# Symmetry

## University of Cambridge Part II Natural Sciences Tripos

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# Acknowledgements

# 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.

# Contents

# 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. $|2s\rangle$ to $|2p_z\rangle$, but there do exists symmetry operators that transforms $|2s\rangle$ 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

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

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

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

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.

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[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 $\alpha$ 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 $H - O - H$ 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.
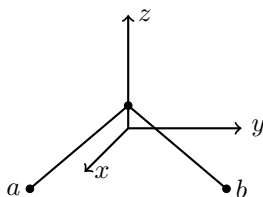


Let's associate some orbitals and vectors to track what everything is going on. Consider a nuclear permutation operator $(ab)$ that permutes the labels of the hydrogen nuclei $a$ and $b$ only, leaving everything else unchanged. The action of this operator is shown in figure 1.1. Notice that since the 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 $\sigma_v^{yz}$ to the associated objects (vectors, functions etc.), as shown in figure 1.2, and the action of $(ab)E^*$ is the same as $\sigma_v^{xz}$ to the associated objects as shown in figure 1.3.
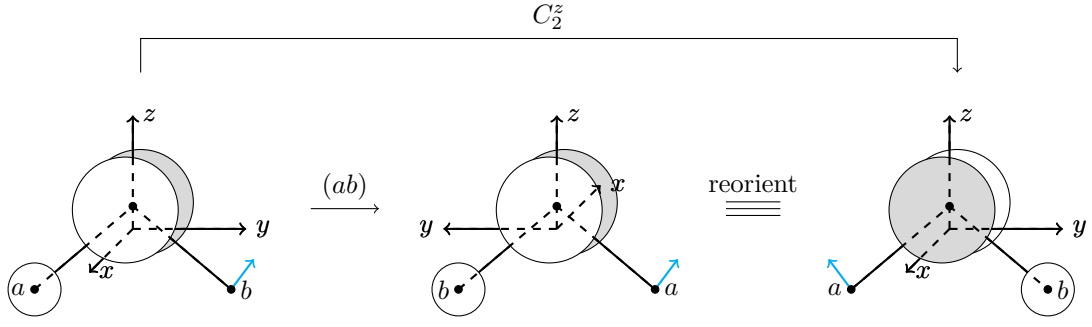
Figure 1.1: The action of a nuclear permutation operator $(ab)$ on $H_2O$ is equivalent to $C_2^z$ on associated objects.
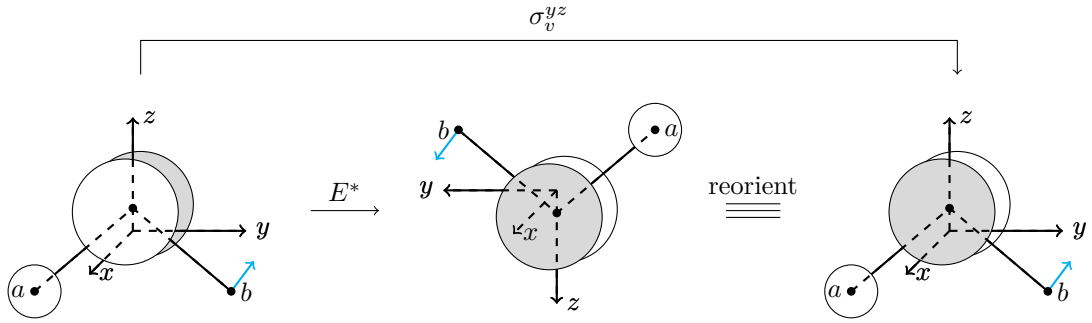


Figure 1.2: The action of a parity inversion operator $E^*$ on $H_2O$ is equivalent to $\sigma_v^{yz}$ on associated objects.
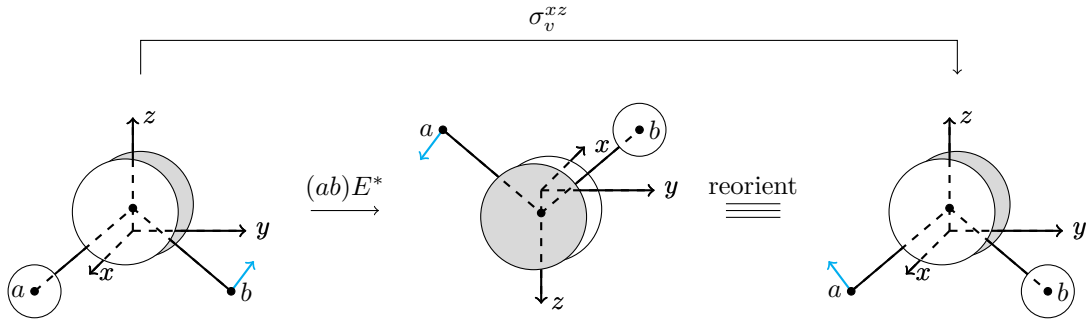


Figure 1.3: The action of a parity inversion operator $(ab)E^*$ on $H_2O$ is equivalent to $\sigma_v^{xz}$ on associated objects.

### 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, $\psi_{\text{rot}}$ is a spherical harmonic $Y_{JM}(\theta, \varphi)$, where $\theta$ and $\varphi$ 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.

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[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 $P_\ell^m$ 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, $\theta$ becomes $\pi - \theta$ and $\varphi$ 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 $\psi_{ns} = 1$. 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 $\varphi$ 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

$$X = \left\{ \triangle, \triangle, \triangle \right\}. \tag{2.1}$$

Then we have, for example,

$$E * \triangle = \triangle. \tag{2.2}$$

$$C_3 * \triangle = \triangle. \tag{2.3}$$

$$C_3 * \left( C_3 * \triangle \right) = C_3 * \triangle = \triangle \tag{2.4}$$

$$= C_3^2 * \triangle = \triangle \tag{2.5}$$

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.

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[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 will omit $\cdot$ and $*$ because it will be clear that we are taking group product/group action from the context. However, note that $RS\psi$ means $R*(S*\psi)$. We act $S$ on $\psi$ 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.
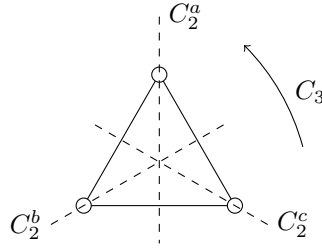


Then the symmetries form a $D_3$ group, whose group table can be obtained as following.

|       | $E$     | $C_3$   | $C_3^2$ | $C_2^a$ | $C_2^b$ | $C_2^c$ |
|-------|---------|---------|---------|---------|---------|---------|
| $E$     | $E$     | $C_3$   | $C_3^2$ | $C_2^a$ | $C_2^b$ | $C_2^c$ |
| $C_3$   | $C_3$   | $C_3^2$ | $E$     | $C_2^c$ | $C_2^a$ | $C_2^b$ |
| $C_3^2$ | $C_3^2$ | $E$     | $C_3$   | $C_2^b$ | $C_2^c$ | $C_2^a$ |
| $C_2^a$ | $C_2^a$ | $C_2^b$ | $C_2^c$ | $E$     | $C_3$   | $C_3^2$ |
| $C_2^b$ | $C_2^b$ | $C_2^c$ | $C_2^a$ | $C_3^2$ | $E$     | $C_3$   |
| $C_2^c$ | $C_2^c$ | $C_2^a$ | $C_2^b$ | $C_3$   | $C_3^2$ | $E$     |

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 $H \le G$, if $H$ is a non-empty subset of $G$, and $H$ is a group on its own under the same group product $\cdot$.

*Example. $C_3 \le D_3$.* 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) $(g, I) \circ (E, h) = (g, h) = (E, h) \circ (g, I)$. $\qquad\qquad\square$

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

| | $E$ | $C_3$ | $C_3^2$ | $C_2^a$ | $C_2^b$ | $C_2^c$ |
|---|---|---|---|---|---|---|
| $E$ | $E$ | $C_3$ | $C_3^2$ | $C_2^a$ | $C_2^b$ | $C_2^c$ |
| $\sigma_h$ | $\sigma_h$ | $S_3$ | $S_3^2$ | $\sigma_v^a$ | $\sigma_v^b$ | $\sigma_v^c$ |

**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 $\sigma_v^{xz}$ plane to the $\sigma_v^{yz}$ 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 $R = (PQ)T(PQ)^{-1}$. $\qquad\square$

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.
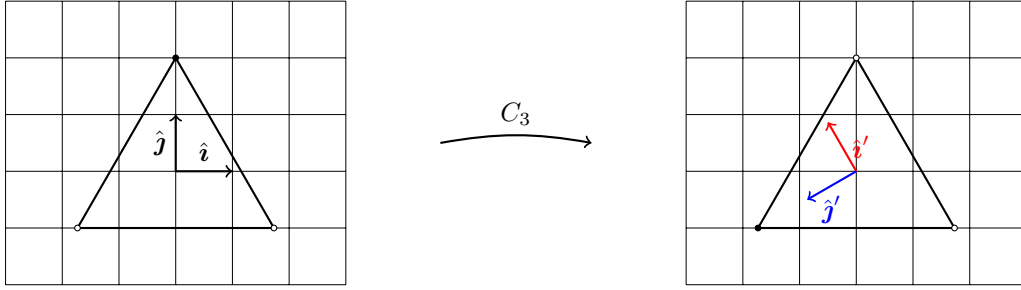


Then to act a $C_3$ operation to the triangle, we can rotate the underlying vector space by $120°$. This operation sends the unit vector $\hat{\imath}$ to $\hat{\imath}' = -\frac{1}{2}\hat{\imath} + \frac{\sqrt{3}}{2}\hat{\jmath}$, and sends $\hat{\jmath}$ to $\hat{\jmath}' = -\frac{\sqrt{3}}{2}\hat{\imath}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

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

Then for any vector

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

we have

$$C_3 * \mathbf{v} = C_3 * \begin{pmatrix} \hat{\imath} & \hat{\jmath} \end{pmatrix} \begin{pmatrix} v_x \\ v_y \end{pmatrix}$$

$$= \begin{pmatrix} \hat{\imath} & \hat{\jmath} \end{pmatrix} \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} v_x \\ v_y \end{pmatrix}. \tag{3.4}$$

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

$$R \cdot S = T, \tag{3.9}$$

we have the corresponding relationship for the representation matrices under matrix multiplication

$$\mathsf{D}(R)\mathsf{D}(S) = \mathsf{D}(T). \tag{3.10}$$

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

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

$$= \begin{pmatrix} \hat{\boldsymbol{\imath}} & \hat{\boldsymbol{\jmath}} \end{pmatrix} \mathsf{D}(R)\mathsf{D}(S) \begin{pmatrix} v_x \\ v_y \end{pmatrix}, \tag{3.12}$$

while by the compatibility of group actions, we also have

$$R * (S * \mathbf{v}) = (R \cdot S) * \mathbf{v} = \begin{pmatrix} \hat{\boldsymbol{\imath}} & \hat{\boldsymbol{\jmath}} \end{pmatrix} \mathsf{D}(R \cdot S) \begin{pmatrix} v_x \\ v_y \end{pmatrix}. \tag{3.13}$$

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 $R, S \in G$,

$$\phi(R) \circ \phi(S) = \phi(R \cdot S). \tag{3.14}$$

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 $\mathrm{GL}(n, \mathrm{R})$ (or $GL(n, \mathbb{C})$ 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 $2 \times 2$ 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 the representation is the dimension of the representation matrix.

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

$$\mathsf{D}(R)\mathsf{D}(S) = (1)(1) = (1) = \mathsf{D}(RS) \tag{3.15}$$

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. 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

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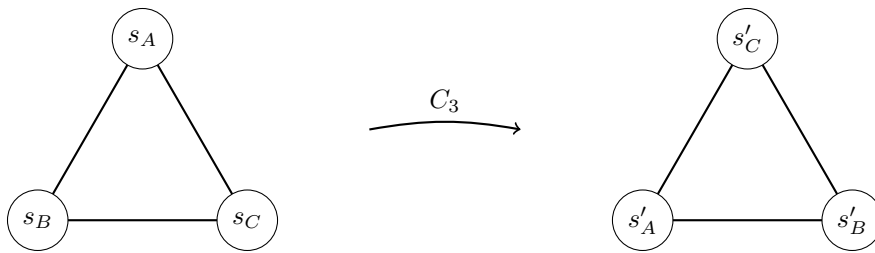


Then, for example, since we have

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

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 $(\varphi_1, \varphi_2, \dots, \varphi_n)$ 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 $\mathsf{D}$ 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 $\mathsf{T}$ 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

$$R * \mathbf{v} = \begin{pmatrix} \hat{\boldsymbol{\imath}} & \hat{\boldsymbol{\jmath}} & \hat{\mathbf{k}} \end{pmatrix} \mathsf{T} \mathsf{T}^{-1} \mathsf{D}(R) \mathsf{T} \mathsf{T}^{-1} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

$$= \begin{pmatrix} \hat{\boldsymbol{\imath}}' & \hat{\boldsymbol{\jmath}}' & \hat{\mathbf{k}}' \end{pmatrix} \mathsf{D}(R)' \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix}. \tag{3.29}$$

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 $\mathsf{D}$ and $\mathsf{D}'$ 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

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

$\omega$ 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, $\text{span}(p_x, p_y)$ and $\text{span}(p_z)$, the *invariant subspaces* of the whole vector space $\text{span}(p_x, p_y, p_z)$. Then if we use this three dimensional basis set to form a representation, it will look like this.

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

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

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

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 $(p_z)$.

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

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

$$\varphi_1 = \sqrt{\frac{1}{3}}(s_a + s_b + s_c)$$

$$\varphi_2 = \sqrt{\frac{1}{6}}(2s_a - s_b - s_c) \tag{3.38}$$

$$\varphi_3 = \sqrt{\frac{1}{2}}(s_b - s_c).$$

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

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

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

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

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 $DD^{xy}$, 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).

# 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 is the traces of the representation matrices.

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

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

*Proof.*

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

$\square$

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,

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

so their traces are equal.

## 4.2 Orthogonality Theorems