-i\alpha\hat{J}_z/\hbar} \,. \tag{5.10}$$

This allows us to use the eigenstates of the angular momentum operator (spherical harmonics) as the basis, which are

We can then work out the character of the irreducible representations of SO(3). The spherical harmonics are

$$Y_{JM}(\theta,\varphi) = C_{JM} P_J^{|M|}(\cos\theta) e^{iM\varphi}\,, \tag{5.14}$$

where $P_J^{|M|}$ is the *associated Legendre polynomial*. Since the rotation of the same angle about any axis are in the same conjugacy class, they have the same character, so it is the easiest to consider the rotation about the z axis. We have

$$R(\alpha\hat{\mathbf{z}}) * Y_{JM} = Y_{JM}(\theta,\varphi-\alpha) = e^{-iM\alpha} Y_{JM}\,, \tag{5.15}$$

so the Mth diagonal component of the irreducible representation Γ^J is

$$\mathsf{D}^J_{MM}(\alpha) = e^{-iM\alpha}\,. \tag{5.16}$$

The character is then

$$\begin{aligned}\chi^J(\alpha) &= \sum_{M=-J}^{J} e^{-iM\alpha} \\ &= \frac{e^{iJ\alpha}[1-e^{-i(2J+1)\alpha}]}{1-e^{-i\alpha}} \\ &= \frac{\sin(J+\frac{1}{2})\alpha}{\sin\frac{1}{2}\alpha}\,.\end{aligned} \tag{5.17}$$

---

labelled by $|J,M\rangle$, with

$$\hat{\mathbf{J}}^2 |J,M\rangle = \hbar^2 J(J+1)|J,M\rangle \tag{5.11}$$

$$\hat{J}_z |J,M\rangle = \hbar M |J,M\rangle\,. \tag{5.12}$$

For any value of J, $M_J \in \{-J,-J+1,\ldots,J\}$, so there are $2J+1$ of them. $\{|J,M\rangle\}_{M=-J}^J$ is therefore a $2J+1$ dimensional basis, and rotation along the z axis acting on them by

$$R(\alpha\hat{z}) * |J,M\rangle = e^{-i\alpha\hat{J}_z/\hbar}|M,J\rangle = e^{-iM\alpha}|M,J\rangle\,. \tag{5.13}$$

For this to be a homomorphism, we require $R(2\pi\hat{z})$ to be mapped to the identity, so we must have $e^{-2\pi iM}=1$. This is true if and only if M is an integer, which is true if and only if J is an integer. Hence, these representations are $2J+1$ dimensional with J an integer, and the basis functions are the spherical harmonics. However, we haven't shown that they are exactly the irreducible ones. Moreover, there are some subtle details with those half-integer J states. Roughly speaking, the half-integer J states form the *projective representations*, when you consider all states $\lambda|\psi\rangle$, $\lambda\in\mathbb{C}$ to be the same as $|\psi\rangle$ as in quantum mechanics, and those particles with half-integer spin values (internal J value) are known as the *spinors*. For example, when $J=\frac{1}{2}$ and $M=\pm\frac{1}{2}$, you can see $e^{-iM\alpha}$ returns to 1 when $\alpha=720°$! You will need to rotate a electron ($s=\frac{1}{2}$) by 720° for it to go back to its original state!

6 Symmetric Representation and Direct Product Representations

6.1 Symmetric Representation

Every group has a special one-dimensional representation called the symmetric representation, where the representation matrices of all elements are (1), and the characters are all (1). In different groups, they might have different conventional notations ($A_1, A_{1g}, A_1', \Sigma_g^+, S$ *etc.*), but here we call it $\Gamma^{(1)}$ for simplicity.

In in the great orthogonality theorem, we use the totally symmetric representation $\Gamma^{(1)}$ as one of the representation, then we get a useful formula

$$\frac{1}{|G|}\sum_{R\in G} D^{\Gamma}_{jq}(R) = \begin{cases} 0 & \text{if } \Gamma \neq \Gamma^{(1)} \\ 1 & \text{if } \Gamma = \Gamma^{(1)} \,. \end{cases} \tag{6.1}$$

Next, let's consider the behaviour of physical properties of molecules, such as charge or dipole moment. If a molecule belongs to a certain point group, then all the action of all the symmetry operations should, by definition, leave the appearance of the molecule unchanged, and so it cannot change the value of any physical quantity. Let's consider a physical quantity μ of a molecule, the components of which spans a representation Γ^{μ}. For example, if $\boldsymbol{\mu} = (\mu_x, \mu_y, \mu_z)$ is a vector, then its three components will transform as vectors $\mathbf{x}$, $\mathbf{y}$ and $\mathbf{z}$ (or equivalently Cartesian functions x, y and z) respectively, which spans a three dimensional representation. Then for any component of the quantity μ_i, the action of any symmetry operation R should leave it unchanged:

$$\mu_i = R * \mu_i = \sum_j \mu_j D^{\Gamma^{\mu}}_{ji}(R)\,. \tag{6.2}$$

Then if we sum over the operations in the group, we get

$$|G|\,\mu_i = \sum_{R\in G} R * \mu_i = \sum_j \mu_j \sum_R \mathsf{D}^{\Gamma^{\mu}}_{ji}(R)\,. \tag{6.3}$$

Then if Γ^{μ} is irreducible, by (6.1), we have

$$\mu_i = 0 \tag{6.4}$$

unless $\Gamma^{\mu} = \Gamma^{(1)}$. On the other hand, if $\Gamma^{i} = \Gamma^{(1)}$, then this equation is simply $\mu_i = \mu_i$. It tells us nothing about this quantity — it can be any value.

If Γ^{μ} is reducible, then we can reduce it and then apply it to each irreducible components of it. Only the components that transforms as $\Gamma^{(1)}$ can be non-zero.

This leads to an important conclusion. The number of independent nonzero components of a physical quantity μ is the number of times that the symmetric representation occurs in Γ^{μ}.

Example. The polarisability α is a rank 2 symmetric tensor describing the dipole moment of an object induced by an electric field

$$\mu_i = \sum_j \alpha_{ij} E_j\,, \tag{6.5}$$

where $i, j \in \{x, y, z\}$, and $\alpha_{ij} = \alpha_{ji}$ by symmetry. It therefore has six independent components and the component α_{ij} transforms like the quadratic Cartesian function ij.

The BF_3 molecule belongs to the D_{3h} point group, and the character table of D_{3h} tells us how does the quadratic functions transforms in D_{3h}.

Component	Cartesian function	Irrep	Conclusion
α_{zz}	z^2	A_1'	$\alpha_{zz} \neq 0$
$\alpha_{xx} + \alpha_{yy}$	$x^2 + y^2$	A_1'	$\alpha_{xx} + \alpha_{yy} \neq 0$
$\alpha_{xx} - \alpha_{yy}$	$x^2 - y^2$	E'	$\alpha_{xx} - \alpha_{yy} = 0$
α_{xy}	xy		$\alpha_{xy} = 0$
α_{xz}	xz	E''	$\alpha_{xz} = 0$
α_{yz}	yz		$\alpha_{yz} = 0$

Table 1: The component of polarisability tensor in D_{3h}, the Cartesian function and hence the irreducible representation they transforms as.

The representation spanned by the polarisability components, Γ^α, has two A_1' components, and so the polarisability of BF_3 can only have two independent components: $\alpha_{zz} = \alpha_\parallel$ and $\alpha_{xx} = \alpha_{yy} = \alpha_\perp$.

In quantum mechanics, we often encounter integrals, like $\left\langle \psi \middle| \hat{Q} \middle| \phi \right\rangle = \int \mathrm{d}\tau \, {}^*\psi \hat{Q} \phi$ which frequently arise in spectroscopy. We are often not particularly interested in the exact value of the integral — we just want to know whether it is zero or not. Then symmetry can be a particularly useful argument.

Let's consider a simple integral $\int \mathrm{d}\tau \, F_i^\Gamma$, whose integrand transform as the ith component of the irreducible representation Γ. The integral is over all space, so we can freely transform our integrand without affecting the value of the Integral

$$|G| \int \mathrm{d}\tau \, F_i^\Gamma = \sum_{R \in G} \int \mathrm{d}\tau \, R * F_i^\Gamma = \sum_{R \in G} \int \mathrm{d}\tau \, F_j^\Gamma \mathsf{D}_{ji}^\Gamma(R) \,, \tag{6.6}$$

where F_j^Γ is the corresponding function transforming as the jth component of Γ. Then since (6.1),

$$\sum_{R \in G} \mathsf{D}_{ji}^\Gamma(R) = 0 \tag{6.7}$$

unless Γ is the totally symmetric representation. Hence, we conclude that a integral can be non-zero only if the integrand transforms as the totally symmetric representation.

However, if the integrand is a product of functions and operators, like in $\int \mathrm{d}\tau \, \psi^* \hat{Q} \phi$, where each function and operator transform as some representation on their own, we need to work out how their product transforms. To do this, we need the direct product representation.

6.2 Direct Product Representation

Suppose we have a m-dimensional representation Γ^a generated by a basis $(\mathbf{u}_1, \ldots, \mathbf{u}_m)$ and a n-dimensional representation generated by a basis $(\mathbf{v}_1, \ldots, \mathbf{v}_n)$. We can define a *direct product basis*, $\{\mathbf{u}_i \otimes \mathbf{v}_j\}_{i=1}^{m}{}_{j=1}^{n}$ composed of mn 'combined basis vectors' composed of one basis taken from each basis set. We can then use this to define the *direct product representation*, $\Gamma^a \otimes \Gamma^b$, defined by the action[8]

$$
\begin{aligned}
R * (\mathbf{u}_i \otimes \mathbf{v}_j) \coloneqq (R * \mathbf{u}_i) \otimes (R * \mathbf{v}_j) &= \left(\sum_{k=1}^{m} \mathbf{u}_k \mathsf{D}^a_{ki}(R) \right) \otimes \left(\sum_{l=1}^{n} \mathbf{v}_l \mathsf{D}^b_{lj}(R) \right) \\
&= \sum_{k=1}^{m} \sum_{l=1}^{n} \mathbf{u}_k \otimes \mathbf{v}_l \mathsf{D}^a_{ki}(R) \mathsf{D}^b_{lj}(R) \qquad (6.9) \\
&\eqqcolon \sum_{k=1}^{m} \sum_{l=1}^{n} \mathbf{u}_k \otimes \mathbf{v}_l \mathsf{D}^{\Gamma^a \otimes \Gamma^b}_{(k,l),(i,j)}(R) \,, \qquad (6.10)
\end{aligned}
$$

and so

$$
\mathsf{D}^{\Gamma^a \otimes \Gamma^b}_{(k,l),(i,j)} \coloneqq \mathsf{D}^a_{ki}(R) \mathsf{D}^b_{lj}(R) \,. \qquad (6.11)
$$

The resulting representation is mn dimensional, for which both the indices of the rows and the columns run from $(1,1)$ to (m,n). Of course, you have the freedom to relabel them as a single number from 1 to mn.

We can also find the character of the direct product representation

$$
\begin{aligned}
\chi^{\Gamma^a \otimes \Gamma^b}(R) &= \sum_{(k,l)=(1,1)}^{(m,n)} \sum_{(i,j)=(1,1)}^{(m,n)} \delta_{ki} \delta_{lj} \mathsf{D}^{\Gamma^a \otimes \Gamma^b}_{(k,l),(i,j)} \\
&= \sum_{i,j} \mathsf{D}^{\Gamma^a}_{ii}(R) \mathsf{D}^b_{jj}(R) \\
&= \chi^{\Gamma^a}(R) \chi^{\Gamma^b}(R) \,. \qquad (6.12)
\end{aligned}
$$

The character of a direct product is the product of the characters.

Proposition 6.1. The direct product is distributive on direct sums.

$$
(\Gamma^a \oplus \Gamma^b) \otimes (\Gamma^c \otimes \Gamma^d) = (\Gamma^a \otimes \Gamma^c) \oplus (\Gamma^a \otimes \Gamma^d) \oplus (\Gamma^b \otimes \Gamma^c) \oplus (\Gamma^b \otimes \Gamma^d) \,. \qquad (6.13)
$$

Remark. This allows us to take the direct product of reducible representations as well as the irreducible ones.

Proof. This is the easiest seen by examining the characters of both sides. The character of the left-hand side is

$$
(\chi^a + \chi^b) \times (\chi^c + \chi^d) = \chi^a \chi^c + \chi^a \chi^d + \chi^b \chi^d + \chi^b \chi^d \,, \qquad (6.14)
$$

[8] More formally in pure mathematics, they are known as the *tensor product representations* as they are representations on the tensor product spaces. So in more formal representation theories, all those 'direct products' should be replaced by *tensor products* as tensor products has more algebraic structures than the direct product that we have assumed throughout our calculations below. The tensor product can be though of as the direct product, but with the following few extra equivalence relations imposed (mathematically, this is called taking a quotient)

$$
(v,w) + (v',w) \sim (v+v',w) \,,\ (v,w) + (v,w') \sim (v,w+w') \text{ and } c(v,w) \sim (cv,w) \sim (v,cw) \,. \qquad (6.8)
$$

See more details in section A. However, this is a chemistry course so we will stick to chemists' conventions and call them direct products.

which is exactly the character of the right hand side. The characters are the same so the representations are the same (up to a similarity transform) — remember that the character uniquely determines the irreducible representation decomposition of a reducible representation. □

Now let's consider how a group element act on a product of functions $f(\mathbf{r})g(\mathbf{r}) \equiv fg(\mathbf{r})$:

$$\begin{aligned} R * (fg(\mathbf{r})) &= fg(R^{-1} * \mathbf{r}) && (6.15)\\ &= f(R^{-1} * \mathbf{r})g(R^{-1} * \mathbf{r}) && (6.16)\\ &= (R * f(\mathbf{r}))(R * g(\mathbf{r}))\,. && (6.17) \end{aligned}$$

A symmetry operator R affects each function individually — this is exactly how we defined the direct product representation. Therefore, if some functions $(\xi_1, \ldots, \xi_m)$ transform as a representation Γ^a and some functions $(\eta_1, \ldots, \eta_n)$ transform as a representation Γ^b, then their products $\{\xi_i\eta_j\}$ transforms as the direct product representation $\Gamma^a \otimes \Gamma^b$.

To be more explicit, suppose the representation spanned by the set of functions $\{\xi_i\eta_j\}$ is Γ, then the component of $\xi_i\eta_j$ along $\xi_i\eta_j$ after the action of R is

$$\begin{aligned} \mathsf{D}^{\Gamma}_{(i,j),(i,j)}(R) &= R * (\xi_i\eta_j) \cdot \xi_i\eta_j \\ &= (R * \xi_i \cdot \xi_i)(R * \eta_j \cdot \eta_j) \\ &= \mathsf{D}^a_{ii}(R)\mathsf{D}^b_{jj}(R)\,, && (6.18) \end{aligned}$$

and so the character of R is

$$\chi^{\Gamma}(R) = \sum_{(i,j)=(1,1)}^{(m,n)} \mathsf{D}^{\Gamma}_{(i,j),(i,j)}(R) = \sum_{i,j} \mathsf{D}^a_{ii}(R)\mathsf{D}^b_{jj}(R) = \chi^a(R)\chi^b(R)\,. \tag{6.19}$$

This is indeed the direct product representation.

It is useful to know how many times the symmetric representation occurs in a direct product.

Proposition 6.2. If Γ^a and Γ^b are irreducible, then the direct product $\Gamma^{a*}\otimes\Gamma^b$ (formed by the basis $\{\xi_i^*\eta_j\}$) contains the symmetric representation once if $\Gamma^a \sim \Gamma^b$, and otherwise not at all.

Proof. We use the reduction formula to find the multiplicity of $\Gamma^{(1)}$ in the direct product representation.

$$\begin{aligned} m_1 &= \frac{1}{|G|}\sum_c h_c \chi^1(c)^* \chi^{\Gamma^{a*}\otimes\Gamma^b} \\ &= \frac{1}{|G|}\sum_c h_c \chi^a(c)^* \chi^b(c) \\ &= \delta_{ab}\,. && (6.20) \end{aligned}$$

□

It is also possible to work out such symmetric component.

Proposition 6.3. Suppose two bases $\{\xi_i\}$ and $\{\eta_j\}$ span two identical (not just equivalent) irreducible representations $\Gamma^a = \Gamma^b = \Gamma$, then the symmetric component of a basis vector $\xi_i^*\eta_j$ that transforms as the symmetric representation is

$$(\xi_i^*\eta_j)^{\Gamma^{(1)}} = \delta_{ij}\frac{1}{n_\Gamma}\sum_k \xi_k^*\eta_k\,. \tag{6.21}$$

Proof. We can project the direct product basis vector $\xi_i^*\eta_j$ to A_1.

$$\begin{aligned}
(\xi_i^*\eta_j)^{\Gamma^{(1)}} &= \frac{1}{|G|}\sum_R \mathsf{D}_{11}^{\Gamma^{(1)}}(R)R*(\xi_i^*\eta_j) \\
&= \frac{1}{R}\sum_{k,l}\xi_k^*\eta_l\mathsf{D}_{kl}^{\Gamma}(R)^*\mathsf{D}_{lj}^{\Gamma}(R) && (6.22)\\
&= \frac{1}{n_\Gamma}\sum_{k,l}\delta_{kl}\delta_{ij}\xi_k^*\eta_l && (6.23)\\
&= \delta_{ij}\frac{1}{n_\Gamma}\sum_k \xi_k^*\eta_k\,. && (6.24)
\end{aligned}$$

We can see that a basis function $\xi_i^*\eta_j$ has a symmetric component if and only if $i = j$. This is exactly the (unnormalised) function in the span of the direct product basis that transforms as the symmetric representation. □

Example. For example, in the BF_3 molecule under D_3,

$$\begin{aligned}
\xi_x &= \frac{1}{\sqrt{2}}(s_c - s_b) \\
\xi_y &= \frac{1}{\sqrt{6}}(2s_a - s_b - s_c)
\end{aligned} \tag{6.25}$$

transform as the x and y components of the E representation respectively. We also have

$$\begin{aligned}
\eta_x &= p_x \\
\eta_y &= p_y
\end{aligned} \tag{6.26}$$

transform as the x and y components of the E representation respectively. Then we know that

$$\xi_x^*\eta_x + \xi_y^*\eta_y \tag{6.27}$$

transforms as the symmetric representation A_1. If we, for any reason, want to work out the components of the boron p orbitals and the fluorine s orbitals that gives non-zero overlap integral, than this is the one.

Let's conclude everything up. If ξ_i^a transforms as the component i of irreducible representation Γ^a and η_j^n transforms as the component j of the irreducible representation Γ^b:

- The overlap integral

$$\int \mathrm{d}\tau\, \xi_i^{a*} \eta_j^b = 0 \tag{6.28}$$

unless $\Gamma^a \sim \Gamma^b$.

- If $\Gamma^a = \Gamma^b = \Gamma$, then

$$\int \mathrm{d}\tau\, \xi_i^{\Gamma*} \eta_j^{\Gamma} = 0\,. \tag{6.29}$$

- If $\Gamma^a = \Gamma^b = \Gamma$ and $i = j$, then

$$\int \mathrm{d}\tau\, \xi_i^{\Gamma*} \eta_i^{\Gamma} = \frac{1}{n_\Gamma} \int \mathrm{d}\tau \sum_k \xi_k^{\Gamma*} \eta_k^{\Gamma}\,, \tag{6.30}$$

which implies that the integral is the same for all i.

If, in addition, we have an operator $\hat{Q}_k^c$ transforming as the component k of the irreducible representation, then

- The integral

$$\int \mathrm{d}\tau\, \xi_i^{a*} \hat{Q}_k^c \eta_j^b = 0 \tag{6.31}$$

unless $\Gamma^a \in \Gamma^b \otimes \Gamma^c$.

- The operator is totally symmetric e.g. the Hamiltonian, then

$$\int \mathrm{d}\tau\, \xi_i^{a*} \hat{Q}^{\Gamma^{(1)}} \eta_j^b = 0 \tag{6.32}$$

unless $\Gamma_a \sim \Gamma_b$.

- If the operator is totally symmetric and $\Gamma^a = \Gamma^b = \Gamma$, then

$$\int \mathrm{d}\tau\, \xi_i^{\Gamma*} \hat{Q}^{\Gamma^{(1)}} \eta_j^{\Gamma} = 0 \tag{6.33}$$

unless $i = j$, in which case the result will be the same for all i.

6.3 The Symmetrised and Antisymmetrised Square

If we have two bases $(\xi_1, \ldots, \xi_n)$ and $(\eta_i, \ldots, \eta_n)$ spanning the same representation Γ, then it turns out to be more useful to consider a transformed direct product basis, known as the *symmetrised* and *antisymmetrised square basis*. The *symmetrised square basis* are functions of the form $\{\xi_i\eta_j + \xi_j\eta_i\}$ that are symmetric with respect to the exchange of η and ξ, and the *antisymmetrised square basis* are those of the form $\{\xi_i\eta_j - \xi_j\eta_i\}$ that are antisymmetric with respect to the exchange of η and ξ.

In turns out that the symmetrised basis transform only among themselves, and so they span a representation of dimension $\frac{1}{2}n(n+1)$ called the *symmetric square* of Γ and

denoted $(\Gamma \otimes \Gamma)_+$. Similarly, the antisymmetrised square basis span a representation of dimension $\frac{1}{2}n(n-1)$ called the *antisymmetrised square*, denoted $(\Gamma \otimes \Gamma)_-$.[9]

Proposition 6.4. The symmetrised and antisymmetrised square have characters

$$\chi^{(\Gamma\otimes\Gamma)_\pm}(R) = \frac{1}{2}[(\chi^\Gamma(R))^2 \pm \chi^\Gamma(R^2)]\,. \tag{6.34}$$

We are not proving this.[10]

It is possible to construct higher powers of a representation as well as their symmetrised and antisymmetrised parts, but they are in general of less interest. You will meet the symmetrised cube in one of the exercises.

Example. If we have two sets of basis functions, (ξ_x, ξ_y) and (η_x, η_y), both transforming as the irreducible representation E in D_3. Then the direct product basis is $(\xi_x\eta_x, \xi_x\eta_y, \xi_y\eta_x, \xi_y\eta_y)$, and the direct product transforms as $E \otimes E = A_1 \oplus A_2 \oplus E$.

We can transform this into symmetrised and antisymmetrised basis. The symmetrised basis is $(\xi_x\eta_x, \xi_y\eta_y, \xi_x\eta_y + \xi_y\eta_x)$ and the antisymmetrised basis is $(\xi_x\eta_y - \xi_y\eta_x)$. The symmetrised square is $(E \otimes E)_+ = A_1 \oplus E$, and the antisymmetrised square is $(E \otimes E)_- = A_2$. We can also work out the symmetry adapted functions using the projection formula.

A_1:	$\xi_x\eta_x + \xi_y\eta_y$	symmetric
A_2:	$\xi_x\eta_y - \xi_y\eta_x$	antisymmetric
E:	$\xi_x\eta_y + \xi_y\eta_x$ $\xi_x\eta_x - \xi_y\eta_y$	symmetric

6.4 Electronic Terms

An important application of this is in the electronic configuration of molecules. If we have two electrons in the same degenerate set of orbitals $\{\psi_i\}$, then we can take the wavefunctions of the first electron as a basis $\xi_i = \psi_i(\mathbf{r}_1)$ and the wavefunctions of the second electron as a basis $\eta_i = \psi_i(\mathbf{r}_2)$. We can construct orbitally symmetric functions

$$\xi_i\eta_j + \xi_j\eta_i = \psi_i(\mathbf{r}_1)\psi_j(\mathbf{r}_2) + \psi_j(\mathbf{r}_1)\psi_i(\mathbf{r}_2) \tag{6.35}$$

and orbitally antisymmetric ones

$$\xi_i\eta_j - \xi_j\eta_i = \psi_i(\mathbf{r}_1)\psi_j(\mathbf{r}_2) - \psi_j(\mathbf{r}_1)\psi_i(\mathbf{r}_2)\,. \tag{6.36}$$

The orbitally symmetric ones, i.e. the components of the symmetrised square, are by construction symmetric with respect to the exchange of the electrons' spatial coordinates $\mathbf{r}_1 \leftrightarrow \mathbf{r}_2$, so by the Pauli's principle, they have to be combined with antisymmetric (singlet) spin functions to maintain the overall antisymmetry of the electronic

[9] You can choose any distinct i and j to form a symmetric and antisymmetric basis vector — these account for $\frac{1}{2}n(n-1)$ of them each. In addition to that, symmetric basis can also have $\xi_i\eta_i + \xi_i\eta_i \sim \xi_i\eta_i$, which would vanish for the antisymmetric case, so the symmetric basis has n more basis vectors. The symmetric and antisymmetric basis sum up to n^2 basis vectors as expected, as they are a basis transformation of the direct product basis so they should span the same vector space, and we should apparently have $\Gamma \otimes \Gamma = (\Gamma \otimes \Gamma)_+ \oplus (\Gamma \otimes \Gamma)_-$.

[10] See Dexter Chua's notes on Mathematical Tripos Part II: *Representation Theory*.

wavefunction. Similarly, the orbitally antisymmetric ones are the components of the antisymmetrised square, and should be combined with the symmetric (triplet) spin wavefunction.

Example. In D_3 group, we have

$$E \otimes E = A_1 \oplus [A_2] \oplus E\,, \tag{6.37}$$

where the antisymmetrised square are in the square bracket. For a e^2 configuration of a D_3 molecule, with two electrons in a get of degenerate E orbitals. By the above argument, the allowed molecular terms are ${}^1A_1$, ${}^3A_2$ and ${}^1E$, and ${}^3A_2$ is the ground state by Hund's first rule.

In O_h group,

$$T_{2g} \otimes T_{2g} = A_{1g} \oplus E_g \oplus [T_{1g}] \oplus T_{2g}\,, \tag{6.38}$$

so the configuration t_{2g}^2 leads to the molecular terms ${}^1A_{1g}$, ${}^1E_g$, ${}^1T_{2g}$ and ${}^3T_{1g}$, and the term ${}^3T_{1g}$ is the lowest energy one.

6.4.1 Direct Product of Representations of the Full Rotation Group

Proposition 6.5 (Clebsch–Gordan Rule).

$$\Gamma^{J_1} \otimes \Gamma^{J_2} = \Gamma^{(J_1+J_2)} \oplus \Gamma^{(J_1+J_2-1)} \oplus \cdots \oplus \Gamma^{|J_1-J_2|}\,. \tag{6.39}$$

You will prove this in one of the exercises.

Proposition 6.6. The symmetrised and antisymmetrised squares of Γ^J are

$$\begin{aligned}(\Gamma^J \otimes \Gamma^J)_+ &= \Gamma^{(2J)} \oplus \Gamma^{(2J-2)} \oplus \cdots \oplus \Gamma^{(0)} \\ (\Gamma^J \otimes \Gamma^J)_- &= \Gamma^{(2J-1)} \oplus \Gamma^{(2J-3)} \oplus \cdots \oplus \Gamma^{(1)}\,.\end{aligned} \tag{6.40}$$

We will not prove this, but this is rather useful. It allows us to construct the atomic terms.

Example. For the p^2 configuration of an atom,

$$\begin{aligned}(P \otimes P)_+ &= \Gamma^{(2)} \oplus \Gamma^{(0)} = D \oplus S \\ (P \otimes P)_- &= \Gamma^{(1)} = P\,,\end{aligned} \tag{6.41}$$

so the allowed terms are ${}^1D$, ${}^3P$ and ${}^1S$. ${}^3P$ has the lowest energy.

Similarly the allowed terms for the d^2 configuration are ${}^1G$, ${}^3F$, ${}^1D$, ${}^3P$ and ${}^1S$. ${}^3F$ has the lowest energy.

6.5 Jahn–Teller Theorem

Consider a molecule with a electronic term Γ, where the dimension of the irreducible representation Γ is $n \geq 1$. If $n = 1$, then this is a non-degenerate electronic state

$|\psi\rangle$, while if $n > 1$, we have n degenerate electronic states $\{|\psi_1\rangle, |\psi_2\rangle, \ldots, |\psi_n\rangle\}$. You probably have met Jahn–Teller effect in coordination chemistry, where an asymmetric distortion of a complex breaks this degeneracy and results in a decrease/increase of the energy. This is in fact a general phenomenon.

Theorem 6.7 (Jahn–Teller Theorem). Consider a distortion of symmetry $\Gamma^Q \neq \Gamma^{(1)}$ to the molecule.

- If the electronic state Γ is non-degenerate, then the distortion will not change the energy of $|\psi\rangle$ to the first order, i.e. the molecule is stable against distortion.
- If the electronic state Γ is degenerate, then the distortion will lower the energy of at least one of the n degenerate electronic states $\{|\psi_1\rangle, |\psi_2\rangle, \ldots, |\psi_n\rangle\}$ if and only if $\Gamma^Q \in (\Gamma \otimes \Gamma)_+$. This is known as the *Jahn–Teller condition.*

This distortion can be done by simply by a vibration of the atoms if there is a normal mode with appropriate symmetry, so degenerate states of molecules naturally unstable and would spontaneous break its symmetry to reduce its energy.

Proof. If a molecule is distorted away from its original symmetric geometry, the Hamiltonian will change. We can view this as introducing a perturbation V_Q to the Hamiltonian of the symmetry Γ^Q. From non-degenerate perturbation theory[11], if Γ is one-dimensional, then the first order change in energy is

$$\epsilon = \left\langle \psi \middle| \hat{V}_Q \middle| \psi \right\rangle , \tag{6.42}$$

which transforms as $\Gamma^* \otimes \Gamma^Q \otimes \Gamma = \Gamma^Q \neq \Gamma^{(1)}$. Therefore, this first order energy change will be evaluated to zero. A closed shell molecule is stable against distortion.

Now consider the case where Γ is degenerate. Degenerate perturbation theory shows that the energy changes are, to the first order, the eigenvalues ϵ_i of the matrix V with matrix elements

$$V_{ij} = \left\langle \psi_i \middle| \hat{V}_Q \middle| \psi_j \right\rangle . \tag{6.43}$$

We will assume that the functions ψ_i are all real (which can always be made so for degenerate orbitals) are note that the perturbation $\hat{V}_Q$ is just a change in potential, which is a real function, so

$$V_{ij} = \int \mathrm{d}\tau\, \psi_i \psi_j V_Q = \frac{1}{2} \int \mathrm{d}\tau\, (\psi_i \psi_j + \psi_j \psi_i) V_Q . \tag{6.44}$$

This will be non-zero if and only if $\Gamma^Q \in (\Gamma \otimes \Gamma)_+$. We will show that at least one of the energy changes ϵ_i are negative.

The sum of the energy changes is zero since

$$\sum \epsilon_i = \sum V_{ii} = \int \mathrm{d}\tau \left(\sum_i \psi_i^2 \right) V_Q , \tag{6.45}$$

[11] See my notes on C7: *Further Quantum Mechanics* or Mathematical Tripos Part II: Principles of Quantum Mechanics.

and $\sum_i \psi_i^2$ transforms as the totally symmetric representation. Hence, this sum vanishes provided $\Gamma^Q \neq \Gamma^{(1)}$. However, the sum of the square of the energy changes is

$$\sum_i \epsilon_i^2 = \mathrm{tr}(\mathsf{V}^2) = \sum_{ij} V_{ij} V_{ji} = \sum_{ij} |V_{ij}|^2 \ , \tag{6.46}$$

which will be non-zero if any of the elements of V is non-zero. This is true if $\Gamma^Q \in (\Gamma \otimes \Gamma)_+$. Combining these two results, at least one of the energy changes should be negative. □

Claim 6.8. For all non-linear molecules, there is always a distortion with symmetry $\Gamma^Q \in (\Gamma \otimes \Gamma)_+$. However, for linear molecules, there is never a distortion satisfying the Jahn–Teller condition.

Proof. The first claim is difficult to prove. See Landau and Lifshitz, *Quantum Mechanics (Non-Relativistic Theory)*, 3rd edition, pp. 407-412 for a discussion. The second claim is not difficult, and is one of your exercises. □

Stability and degeneracy are not possible simultaneously unless the molecule is a linear one.

6.5.1 Jahn–Teller Distrotion in Octahedral d^9 Complexes

The classical example of Jahn–Teller distortion is the octahedral d^9 complex. The ground electronic state is ${}^1E_g$, with symmetrised square $A_{1g} \oplus E_g$. Hence a E_g distortion will meet the Jahn–Teller condition. Vibration modes with E_g symmetry will break the degeneracy of the two ${}^1E_g$ states (which technically should no longer be labelled ${}^1E_g$ after distortion). The first component of the E_g ligand vibration mode is when ligands along z direction move out and the x and y ones move in, and the other component of this E_g mode has the x ligands moving out and the y ligands moving in, while the z ligands are stationary. Any linear combination of these two degenerate normal modes will lead to a splitting of the e_g orbitals in first order, giving one orbital lowered in energy and the other raised. For large distortions the repulsion between the ligands and the central ion causes the energy to rise.

Therefore, the d^9 complexes will be distorted and the double degeneracy of the two ${}^1E_g$ electronic states will be broken to allow the molecule to sit in a lower energy non-degenerate electronic state.

6.5.2 Jahn–Teller Distrotion in Octahedral d^8 Complexes

The situation for the d^8 complexes are more subtle. The electron configuration is e_g^2 and the allowed terms are ${}^1E_g$, ${}^1A_{1g}$ and ${}^3A_{2g}$. By Hund's first rule, the lowest energy state in the octahedral geometry is ${}^3A_{2g}$, with ${}^1E_g$ above it and the ${}^1A_{1g}$ above that. However, ${}^1E_g$ is degenerate, so it is subjected to Jahn–Teller distortion of E_g symmetry, which may reduce the energy below that of triplet. Consequently in d^8 we may get either a symmetric triplet state or a distorted singlet state.

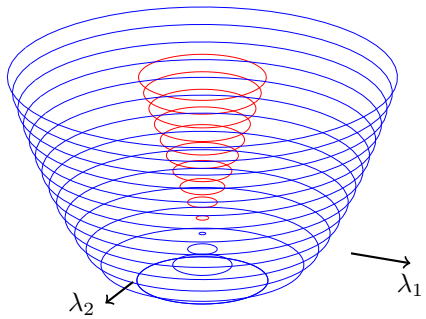


Figure 6.1: The energy of the two ^1E_g electronic states of a d^9 complex against two vibration coordinates of E_g symmetry. The scale of the distortion along the two modes are λ_1 and λ_2 respectively, and the energy of one of the electronic states (the blue one) has its minima at non-zero magnitude of distortions, leading to the spontaneous symmetry breaking of the complex.

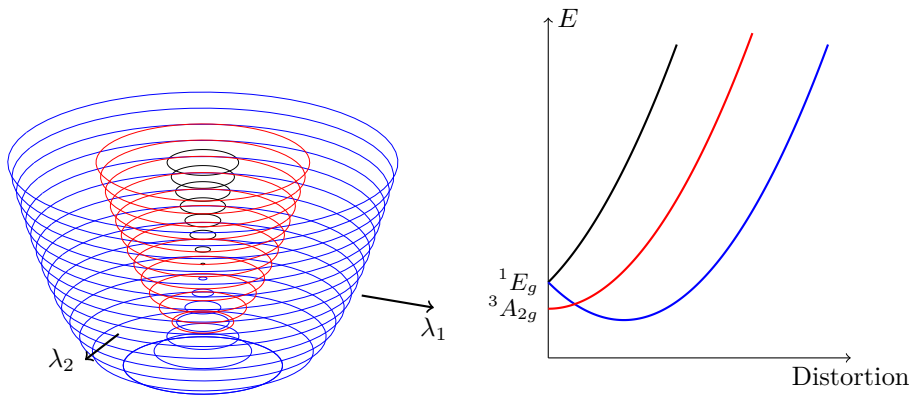


Figure 6.2: The energy of the electronic states of a d^8 complex against distortion. In the undistorted octahedral complex, the $^3A_{2g}$ is the ground state, but the ^1E_g state is subjected to Jahn–Teller distortion, which may or may not reduce its energy below the triplet state.

6.5.3 The Dynamical Jahn–Teller Effect

In some molecules the energy associated with the Jahn–Teller distortion is small compared with $k_B T$, and then the distortion is not static but dynamic. This does not occur in the octahedral d^9 complexes, where there is a strong interaction between the e_g orbitals and the ligands, but it is common in complexes where only the t_{2g} orbitals are occupied, since these interact much more weakly with the ligands.

7 Vibrational Coordinates

8 More on Symmetry Operations

9 Selection Rules

Appendices

A Tensor Product

There are many ways to define a tensor product space. The definition we will take here is a rather hands-on construction of the space, which involves picking a basis.

Definition A.1. Let V and W be vector spaces over $\mathbb{F}$ (always C in our cases). Let $(\mathbf{v}_1, \ldots, \mathbf{v}_m)$ and $(\mathbf{w}_1, \ldots, \mathbf{w}_n)$ be the bases of V and W respectively. The *tensor product space* $V \otimes W$ is a nm-dimensional vector space over $\mathbb{F}$ with basis given by formal symbols

$$\{\mathbf{v}_i \otimes \mathbf{w}_j \mid 1 \leq i \leq m, 1 \leq j \leq n\} \tag{A.1}$$

and thus

$$V \otimes W = \left\{ \sum_{i,j} \lambda_{ij} \mathbf{v}_i \otimes \mathbf{w}_j \,\middle|\, \lambda_{ij} \in \mathbb{F} \right\} \tag{A.2}$$

with addition

$$\sum_{i,j} \lambda_{ij} \mathbf{v}_i \otimes \mathbf{w}_j + \sum_{i,j} \mu_{ij} \mathbf{v}_i \otimes \mathbf{w}_j = \sum_{i,j} (\lambda_{ij} + \mu_{ij}) \mathbf{v}_i \otimes \mathbf{w}_j \tag{A.3}$$

and scalar product define via basis

$$(\mathbf{v}_i \otimes \mathbf{w}_j) \cdot (\mathbf{v}_k \otimes \mathbf{w}_l) = (\mathbf{v}_i \cdot \mathbf{v}_k)(\mathbf{w}_j \cdot \mathbf{w}_l)\,. \tag{A.4}$$

If

$$\mathbf{v} = \sum_i \alpha_i \mathbf{v}_i \in V\,, \quad \mathbf{w} = \sum_j \beta_j \mathbf{w}_j\,, \tag{A.5}$$

then their tensor product is defined as

$$\mathbf{v} \otimes \mathbf{w} = \sum_{i,j} \alpha_i \beta_j (\mathbf{v}_i \otimes \mathbf{w}_j)\,. \tag{A.6}$$

Remark. This allows as to compactly write a vector in a tensor product space as a matrix, with components λ_{ij}, and hence a matrix is also known as a *rank-two tensor*.

Definition A.2. Let $P : V \to V$ and $Q : W \to W$ be linear maps (matrices) on V and W respectively. Then we define $P \otimes Q$ to be a linear map on $V \otimes W$, defined by

$$(P \otimes Q)(\mathbf{v}_i \otimes \mathbf{w}_j) = (P\mathbf{v}_i) \otimes (Q\mathbf{w}_j)\,. \tag{A.7}$$

A direct product representation, which should really be called a *tensor product representation*, is then defined as the tensor product of representations.

Definition A.3. Let G be a finite group and $\Gamma^V : G \to \mathrm{GL}(V)$ and $\Gamma^W : G \to \mathrm{GL}(W)$ be representations of G. Then the *tensor product representation* $\Gamma^V \otimes \Gamma^W$ is defined by

$$\begin{aligned} \Gamma^V \otimes \Gamma^W : G &\to \mathrm{GL}(V \otimes W) \\ g &\mapsto \Gamma^V(g) \otimes \Gamma^W(g)\,. \end{aligned} \tag{A.8}$$

Proposition A.4. If the character of Γ^V is χ^V and the character of Γ^W is χ^W, then the character of $\Gamma^V \otimes \Gamma^W$ is $\chi_V \chi^W$.

Proof. For $g \in G$, let $(\mathbf{v}_1, \ldots, \mathbf{v}_m)$ be a basis of V of eigenvectors of $\Gamma^V(g)$ and let $(\mathbf{w}_1, \ldots, \mathbf{w}_m)$ be a basis of eigenvectors of $\Gamma^W(g)$, with

$$\Gamma^V(g)\mathbf{v}_i = \lambda_i \mathbf{v}_i \,, \quad \Gamma^W \mathbf{w}_j = \mu_j \mathbf{w}_j \,. \tag{A.9}$$

Then

$$\begin{aligned}(\Gamma^V \otimes \Gamma^W)(g)(\mathbf{v}_i \otimes \mathbf{w}_j) &= \Gamma^V(g)\mathbf{v}_i \otimes \Gamma^W(g)\mathbf{w}_j \\ &= \lambda_i \mathbf{v}_i \otimes \mu_j \mathbf{w}_j \\ &= (\lambda_i \mu_i)(\mathbf{v}_i \otimes \mathbf{v}_j) \,. \end{aligned} \tag{A.10}$$

So

$$\chi^{\Gamma^V \otimes \Gamma^W}(g) = \sum_{i,j} \lambda_i \mu_j = \left(\sum_i \lambda_i \right) \left(\sum_j \mu_j \right) = \chi^V(g)\chi^W(g) \,. \tag{A.11}$$

□

If you are interested in more of this, see e.g. Dexter Chua's notes on Mathematical Tripos Part II: *Representation Theory*.