

Symmetry

University of Cambridge Part II Natural Sciences Tripos

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Nothing in these lecture notes is original. They are largely based on the notes by Prof. Ali Alavi, who lectured this course in 2024. They are nowhere near accurate representations of what was actually lectured, and in particular, all errors are almost surely mine.

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	4
1.1	Molecular Symmetry	4
1.2	Internal Frame of Reference	7

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

$$\hat{R}\hat{H} = \hat{H}\hat{R}. \quad (1.1)$$

The above condition can be trivially rewritten as

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

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

$$\hat{H}|\psi\rangle = E|\psi\rangle, \quad (1.3)$$

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

$$\hat{H}\hat{R}|\psi\rangle = \hat{R}\hat{H}|\psi\rangle = \hat{R}E|\psi\rangle = E\hat{R}|\psi\rangle. \quad (1.4)$$

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 exist symmetry operators that transform $|2s\rangle$ 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

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

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 it is easy to see that the wavefunction after translation $\psi'(\mathbf{x}_i, \mathbf{x}_j, \dots)$ is given by

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

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

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

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

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

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.

¹A baby version of this Noether's theorem related to the first integral of Lagrangian 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,

$$\mathbf{F} = \frac{dE}{d\mathbf{x}}, \quad (1.9)$$

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

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

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

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

- (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.

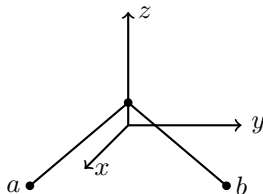
- (iii) *Parity inversion.*

Parity operator inverts the coordinates of the particles through 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{i} , 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 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.

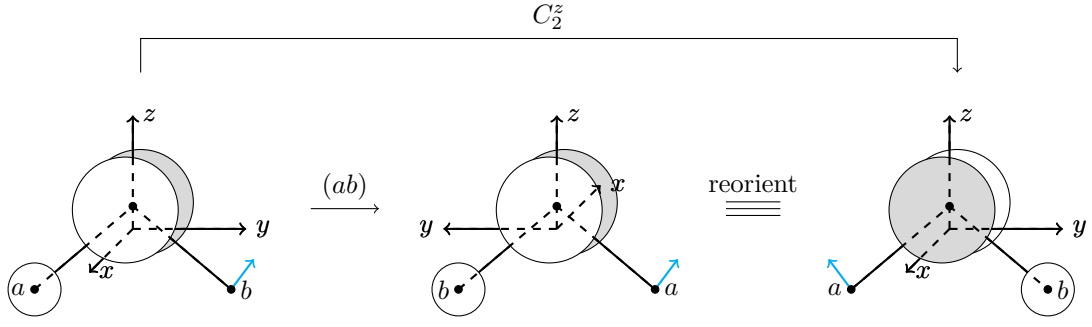


Figure 1.1: The action of a nuclear permutation operator (ab) on H_2O is equivalent to C_2^z on associated objects.

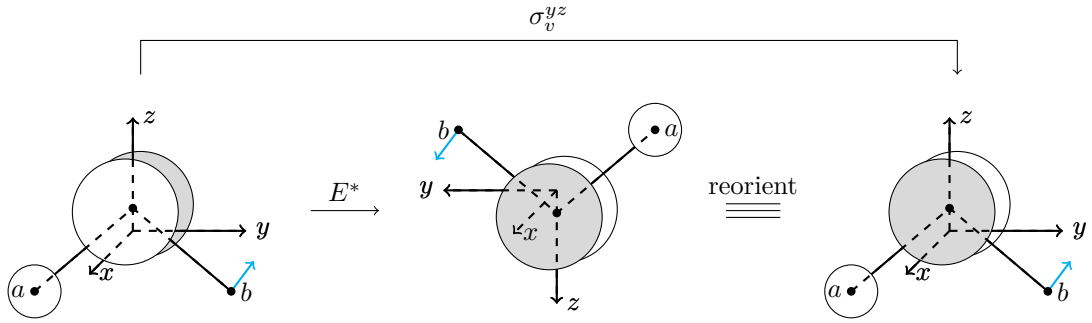


Figure 1.2: The action of a parity inversion operator E^* on H_2O is equivalent to σ_v^{yz} on associated objects.

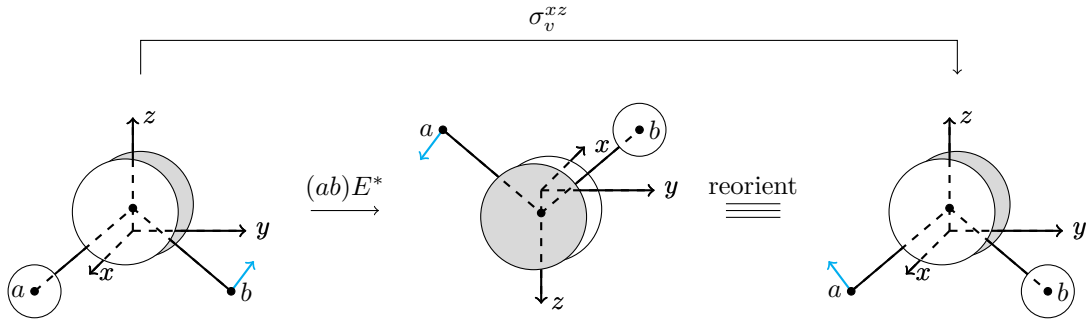


Figure 1.3: The action of a parity inversion operator $(ab)E^*$ on H_2O is equivalent to σ_v^{xz} on associated objects.

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

$$\Psi = \psi_{\text{elec}} \psi_{\text{vib}} \psi_{\text{rot}} \psi_{\text{trans}} \psi_{\text{ns}}. \quad (1.11)$$

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

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

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

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

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.

²The 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

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

where P_{ℓ}^m is the associated Legendre polynomial, defined by

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

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

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