

**Part II Chemistry 2009–10**

**Course B7: Symmetry and Perturbation Theory**

# **Symmetry**

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# Outline

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The purpose of this course is

- To explore the foundations of the theory in a bit more detail;
- In particular, to introduce the Great Orthogonality Theorem and to show how it leads to the important theorems of representation theory;
- To extend the methods introduced in previous courses;
- To investigate a wider range of applications.

Assumed:

- Basic practical use of group theoretical methods as outlined in IB Symmetry and Bonding;
- Matrix methods from the Part IA NST Maths course (there is a reminder of basic definitions in Appendix A);
- Some Perturbation Theory results from the first half of this course.

Not assumed:

- Anything from the Part IB Maths course.

# Recommended books

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- **A. Vincent**, '*Molecular Symmetry and Group Theory*' (Wiley)  
An excellent elementary introduction. Relatively cheap. (If you don't know most of the material in this book you should review it before continuing this course.)
- **A. Cotton**, '*Chemical Applications of Group Theory*' (Wiley)  
Expensive but useful for chemical applications. Don't use the first edition, which contains many errors.
- **P. W. Atkins**, '*Molecular Quantum Mechanics*' (O.U.P.)  
A very good account of theoretical methods and applications, with useful coverage of Group Theory. Recommended for theoretical specialists.
- **J. W. Leech and D. J. Newman**, '*How to use Groups*' (Methuen)  
Short and approachable. Out of print but may be in College libraries.
- **J. P. Elliott and P. G. Dawber**, '*Symmetry in Physics*', vol. 1 (Macmillan)  
Good on basic principles but intended for physicists.

# 1. What is a symmetry operator?

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We define a symmetry operator generally as any operator  $R$  that has an inverse and that commutes with the Hamiltonian:

$$R\mathcal{H} = \mathcal{H}R \quad (1.1)$$

or, equivalently, that leaves the Hamiltonian unchanged:

$$R\mathcal{H}R^{-1} = \mathcal{H}. \quad (1.2)$$

Then, if we have a wavefunction  $\psi$  that satisfies the Schrödinger equation, with energy  $W$ :

$$\mathcal{H}\psi = W\psi,$$

the wavefunction  $R\psi$  also satisfies it, with the same energy:

$$\mathcal{H}(R\psi) = R\mathcal{H}\psi = RW\psi = W(R\psi). \quad (1.3)$$

## Symmetry and degeneracy

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If  $\mathcal{H}\psi = W\psi$  then  $\mathcal{H}(R\psi) = W(R\psi)$ .

$R\psi$  may be the same function as  $\psi$  (possibly multiplied by  $-1$  or some other number). For example, we might find that for some functions  $R\psi = \psi$  and for others  $R\psi = -\psi$ . This allows us to classify functions according to their symmetry behaviour.

But if  $\psi$  and  $R\psi$  are different, symmetry leads to degeneracy: the functions  $\psi$  and  $R\psi$  have the same energy.

We *postulate* that if a set of wavefunctions is degenerate, the degeneracy must be a consequence of some kind of symmetry. Another way of expressing this postulate is

**Accidental degeneracy doesn't happen.**

By 'accidental degeneracy' we mean degeneracy that isn't due to symmetry.

## What kinds of symmetry are there?

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We need to look for operators that don't change the Hamiltonian. We consider isolated molecules.

### 1. Any translation of all particles by the same distance.

If we move all particles by the same amount, then all distances between particles stay the same, so the potential energy doesn't change.

If  $x' = x - d$  then  $\partial/\partial x' = \partial/\partial x$  (by the chain rule), so the  $\nabla^2$  kinetic energy terms in  $\mathcal{H}$  don't change either.

So the Hamiltonian is unchanged if we move the whole molecule to a new position.

This means that moving a molecule to a new position doesn't change its energy. Consequently the force on the molecule (derivative of energy with respect to position) is zero, and so there is no change in momentum.

Thus this symmetry leads to *conservation of linear momentum*.

## Symmetry operations

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### 2. Any rotation of the whole system.

This also leaves all distances unchanged and doesn't affect the potential energy.

Rotation doesn't affect  $\nabla^2$  either (this too can be shown using the chain rule), so the kinetic energy operators stay the same.

We conclude that rotating the whole molecule doesn't change its energy. Consequently the torque (derivative of energy with respect to orientation) is zero, and there is no change in angular momentum.

Thus rotational symmetry of isolated molecules leads to *conservation of angular momentum*.

If  $R_z(\delta\phi)$  is a rotation about the  $z$  axis, we can see that

$$\lim_{\delta\phi \rightarrow 0} \frac{R_z(\delta\phi) - E}{\delta\phi} \psi = \frac{\partial}{\partial \phi} \psi \propto J_z \psi,$$

where  $J_z$  is the usual angular momentum operator. Consequently the theory of rotational symmetry and the theory of angular momentum are one and the same.

## Symmetry operations: electron permutations

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### 3. Any permutation of the electrons.

All electrons are equivalent — the Hamiltonian has a kinetic energy term of the same form for each one, and the potential energy terms also have the same form for every electron. Therefore permuting the electrons has no effect on the Hamiltonian, and any such permutation is a symmetry operation.

Experimental observations can only be explained by quantum mechanics if we require that all wavefunctions are antisymmetric with respect to exchange of electrons. This is the *Pauli principle*.

More generally, it is found experimentally that all wavefunctions have to be *antisymmetric* with respect to exchange of identical fermions of any kind, and *symmetric* with respect to exchange of identical bosons of any kind. For chemistry, we are concerned only with electrons and nuclei. Nuclei with even mass number are bosons, and those with odd mass number are fermions.

## Symmetry operations: nuclear permutations

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### 4. Any permutation of a set of identical nuclei.

Just as for electrons, the Hamiltonian is unchanged in form if we permute the labels of a set of identical nuclei.

### 5. Parity: inversion of every particle in the centre of mass

Again, this leaves particle–particle distances and  $\nabla^2$  terms unchanged and leaves the Hamiltonian invariant. It is called the parity operation, and denoted  $E^*$ , to distinguish it from the inversion operation of finite symmetry groups, usually denoted  $\hat{i}$ .

These are the operations that make up the elements of the ordinary molecular symmetry group.

## Example: the water molecule

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We need to understand the relationship between these operations of inversion and nuclear permutation and the conventional geometrical symmetry operations. This will give us a deeper and more secure understanding of what symmetry operations do.

We are mainly interested in *internal* degrees of freedom — electronic and vibrational — but also sometimes in overall rotation of the molecule. We need a local molecular coordinate frame  $(x, y, z)$ , fixed in the molecule. Internal degrees of freedom are referred to this frame, while the rotational wavefunction depends on the orientation of this local frame relative to the global frame  $(X, Y, Z)$ .

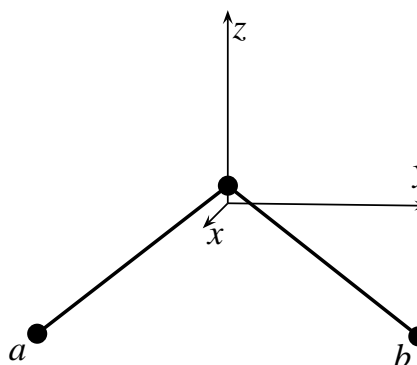
This local frame can usually be defined only in terms of the nuclear labels. If the labels change as the result of a nuclear permutation, the axes may change.

## Symmetry operations of the water molecule

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The local axes have to take account of the fact that the molecule is constantly vibrating, so that at any particular instant its particles are in an unsymmetrical configuration.

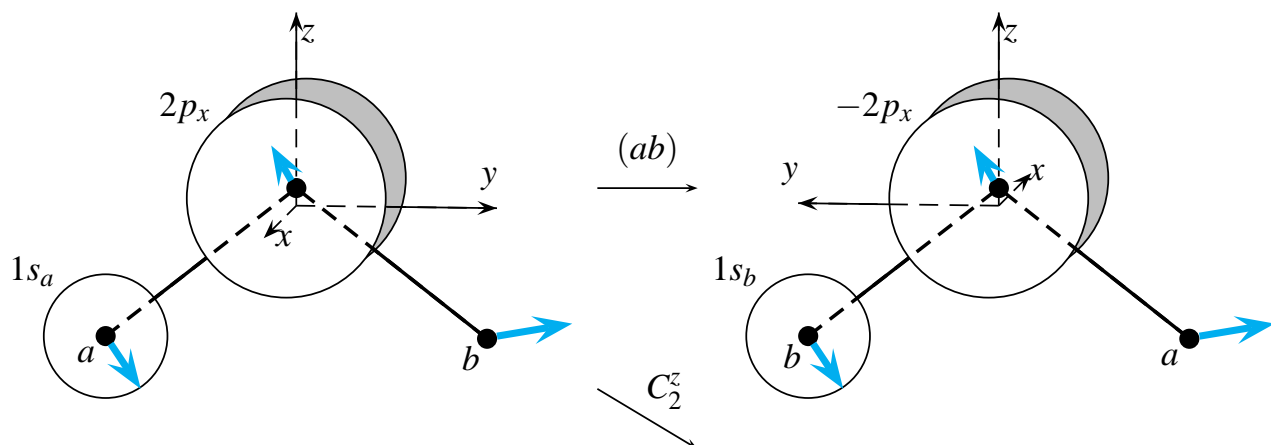
For the water molecule, we define the origin of the local axis system as the centre of mass. The  $z$  axis is parallel to the bisector of the HOH angle. The  $y$  axis is perpendicular to the  $z$  axis, in the molecular plane, and in the general direction from proton  $a$  to proton  $b$ . The  $x$  axis completes a right-handed set. (Other definitions are possible.)



The symmetry operations are  $(ab)$  (i.e. exchange of proton labels  $a$  and  $b$ ), the inversion  $E^*$ , and their product  $(ab)E^*$ , usually abbreviated to  $(ab)^*$ . The identity operation  $E$  completes the group.

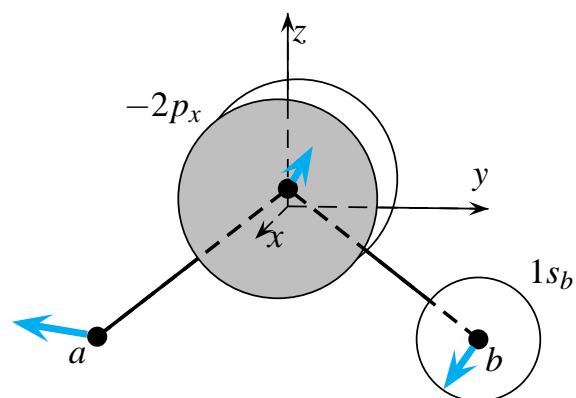
## Symmetry operations of the water molecule: $(ab)$

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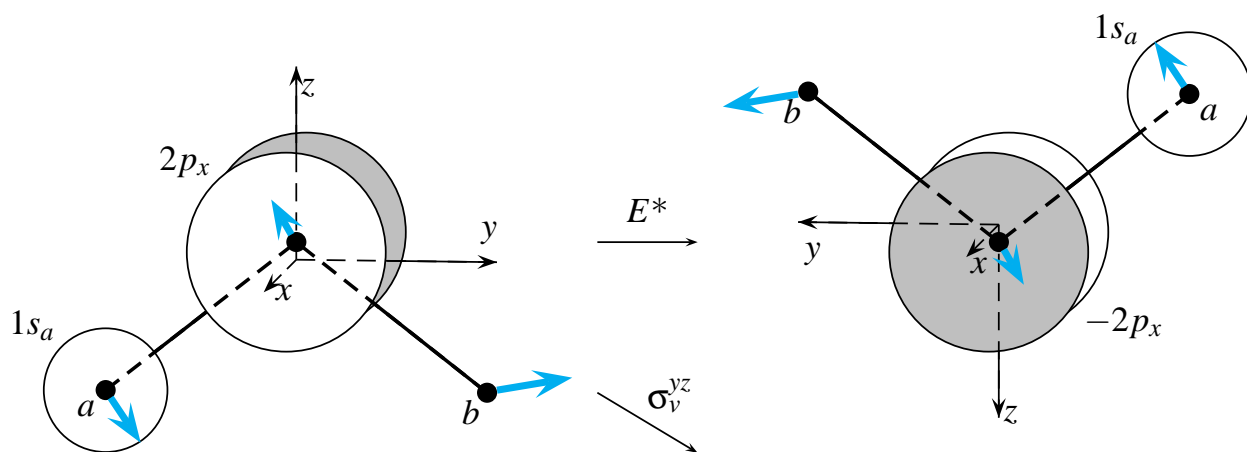
Because the  $y$  axis changes direction when  $a$  and  $b$  are exchanged, the  $x$  axis also has to change direction to maintain a right-handed coordinate frame.

The effect of the  $(ab)$  operation on *internal* coordinates is the same as that of  $C_2^z$ . We see that  $C_2^z$  rotates functions and coordinates but not the nuclear labels.

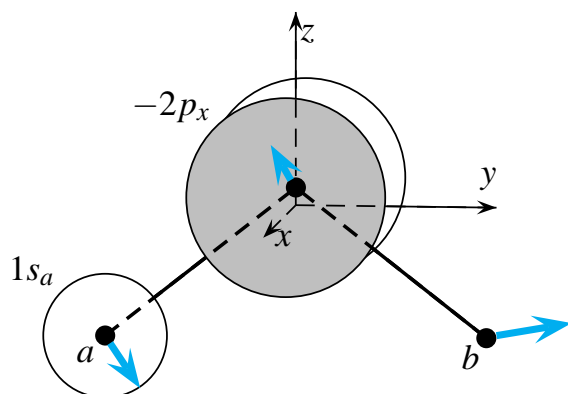


## Symmetry operations of the water molecule: $E^*$

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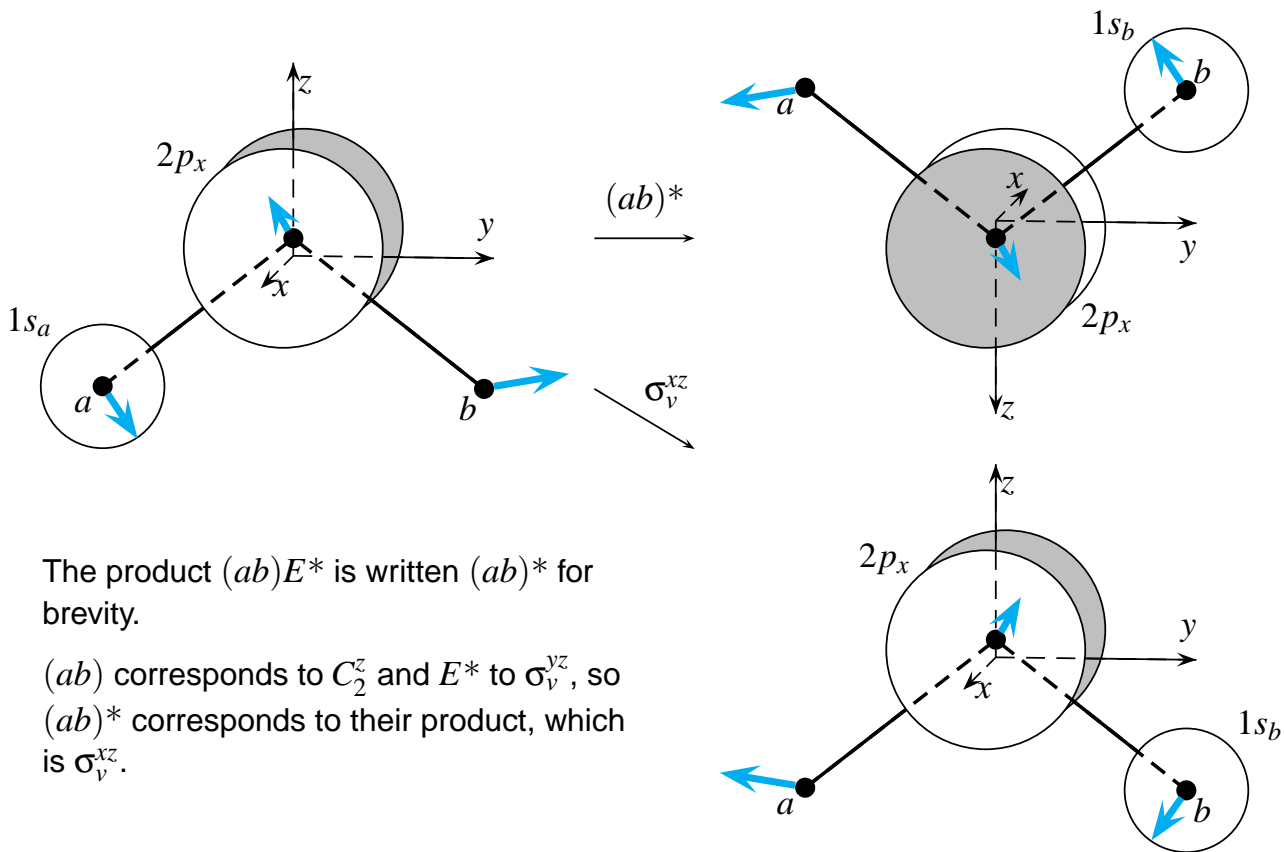


The  $E^*$  operation corresponds to reflection of the internal coordinates in the plane of the nuclei.



# Symmetry operations of the water molecule: $(ab)^*$

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The product  $(ab)E^*$  is written  $(ab)^*$  for brevity.

$(ab)$  corresponds to  $C_2^z$  and  $E^*$  to  $\sigma_v^{yz}$ , so  $(ab)^*$  corresponds to their product, which is  $\sigma_v^{xz}$ .

## Ortho and para hydrogen

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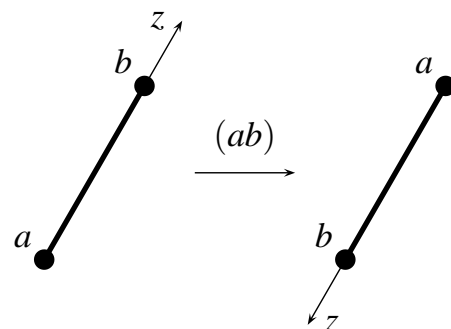
The Pauli principle applies in a more general form to nuclear permutations as well as to electrons. The complete molecular wavefunction has to be antisymmetric with respect to exchange of identical nuclei if they are fermions (i.e. if they have half-odd-integer spin) and symmetric if they are bosons (i.e. if they have integer spin).

The wavefunction of an  $H_2$  molecule is a product of electronic, vibrational, rotational and nuclear-spin factors:

$$\Psi = \Psi_{\text{elec}} \Psi_{\text{vib}} \Psi_{\text{rot}} \Psi_{\text{ns}}$$

The symmetry operation  $(ab)$  which exchanges the proton labels can in principle affect these factors. The ground electronic state of  $H_2$  is  $^1\Sigma_g^+$ , i.e. totally symmetric, so it is unchanged.  $\Psi_{\text{vib}}$  depends only on the bond length  $|\mathbf{r}_a - \mathbf{r}_b|$ , which is unchanged by exchange of  $a$  and  $b$ .

However  $\Psi_{\text{rot}}$  is a spherical harmonic  $Y_{JM}(\theta, \varphi)$ , where  $\theta$  and  $\varphi$  specify the direction of the molecular axis. This axis is reversed when  $a$  and  $b$  are interchanged, and the rotational wavefunction changes sign if  $J$  is odd, and is unchanged if  $J$  is even.





## Ortho and para hydrogen *contd.*

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Finally the nuclear spin function is either a singlet function  $\sqrt{\frac{1}{2}}(\alpha_a\beta_b - \beta_a\alpha_b)$  (antisymmetric under exchange of  $a$  and  $b$ ) or one of the triplet functions  $\alpha_a\alpha_b$ ,  $\sqrt{\frac{1}{2}}(\alpha_a\beta_b + \beta_a\alpha_b)$  and  $\beta_a\beta_b$  (symmetric).

Because the nuclear spins interact only very weakly with the environment, the spin state doesn't change easily, and we speak of *ortho* hydrogen (triplet nuclear spin) and *para* hydrogen (singlet nuclear spin).

For the overall wavefunction to be antisymmetric under exchange of  $a$  and  $b$ , the rotational wavefunction can only have odd  $J$  for ortho hydrogen, and even  $J$  for para hydrogen. Because of the nuclear-spin degeneracy, there is three times as much ortho hydrogen as para at equilibrium at high temperatures, and the line intensities in the rotational Raman spectrum alternate accordingly.

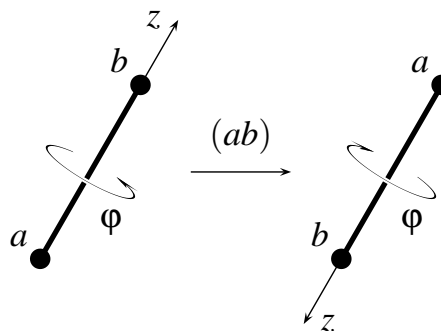
## Carbon dioxide

In  $\text{CO}_2$ , the O atoms have zero spin, so their nuclear spin function is just  $\psi_{\text{ns}} = 1$ . As they are bosons (integer spin) the overall wavefunction must be unaffected by exchange of the O atom labels. Consequently only even- $J$  rotational functions are allowed, and rotational Raman or vibration-rotation transitions involving the odd  $J$  levels are absent.

## Oxygen

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The oxygen molecule,  $\text{O}_2$ , has a  ${}^3\Sigma_g^-$  ground state. The  $(ab)$  operation which exchanges the O nuclei switches the direction of the local  $z$  axis, which we take from nucleus  $a$  to  $b$ . This has the effect of changing the sign of internal  $\varphi$  coordinates, which are measured corkscrew-wise around the  $z$  axis.



The dependence of the  ${}^3\Sigma_g^-$  wavefunction on the  $\varphi$  coordinates of the unpaired electrons is  $\sin(\varphi_1 - \varphi_2)$ . This is the reason for the minus sign on the term symbol, denoting that the wavefunction changes sign under reflection in planes containing the molecular axis.

Consequently the electronic wavefunction changes sign under  $(ab)$ , while the nuclear wavefunction is unchanged, as for  $\text{CO}_2$ . In order for the overall wavefunction to be unchanged, the rotational wavefunction must have odd  $J$ , and the even- $J$  levels are absent.

## 2. Groups

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A *group* is a set of elements, together with a rule for combining them, which together satisfy the *group postulates*:

**Postulate 1:** (*Closure*) The result  $R * S$  of combining any two elements is defined and is an element of the set.

**Postulate 2:** (*Associativity*) Combination is associative:  $(R * S) * T = R * (S * T)$ .

**Postulate 3:** (*Identity*) The set contains an identity  $E$  such that  $E * R = R * E = R$  for any element  $R$  of the set.

**Postulate 4:** (*Inverses*) Every element  $R$  has an inverse  $R^{-1}$  such that  $R * R^{-1} = R^{-1} * R = E$ .

For symmetry operators, the product  $R * S$  (usually written simply as  $RS$ ) is defined as the operator whose effect is that of operating first with  $S$  and then with  $R$ :

$$(RS)\psi \equiv R(S\psi). \quad (2.1)$$

Associativity follows at once:

$$((RS)T)\psi = (RS)(T\psi) = R(S(T\psi)) = R((ST)\psi) = (R(ST))\psi,$$

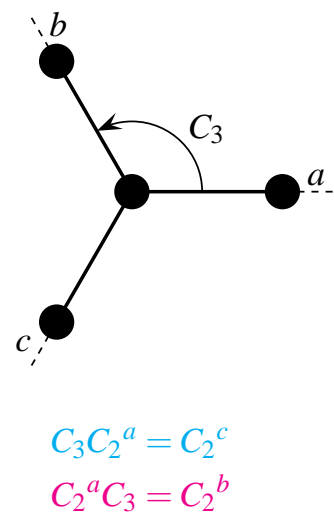
while the Identity and Inverse postulates are satisfied because of the nature of symmetry operations as coordinate transformations.

## Multiplication tables

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A group is summarized in its *multiplication table*, shown below for  $\mathcal{D}_3$ . The product  $RS$  appears in the row labelled  $R$  and the column labelled  $S$ . If  $RS = SR$  for all pairs of elements  $R$  and  $S$ , the group is said to be *Abelian*. This is evidently not the case for  $\mathcal{D}_3$ .

$\mathcal{D}_3$	first					
	$E$	$C_3$	$C_3^{-1}$	$C_2^a$	$C_2^b$	$C_2^c$
second						
$E$	$E$	$C_3$	$C_3^{-1}$	$C_2^a$	$C_2^b$	$C_2^c$
$C_3$	$C_3$	$C_3^{-1}$	$E$	$C_2^c$	$C_2^a$	$C_2^b$
$C_3^{-1}$	$C_3^{-1}$	$E$	$C_3$	$C_2^b$	$C_2^c$	$C_2^a$
$C_2^a$	$C_2^a$	$C_2^b$	$C_2^c$	$E$	$C_3$	$C_3^{-1}$
$C_2^b$	$C_2^b$	$C_2^c$	$C_2^a$	$C_3^{-1}$	$E$	$C_3$
$C_2^c$	$C_2^c$	$C_2^a$	$C_2^b$	$C_3$	$C_3^{-1}$	$E$



The number of possible groups is severely limited by the group postulates.

For example, if a group contains  $C_n$ , then it must contain  $C_n C_n = C_n^2$ ,  $C_n^2 C_n = C_n^3, \dots$ , and  $C_n^n = E$ . The set of  $n$  elements obtained from  $C_n$  in this way is a group (called  $C_n$ ); we say that  $C_n$  *generates* the group  $C_n$ .

Many groups need two or more generators. Not every possible set of generators defines a finite group; in all but a few cases more and more elements are generated *ad infinitum*. The possible finite symmetry groups, for rigid molecules, are given in Appendix B. There are also two infinite groups,  $C_{\infty v}$  and  $D_{\infty h}$ , which are appropriate for linear molecules. Note that the choice of generators is not unique; also that any two of the four  $C_3$  axes in the cubic groups generate the others, as do any two of the six  $C_5$  axes for the icosahedral groups.

## Direct product groups

If two groups  $\mathcal{G}$  (with  $n_G$  elements  $g_i$ ) and  $\mathcal{H}$  (with  $n_H$  elements  $h_j$ ) have no element in common except the identity, and have the property that every  $g_i$  commutes with every  $h_j$ , then the products  $g_i h_j$  form a group of order  $n_G n_H$ , called the *direct product group* and written  $\mathcal{G} \otimes \mathcal{H}$ .

For example,  $\mathcal{D}_{3h} = \mathcal{D}_3 \otimes C_s$ :

- Every element of  $\mathcal{D}_3$  commutes with every element of  $C_s$ .
- Each element of  $\mathcal{D}_{3h}$  is the product of an element of  $\mathcal{D}_3$  with an element of  $C_s$ .

		$\mathcal{D}_3$	$E$	$C_3$	$C_3^{-1}$	$C_2^a$	$C_2^b$	$C_2^c$
$C_s$	$E$		$E$	$C_3$	$C_3^{-1}$	$C_2^a$	$C_2^b$	$C_2^c$
	$\sigma_h$		$\sigma_h$	$S_3$	$S_3^{-1}$	$\sigma_v^a$	$\sigma_v^b$	$\sigma_v^c$

If a group can be expressed as a direct product of two smaller groups, the symmetries described by the two groups can be treated independently.

## Classes: equivalent operations

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Two symmetry operators  $R$  and  $S$  are said to be *equivalent* (notation  $R \sim S$ ) if there is an element  $Q$  in the group such that  $S = QRQ^{-1}$ .

The operator  $QRQ^{-1}$  can be thought of as the operator obtained by applying  $Q$  to the operator  $R$  itself; if  $R$  is a rotation through  $\alpha$  about an axis in the direction of the vector  $\xi$ , then  $QRQ^{-1}$  is a rotation through the same angle  $\alpha$  about the rotated axis  $Q\xi$ .

In  $\mathcal{D}_3$ ,

$$C_2^a C_3 (C_2^a)^{-1} = (C_3)^{-1}$$

$$C_3 C_2^a (C_3)^{-1} = C_2^b = (C_3)^{-1} C_2^c C_3$$

so  $(C_3)^{-1}$  is equivalent to  $C_3$  and  $C_2^b$  is equivalent to  $C_2^a$  and  $C_2^c$ .

However, in  $C_{2v}$ , the two reflections,  $\sigma_v^{xz}$  and  $\sigma_v^{yz}$ , are not equivalent, even though they are both reflections, because there is no symmetry operator in the group that transforms one into the other.

## Classes

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- If  $S \sim R$ , so that  $S = QRQ^{-1}$ , then  $R \sim S$ , because  $R = Q^{-1}SQ$ .
- If  $R \sim S$  and  $S \sim T$ , then  $R \sim T$ .
- It follows that the elements of the group can be divided into *equivalence classes* (or just *classes*), so that all the elements in each class are equivalent to each other and to no other element of the group.
- Notice that the identity  $E$  always forms a class by itself, because for any element  $Q$  in the group,  $QEQ^{-1} = E$ .
- Similarly, every element of an Abelian group forms a class by itself, because in that case  $QRQ^{-1} = RQQ^{-1} = R$ , for any  $Q$ .

### 3. Representations

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A vector  $r$  describing some fixed physical quantity can be specified by setting up a coordinate system in terms of vectors  $i$ ,  $j$  and  $k$ . In practice the basis is often suppressed, but when we write

$$r = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

we really mean

$$r = ix + jy + kz = \begin{pmatrix} i & j & k \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}. \quad (3.1)$$

This is a *representation* of vectors  $r$  in the *basis*  $(i, j, k)$ .

It is usually convenient to choose the basis vectors to be orthogonal and normalized, but this is not essential.

### Wavefunctions as basis functions

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Wave functions are dealt with in the same way. If we are studying  $\text{BF}_3$ , we may be interested in boron  $p$  orbitals lying in the plane of the molecule (the  $xy$  plane). We may write any such orbital in the form

$$\Phi = \begin{pmatrix} p_x & p_y \end{pmatrix} \begin{pmatrix} c_x \\ c_y \end{pmatrix},$$

where  $c_x$  and  $c_y$  are numerical coefficients which may be complex.

The set of all functions which can be written in this way (all  $p$  orbitals, normalized or not, that lie in the  $xy$  plane) is called a *vector space*. In this case it is the vector space *spanned* by the basis  $(p_x, p_y)$ .

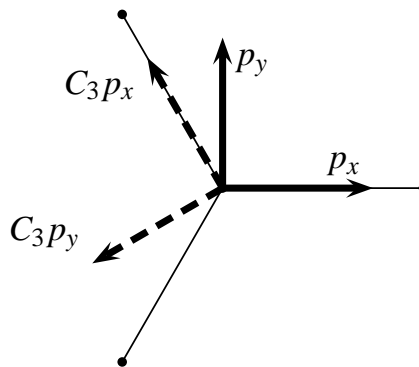
## Representation of symmetry operators

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Now consider the effect of a symmetry operator on such a function. Because

$$\begin{aligned} C_3 p_x &= -\frac{1}{2}p_x + \frac{\sqrt{3}}{2}p_y, \\ C_3 p_y &= -\frac{\sqrt{3}}{2}p_x - \frac{1}{2}p_y, \end{aligned} \quad (3.2)$$

we see that



$$\begin{aligned} C_3 \varphi &= C_3 \begin{pmatrix} p_x & p_y \end{pmatrix} \begin{pmatrix} c_x \\ c_y \end{pmatrix} = \begin{pmatrix} p_x & p_y \end{pmatrix} \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} c_x \\ c_y \end{pmatrix} \\ &= \begin{pmatrix} p_x & p_y \end{pmatrix} D(C_3) \begin{pmatrix} c_x \\ c_y \end{pmatrix}, \end{aligned} \quad (3.3)$$

so for functions of this nature the symmetry operator  $C_3$  can be represented by the matrix  $D(C_3)$ . In a similar way we can set up representations of the other symmetry operators in the group.

## Products of symmetry operators

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If we treat a product  $RS$  as a single element, we obtain

$$(RS) \begin{pmatrix} p_x & p_y \end{pmatrix} \begin{pmatrix} c_x \\ c_y \end{pmatrix} = \begin{pmatrix} p_x & p_y \end{pmatrix} D(RS) \begin{pmatrix} c_x \\ c_y \end{pmatrix}.$$

However we can also treat  $R$  and  $S$  separately:

$$(RS) \begin{pmatrix} p_x & p_y \end{pmatrix} \begin{pmatrix} c_x \\ c_y \end{pmatrix} = R \begin{pmatrix} p_x & p_y \end{pmatrix} D(S) \begin{pmatrix} c_x \\ c_y \end{pmatrix} = \begin{pmatrix} p_x & p_y \end{pmatrix} D(R)D(S) \begin{pmatrix} c_x \\ c_y \end{pmatrix},$$

and we see that  $D(RS) = D(R)D(S)$  — the matrices multiply in the same way as the symmetry operations.

## Some more jargon

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This procedure is one way to generate a *matrix representation* of a group, which is defined as a set of matrices corresponding to the elements  $R$  of the group, and satisfying

$$D(R)D(S) = D(RS) \quad (3.4)$$

for all pairs of elements  $R$  and  $S$  in the group.

The matrices of a representation need not be all different; if they are, the representation is said to be *faithful*.

The *dimension* of a representation is the dimension of each of its matrices.

The set of matrices  $\{D(R)\}$  forms a group, and the relationship expressed by eq. (3.4) between the elements of the original group and the representation matrices is a *homomorphism*.

## Representations *contd.*

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The homomorphism condition is

$$D(R)D(S) = D(RS). \quad (3.4)$$

From (3.4) we see that

$$\begin{aligned} D(R) &= D(ER) = D(E)D(R), \\ D(E) &= D(RR^{-1}) = D(R)D(R^{-1}). \end{aligned}$$

That is,  $D(E)$  is always the unit matrix, and  $D(R^{-1}) = (D(R))^{-1}$ .

There is always a *trivial* or *symmetric* representation, for which  $D(R) = (1)$  (the  $1 \times 1$  unit matrix) for all  $R$ . 'Trivial' is the mathematicians' term; it is particularly important as far as applications are concerned. It may be called  $A_1$ ,  $A_{1g}$ ,  $A'_1$ ,  $\Sigma_g^+$ , etc, in different symmetry groups. Here we shall use the notation  $\Gamma_1$  as a general symbol for the symmetric representation.

## Matrix representations

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If we choose to start with a different set of basis functions we shall get different matrices.

In general the matrix  $D(R)$  representing a symmetry operator  $R$  in a basis  $(\varphi_1, \varphi_2, \dots, \varphi_n)$  is defined by the equation

$$R\varphi_i = \sum_j \varphi_j D_{ji}(R). \quad (3.5)$$

If the representation matrices  $D(R)$  are all unitary then we have a *unitary representation*.

(See Appendix A for a summary of matrix terminology.)

## Using generators

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In working out representation matrices, it isn't necessary to use eq. (3.5) for every  $R$ . Instead, we can use the group generators (see slide 19 and Appendix B) together with the homomorphism, eq. (3.4).

For  $\mathcal{D}_3$  the generators can be taken as  $C_3$  and  $C_2^a$ . (The choice is not unique.) Then, for example,

$$C_3^{-1} = C_3^2, \\ C_2^b = C_2^a C_3.$$

Since the matrices multiply the same way as the operations, according to eq. (3.4), this means that

$$D(C_3^{-1}) = D(C_3)^2, \\ D(C_2^b) = D(C_2^a)D(C_3).$$

So once we have the matrices for  $C_3$  and  $C_2^a$ , it is easy to work out all the others.



$\mathcal{D}_3$		$E$	$C_3$	$C_3^{-1}$	$C_2^a$	$C_2^b$	$C_2^c$
$A_1$	$(s)$	(1)	(1)	(1)	(1)	(1)	(1)
$A_2$	$(p_z)$	(1)	(1)	(1)	(-1)	(-1)	(-1)
$E$	$(p_x, p_y)$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$
	$(p_1, p_{-1})$	$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \omega^* & 0 \\ 0 & \omega \end{pmatrix}$	$\begin{pmatrix} \omega & 0 \\ 0 & \omega^* \end{pmatrix}$	$\begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -\omega \\ -\omega^* & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -\omega^* \\ -\omega & 0 \end{pmatrix}$
$\Gamma^s$	$(s_a, s_b, s_c)$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$

The basis functions are all atomic orbitals for  $\text{BF}_3$ .  $s_a$ ,  $s_b$  and  $s_c$  are fluorine  $2s$  orbitals and the rest are boron orbitals. The functions  $p_1$  and  $p_{-1}$  are defined by

$$p_1 = -\frac{1}{\sqrt{2}}(p_x + ip_y), \quad p_{-1} = +\frac{1}{\sqrt{2}}(p_x - ip_y),$$

and  $\omega = \exp(2\pi i/3) = -\frac{1}{2} + \frac{\sqrt{3}}{2}i$ .

## Equivalent representations

When we set up a representation of ordinary three-dimensional vectors, the basis vectors  $(\mathbf{i}, \mathbf{j}, \mathbf{k})$  are arbitrary, so long as they are linearly independent. If  $T$  is any  $3 \times 3$  matrix possessing an inverse, we can write

$$\begin{pmatrix} \mathbf{i}' & \mathbf{j}' & \mathbf{k}' \end{pmatrix} = \begin{pmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \end{pmatrix} T^{-1} \quad \text{and} \quad \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = T \begin{pmatrix} x \\ y \\ z \end{pmatrix},$$

and then

$$\begin{pmatrix} \mathbf{i}' & \mathbf{j}' & \mathbf{k}' \end{pmatrix} \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \end{pmatrix} T^{-1} T \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} \mathbf{i} & \mathbf{j} & \mathbf{k} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \mathbf{r}.$$

The new representation is *equivalent* to the old one; we can still describe any vector  $\mathbf{r}$  in terms of it, though the numbers will be different. This procedure is just a simple coordinate transformation.

We can apply a similar procedure in the case of group representations. Write the relationship between  $(p_1, p_{-1})$  and  $(p_x, p_y)$  in the form

$$\begin{pmatrix} p_1 & p_{-1} \end{pmatrix} = \begin{pmatrix} p_x & p_y \end{pmatrix} T^{-1} = \begin{pmatrix} p_x & p_y \end{pmatrix} \begin{pmatrix} -1/\sqrt{2} & 1/\sqrt{2} \\ -i/\sqrt{2} & -i/\sqrt{2} \end{pmatrix}.$$

Then if

$$\Phi = \begin{pmatrix} p_x & p_y \end{pmatrix} \begin{pmatrix} c_x \\ c_y \end{pmatrix}$$

we can equivalently write

$$\Phi = \begin{pmatrix} p_x & p_y \end{pmatrix} T^{-1} T \begin{pmatrix} c_x \\ c_y \end{pmatrix} = \begin{pmatrix} p_1 & p_{-1} \end{pmatrix} \begin{pmatrix} c_1 \\ c_{-1} \end{pmatrix}.$$

That is, any  $c_x p_x + c_y p_y$  can be expressed just as well in terms of  $p_1$  and  $p_{-1}$ . The two basis sets *span the same vector space*.

Similarly, from the definition of the representation matrices for the basis  $(p_x, p_y)$ , i.e.

$$R\Phi = \begin{pmatrix} p_x & p_y \end{pmatrix} D(R) \begin{pmatrix} c_x \\ c_y \end{pmatrix},$$

we can obtain the representation matrices for the basis  $(p_1, p_{-1}) = (p_x, p_y)T^{-1}$ :

$$R\Phi = \begin{pmatrix} p_x & p_y \end{pmatrix} T^{-1} T D(R) T^{-1} T \begin{pmatrix} c_x \\ c_y \end{pmatrix} = \begin{pmatrix} p_1 & p_{-1} \end{pmatrix} D'(R) \begin{pmatrix} c_1 \\ c_{-1} \end{pmatrix},$$

so that  $D'(R) = T D(R) T^{-1}$  is the representation matrix for the basis  $(p_1, p_{-1})$ .

Thus the representation matrices  $D'(R)$  for  $(p_1, p_{-1})$  are related to the matrices  $D(R)$  for  $(p_x, p_y)$  by

$$D'(R) = T D(R) T^{-1}.$$

This relationship is called a *similarity* or *equivalence* transformation, and the two representations  $D(R)$  and  $D'(R)$  are said to be *equivalent*. In this example  $T$  is unitary, but any non-singular matrix can be used to generate such a transformation.

Much of the information in the representation matrices therefore depends on the choice of basis, and is irrelevant to the physics of the problem. However the *trace* of a matrix is invariant under equivalence transformations:

$$\text{trace}(A') = \sum_i A'_{ii} = \sum_{ijk} T_{ij} A_{jk} (T^{-1})_{ki} = \sum_{ijk} (T^{-1})_{ki} T_{ij} A_{jk} = \sum_k A_{kk} = \text{trace}(A). \quad (3.6)$$

The set of traces  $\chi(R)$  of the matrices  $D(R)$  is called the *character* of the representation, and it contains all the information that is normally needed.

## Characters for $\mathcal{D}_3$

$\mathcal{D}_3$		$E$	$C_3$	$C_3^{-1}$	$C_2^a$	$C_2^b$	$C_2^c$
$A_1$	$(s)$	1	1	1	1	1	1
$A_2$	$(p_z)$	1	1	1	-1	-1	-1
$E$	$(p_x, p_y)$	2	-1	-1	0	0	0
	$(p_1, p_{-1})$	2	-1	-1	0	0	0
$\Gamma^s$	$(s_a, s_b, s_c)$	3	0	0	1	1	1

Notice that the characters of the equivalent representations based on  $(p_x, p_y)$  and  $(p_1, p_{-1})$  are the same.

Notice also that  $C_3$  and  $C_3^{-1}$  always have the same character, as do  $C_2^a$ ,  $C_2^b$  and  $C_2^c$ .

# Characters for equivalent operations

If two elements  $R$  and  $S$  are in the same class, so that  $S = QRQ^{-1}$ , then because of the homomorphism property of group representations their representation matrices are related by

$$D(S) = D(QRQ^{-1}) = D(Q)D(R)D(Q^{-1}) = D(Q)D(R)D(Q)^{-1},$$

where the last step is again a consequence of the homomorphism, and then

$$\chi(S) = \text{trace} D(S) = \text{trace} D(R) = \chi(R).$$

Because of this it is usual to collect all the elements of each class together in the *character table*.

$\mathcal{D}_3$		$E$	$2C_3$	$3C_2$
$A_1$	$(s)$	1	1	1
$A_2$	$(p_z)$	1	1	-1
$E$	$(p_x, p_y)$	2	-1	0
$\Gamma^s$	$(s_a, s_b, s_c)$	3	0	1

# Reducible and irreducible representations

We might choose to set up a representation for  $\mathcal{D}_3$  using the basis  $(i, j, k)$  of unit vectors in three dimensions.

However the operations of the group all leave the vector  $k$  unchanged or merely change its sign, while vectors in the  $ij$  plane are changed into other vectors in the  $ij$  plane. The one-dimensional space of vectors  $kz$  forms an *invariant subspace* of the original three-dimensional space, as does the two-dimensional space of vectors of the form  $ix + jy$ . This is apparent from the form of the representation matrices, which are

$E$	$C_3$	$C_3^{-1}$	$C_2^a$	$C_2^b$	$C_2^c$
$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & -1 \end{pmatrix}$

Comparison with Table 3 shows that all these matrices are of the form

$$\begin{pmatrix} D^E & 0 \\ & 0 \\ 0 & 0 & D^{A_2} \end{pmatrix}.$$

The matrices generated from the basis  $(i, j, k)$  are all of the form

$$\begin{pmatrix} & & \\ D^E & & 0 \\ & & 0 \\ 0 & 0 & D^{A_2} \end{pmatrix}.$$

They are said to be in *block diagonal* or *direct sum* form (symbol  $\oplus$ ):  $D^E \oplus D^{A_2}$ .

The 3-dimensional representation generated from the basis  $(i, j, k)$  is said to be *reducible*.

## Reducible representations *contd.*

The relationship between the representation  $\Gamma^s$  based on the functions  $(s_a, s_b, s_c)$  and the representations  $A_1, A_2$  and  $E$  goes one stage further. None of these functions forms a basis for an invariant subspace; all of them are transformed into some other function by several of the symmetry operations. However the function  $s_a + s_b + s_c$  is left unchanged by all the symmetry operations, so it corresponds to an invariant subspace, and the representation  $\Gamma^s$  must be reducible.

We can define some new basis functions:

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

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

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

This is a similarity transformation using the matrix

$$T = \begin{pmatrix} \sqrt{\frac{1}{3}} & \sqrt{\frac{1}{3}} & \sqrt{\frac{1}{3}} \\ \sqrt{\frac{2}{3}} & -\sqrt{\frac{1}{6}} & -\sqrt{\frac{1}{6}} \\ 0 & \sqrt{\frac{1}{2}} & -\sqrt{\frac{1}{2}} \end{pmatrix},$$

and  $T$  here is orthogonal so that  $T^{-1} = T^T$ .

Using this transformation we can construct a new representation  $D^\Phi = TD^sT^{-1}$  equivalent to  $D^s$ .

In this case the matrices are

$E$	$C_3$	$C_3^{-1}$	$C_2^a$	$C_2^b$	$C_2^c$
$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & \frac{\sqrt{3}}{2} & \frac{1}{2} \end{pmatrix}$

These matrices are again in direct sum form, this time with  $D^\Phi = D^{A_1} \oplus D^E$ .

## Direct sums

The notation  $D^\Phi = D^{A_1} \oplus D^E$  expresses the direct sum form of  $D^\Phi$ .

Similarly we can write the basis as a direct sum:

$$(\varphi_1, \varphi_2, \varphi_3) = (\varphi_1) \oplus (\varphi_2, \varphi_3).$$

$\varphi_1$  is left unchanged by all symmetry operations, while  $\varphi_2$  and  $\varphi_3$  together transform in exactly the same way as  $p_x$  and  $p_y$ .

We can write  $\Gamma^\Phi = A_1 \oplus E$  too.

We also write  $\Gamma^s \sim A_1 \oplus E$ , indicating that  $\Gamma^s$  is *equivalent* to a direct sum of  $A_1$  and  $E$ .

In practice we often just write this as  $\Gamma^s = A_1 + E$ .

If a representation cannot be reduced to direct sum form (that is, if the space spanned by its basis contains no invariant subspace) then it is *irreducible*.

## The character of a reducible representation

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The character of the direct sum is evidently just the arithmetic sum of the characters of the component representations:

$$\chi^\varphi(R) = \chi^{A_1}(R) + \chi^E(R).$$

Since the characters of equivalent representations are identical, it follows that  $\chi^s(R) = \chi^{A_1}(R) + \chi^E(R)$  also.

How do we find the matrix  $T$  that transforms the representation matrices to block diagonal form? That is just the standard procedure that we use, for example, to find symmetry orbitals.

## 4. The Great Orthogonality Theorem

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This is the fundamental theorem from which most of the useful results of group theory are derived. It states that if  $\Gamma_a$  and  $\Gamma_b$  are two irreducible unitary representations, then their representation matrices satisfy

$$\frac{1}{h} \sum_R D_{ip}^a(R) * D_{jq}^b(R) = \begin{cases} 0 & \text{if } \Gamma_a \not\sim \Gamma_b, \\ \frac{1}{n_a} \delta_{ij} \delta_{pq} & \text{if } \Gamma_a = \Gamma_b, \end{cases} \quad (4.1)$$

- $h$  is the number of elements in the group;
- $n_a$  is the dimension of representation  $\Gamma_a$ .

We do not consider the case where  $\Gamma_a$  and  $\Gamma_b$  are equivalent but not identical; a more complicated formula applies in that case, but we shall not need it.

An outline of the proof is given in Appendix C. (It is not examinable.)

## The first orthogonality theorem for characters

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From the Great Orthogonality Theorem we immediately deduce the *first orthogonality theorem* for the characters of irreducible representations:

$$\begin{aligned} \frac{1}{h} \sum_R \chi^a(R) \chi^b(R) &= \frac{1}{h} \sum_R \sum_{ik} D_{ii}^a(R) D_{kk}^b(R) \\ &= \begin{cases} 0 & \text{if } \Gamma_a \not\sim \Gamma_b, \\ \frac{1}{n_a} \sum_{ki} \delta_{ik} \delta_{ik} = \frac{1}{n_a} \sum_k \delta_{kk} = 1 & \text{if } \Gamma_a = \Gamma_b. \end{cases} \end{aligned} \quad (4.2)$$

The second case in fact applies when  $\Gamma_a$  and  $\Gamma_b$  are equivalent, not necessarily identical, since the characters of equivalent representations are the same. Therefore we can write this result in the form

$$\boxed{\frac{1}{h} \sum_R \chi^a(R) \chi^b(R) = \delta_{\Gamma_a \Gamma_b}}, \quad (4.3)$$

where  $\delta_{\Gamma_a \Gamma_b} = 1$  if  $\Gamma_a \sim \Gamma_b$ , 0 otherwise.

## The first orthogonality theorem for characters *contd.*

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The theorem states that

$$\boxed{\frac{1}{h} \sum_R \chi^a(R) \chi^b(R) = \delta_{\Gamma_a \Gamma_b}}, \quad (4.3)$$

where  $\delta_{\Gamma_a \Gamma_b} = 1$  if  $\Gamma_a \sim \Gamma_b$ , 0 otherwise.

If we use the fact that all elements in a class have the same character, we can express eq. (4.3) in the form

$$\boxed{\frac{1}{h} \sum_c h_c \chi^a(c) \chi^b(c) = \delta_{\Gamma_a \Gamma_b}}. \quad (4.4)$$

In eq. (4.4) the sum is taken over classes  $c$ , and  $h_c$  is the number of elements in class  $c$ .



If we have a reducible representation  $\Gamma = m_1\Gamma^{(1)} \oplus m_2\Gamma^{(2)} \oplus \dots$ , its character is

$$\chi(c) = m_1\chi^{(1)}(c) + m_2\chi^{(2)}(c) + \dots$$

To find how many times a particular representation  $\Gamma_a$  occurs, multiply by  $(h_c/h)\chi^{(a)}(c)^*$  and sum over  $c$ :

$$\begin{aligned} \frac{1}{h} \sum_c h_c \chi^{(a)}(c)^* \chi(c) &= \frac{1}{h} \sum_c h_c \chi^{(a)}(c)^* \sum_i m_i \chi^{(i)}(c) \\ &= \sum_i m_i \delta_{\Gamma_a \Gamma_i} \\ &= m_a. \end{aligned}$$

We have obtained the familiar **reduction formula**:

$$m_a = \frac{1}{h} \sum_c h_c \chi^{(a)}(c)^* \chi(c) \tag{4.5}$$

## The second orthogonality theorem for characters

Eq. (4.4) shows that the *rows* of the character table are orthogonal, and therefore that there cannot be more rows (i.e. irreducible representations) than columns (i.e. classes). The *second orthogonality theorem for characters* (not proved here) states that the columns are orthogonal:

$$\frac{h_c}{h} \sum_{\Gamma} \chi^{\Gamma}(c)^* \chi^{\Gamma}(c') = \delta_{cc'}, \tag{4.6}$$

where  $\Gamma$  runs over the irreducible representations.

From eq. (4.6) we deduce that the number of columns cannot exceed the number of rows, and thus (4.4) and (4.6) together tell us that

*the number of irreducible representations is equal to the number of classes.*

We also observe, by putting  $c = c' = E$  in eq. (4.6), and noting that  $h_E = 1$  and  $\chi^{\Gamma}(E) = n_{\Gamma}$ , that

$$\sum_{\Gamma} (n_{\Gamma})^2 = h. \tag{4.7}$$

For an Abelian group,

- Multiplication is commutative:  $RS = SR$ , for all pairs of elements in the group.
- Therefore  $RSR^{-1} = SRR^{-1} = S$  for any  $R$ , so every element is in a class by itself, and there are  $h$  classes;
- Therefore there are  $h$  representations,
- and because  $\sum_{\Gamma=1}^h (n_{\Gamma})^2 = h$ , every representation is one-dimensional.

## The projection formula

Consider the following operator, in which the coefficient of symmetry operator  $R$  is a component of the representation matrix for the irreducible unitary representation  $\Gamma_a$ :

$$P_i^a = \frac{n_a}{h} \sum_R D_{ii}^a(R)^* R, \quad (4.8)$$

We apply this operator to a function  $\varphi_j^b$  which transforms according to component  $j$  of irreducible representation  $\Gamma_b$ :

$$\begin{aligned} P_i^a \varphi_j^b &= \frac{n_a}{h} \sum_R D_{ii}^a(R)^* R \varphi_j^b \quad (\text{no summation convention}) \\ &= \frac{n_a}{h} \sum_R D_{ii}^a(R)^* \sum_k \varphi_k^b D_{kj}^b(R) \\ &= \sum_k \varphi_k^b \delta_{\Gamma_a \Gamma_b} \delta_{ik} \delta_{ij} \quad \text{using the GOT, eq. (4.1)} \\ &= \begin{cases} \varphi_i^a & \text{if } \Gamma_a = \Gamma_b \text{ and } j = i, \\ 0 & \text{otherwise.} \end{cases} \end{aligned} \quad (4.9)$$

## The usual projection formula

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The operator  $P_i^a$  leaves unchanged a function that transforms according to component  $i$  of representation  $\Gamma_a$ , but annihilates everything else.

This is a powerful result, but is only useful when the representation matrices are tabulated. If however we sum over  $i$ , we get a formula that can be used when only the character is available:

$$P^a = \frac{n_a}{h} \sum_R \sum_i D_{ii}^a(R) * R = \frac{n_a}{h} \sum_R \chi^a(R) * R. \quad (4.10)$$

This is the formula most commonly used. It has the disadvantage, when  $\Gamma_a$  is not one-dimensional, that it yields only a single function, which in general is a mixture of the components of  $\Gamma_a$ .

However the other components may be obtained by *Schmidt orthogonalisation*.

## Schmidt orthogonalisation

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Suppose that the projection formula gave a function  $\varphi_1$ . If  $\Gamma_a$  is not one-dimensional there must be a symmetry operator  $R$  which gives a different function  $R\varphi_1 = \varphi'$ . It is easy to normalise both functions so that

$$\langle \varphi_1 | \varphi_1 \rangle = \langle \varphi' | \varphi' \rangle = 1,$$

but  $\varphi_1$  and  $\varphi'$  may not be orthogonal. In this case a function  $\tilde{\varphi}_2$  which is orthogonal to  $\varphi_1$  (though not normalized) is given by

$$\tilde{\varphi}_2 = \varphi' - \langle \varphi_1 | \varphi' \rangle \varphi_1.$$

We can normalise this to obtain a function  $\varphi_2$  that is normalised and orthogonal to  $\varphi_1$ .

This *Schmidt orthogonalisation* process can be continued if  $n_\Gamma > 2$  until a complete set of orthogonal basis functions has been obtained.

## 5. Spherical harmonics and the full rotation group

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For an isolated atom or molecule, any rotation about any axis through the centre of mass is a symmetry operation, and the symmetry group comprising all these rotations is the Full Rotation Group, also called  $SO(3)$ , the Special Orthogonal Group in 3 dimensions. (If spin is involved, it is necessary to use a different group called  $SU(2)$ , but that is beyond the scope of the present course.)

The theory of the Full Rotation Group is the theory of angular momentum:

- Any rotation is a symmetry operator, i.e. it doesn't change the energy.
- Therefore there are no torques on the system.
- Therefore angular momentum is conserved.

### Rotating functions

Suppose that we want to rotate a function  $\psi$  through  $\alpha$  about the  $z$  axis, giving a new function  $\psi'$ :

$$R(\alpha, z)\psi = \psi'.$$

From the figure, we see that  $\psi'(r') = \psi(r)$ , or (in polar coordinates)

$$\psi'(r, \theta, \varphi + \alpha) = \psi(r, \theta, \varphi).$$

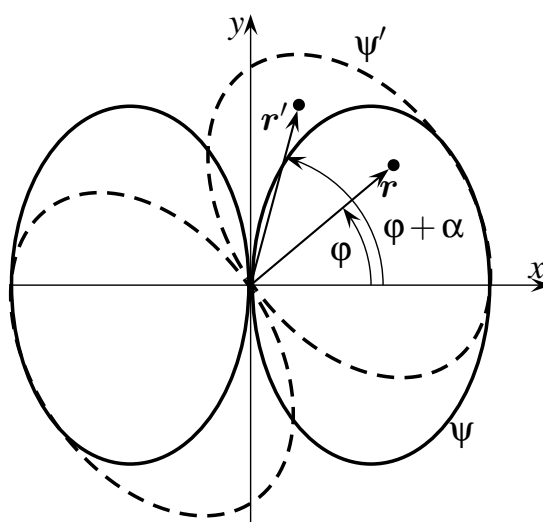
That is,

$$R(\alpha, z)\psi(r, \theta, \varphi) = \psi'(r, \theta, \varphi) = \psi(r, \theta, \varphi - \alpha).$$

In general,

$$R\psi(r) = \psi(R^{-1}r). \quad (5.1)$$

To apply the operation  $R$  to a function, we apply the inverse operation  $R^{-1}$  to its arguments.



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Construct the operator

$$\hat{J}_z = i\hbar \lim_{\alpha \rightarrow 0} \frac{R(\alpha, z) - E}{\alpha}. \quad (5.2)$$

where  $R(\alpha, z)$  is the operator for a rotation through  $\alpha$  about the  $z$  axis.

This operator certainly commutes with the Hamiltonian, since both  $R(\alpha, z)$  and  $E$  commute with the Hamiltonian.

Its effect on some function  $\psi(\varphi)$  is

$$\hat{J}_z \psi(\varphi) = i\hbar \lim_{\alpha \rightarrow 0} \frac{R(\alpha, z) - E}{\alpha} \psi(\varphi) = i\hbar \lim_{\alpha \rightarrow 0} \frac{\psi(\varphi - \alpha) - \psi(\varphi)}{\alpha} = -i\hbar \frac{\partial \psi}{\partial \varphi}, \quad (5.3)$$

so  $\hat{J}_z$  is the angular momentum operator, as the notation suggests.

Consequently the eigenfunctions of the Hamiltonian can be chosen to be also eigenfunctions of angular momentum.

## Implications

The fact that angular momentum can be treated by the methods of group theory has implications that go far beyond the scope of the present course, but some of them are useful here and are quoted without proof:

- The rotation  $R(\alpha, \xi)$  through an angle  $\alpha$  about an axis  $\xi$  belongs to the same class as a rotation  $R(\alpha', \xi')$  if and only if  $\alpha = \alpha'$ . Consequently the class  $C(\alpha)$  of  $SO(3)$  contains all rotations through the angle  $\alpha$ , about any axis.
- The representations of  $SO(3)$  are labelled by the quantum number  $J$  of angular momentum theory. Representation  $J$  has dimension  $2J + 1$ .
- The spherical harmonics  $Y_{JM}$  are basis functions for representation  $J$ .

## Character of representation $J$

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The angular dependence of the spherical harmonics takes the form

$$Y_{JM}(\theta, \varphi) = \Theta_{JM}(\theta) \sqrt{\frac{1}{2\pi}} e^{iM\varphi}. \quad (5.4)$$

When such a function is rotated through  $\alpha$  about the  $z$  axis, we find the new function by replacing  $\varphi$  by  $\varphi - \alpha$ , so that

$$R(\alpha, z)Y_{JM}(\theta, \varphi) = \Theta_{JM}(\theta) \sqrt{\frac{1}{2\pi}} e^{iM(\varphi-\alpha)} = e^{-iM\alpha} Y_{JM}(\theta, \varphi). \quad (5.5)$$

The character  $\chi^J(\alpha)$  for the set of functions with a given value of  $J$  and with  $M = J, J-1, \dots, -J$  is then

$$\chi^J(\alpha) = \sum_{M=-J}^J e^{-iM\alpha}.$$

## Character of representation $J$ *contd*

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The character  $\chi^J(\alpha)$  for the set of functions with a given value of  $J$  and with  $M = J, J-1, \dots, -J$  is

$$\begin{aligned} \chi^J(\alpha) &= \sum_{M=-J}^J e^{-iM\alpha} \\ &= \frac{\exp[(J+1)i\alpha] - \exp[-Ji\alpha]}{\exp[i\alpha] - 1}, \end{aligned}$$

using the geometric series formula. Multiplying top and bottom by  $\exp(-\frac{1}{2}i\alpha)$ ,

$$\boxed{\chi^J(\alpha) = \frac{\sin(J + \frac{1}{2})\alpha}{\sin \frac{1}{2}\alpha}.} \quad (5.6)$$

This result is true for rotations through  $\alpha$  about *any* axis, because all such rotations are in the same class. It allows us to determine the behaviour of a set of atomic orbitals under the rotations of a finite group.

Every group possesses a one-dimensional *symmetric representation*. In this representation the matrix of every operator is (1) and the character is 1. We shall use  $\Gamma_1$  as a general symbol for this representation; in different groups the conventional symbol may be  $A_1$  (as in  $\mathcal{D}_3$ ), or  $A_{1g}$ ,  $A'_1$ ,  $\Sigma_g^+$ ,  $S$ , etc.

If in the G.O.T., eq. (4.1), we put  $\Gamma_a = \Gamma_1$  (so that  $i = p = 1$ ) we have  $D_{11}^{\Gamma_1}(R)^* = 1$ , and we get another useful formula:

$$\frac{1}{h} \sum_R D_{jq}^{\Gamma}(R) = \begin{cases} 0 & \text{if } \Gamma \neq \Gamma_1, \\ 1 & \text{if } \Gamma = \Gamma_1. \end{cases} \quad (6.1)$$

### Physical properties—zero or non-zero?

We consider next the behaviour of physical properties such as charge or dipole moment. There may be just one such quantity for a particular molecule, as in the case of the charge, or there may be several, as for instance the three components of the dipole moment. A symmetry operator will change such a quantity into a linear combination of the several components. However a symmetry operation, by its nature, cannot change the value of any physical quantity. Thus

$$\mu_i = R\mu_i = \sum_j \mu_j D_{ji}^{\Gamma_\mu}(R),$$

and if we now sum over the operations of the group we get

$$h\mu_i = \sum_R R\mu_i = \sum_j \mu_j \sum_R D_{ji}^{\Gamma_\mu}(R). \quad (6.2)$$

If  $\Gamma_\mu$  is irreducible we can use eq. (6.1) to deduce that

$$\mu_i = 0 \quad \text{unless } \Gamma_\mu \text{ is the symmetric representation.}$$

If  $\Gamma_\mu$  is indeed the symmetric representation, then we just get  $\mu_i = \mu_i$ , so the symmetry tells us only whether a quantity is zero or non-zero; it tells us nothing about the magnitude of non-zero quantities.

If  $\Gamma_\mu$  is reducible, it is necessary first to reduce the representation, and then to apply the argument to each irreducible component in turn.

This leads to the conclusion that **the number of independent nonzero components is the number of times that the symmetric representation occurs in  $\Gamma_\mu$ .**

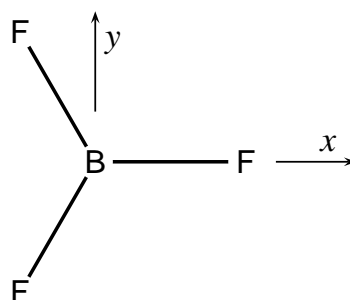
### Example: polarizability of $\text{BF}_3$

The polarizability describes the dipole moment induced by an electric field:  $\Delta\mu_i = \sum_j \alpha_{ij} E_j$ , where  $i$  and  $j$  can be  $x$ ,  $y$  or  $z$ . The component  $\alpha_{ij}$  transforms like  $ij$ , so we can look up the symmetries in the  $D_{3h}$  character table:

$\alpha_{zz}$	transforms like	$z^2$	$A'_1$	so	$\alpha_{zz} \neq 0$
$\alpha_{xx} + \alpha_{yy}$		$x^2 + y^2$	$A'_1$		$\alpha_{xx} + \alpha_{yy} \neq 0$
$\alpha_{xx} - \alpha_{yy}$		$x^2 - y^2$	} $E'$	{	$\alpha_{xx} - \alpha_{yy} = 0$
$\alpha_{xy}$		$xy$			$\alpha_{xy} = 0$
$\alpha_{xz}$		$xz$	} $E''$	{	$\alpha_{xz} = 0$
$\alpha_{yz}$		$yz$			$\alpha_{yz} = 0$

Thus  $\alpha_{xx} + \alpha_{yy} \neq 0$  but  $\alpha_{xx} - \alpha_{yy} = 0$ .

We see that there are two independent non-zero components, corresponding to the two occurrences of  $A'_1$ :  $\alpha_{zz} = \alpha_{||}$  and  $\alpha_{xx} = \alpha_{yy} = \alpha_{\perp}$ .





## When is an integral non-zero?

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In quantum mechanics we often encounter integrals, typically of the form

$\int \psi_1^* \hat{Q} \psi_2 d\tau$ . Sometimes, as in the determination of selection rules for spectroscopy, we don't need to know the exact value of the integral — we just need to know whether it is zero or not. Even when we do need the value, we can avoid the trouble of working out integrals that the group theory tells us are zero.

Consider first a simpler integral,  $\int F_i^\Gamma d\tau$ , whose integrand  $F_i^\Gamma$  transforms according to component  $i$  of representation  $\Gamma$ . The integral is over all space, so rotating or reflecting the function makes no difference. Therefore

$$h \int F_i^\Gamma d\tau = \sum_R \int R F_i^\Gamma d\tau = \sum_R \int F_j^\Gamma D_{ji}^\Gamma(R) d\tau.$$

But  $\sum_R D_{ji}^\Gamma(R) = 0$  unless  $\Gamma$  is the symmetric representation.

We see that **the integral can only be non-zero if the integrand is symmetric.**

To deal with the more general kind of integral that we started with, we need to be able to determine whether an integrand like  $\psi_1^* \hat{Q} \psi_2$  is symmetric. To do this we need **direct products**.

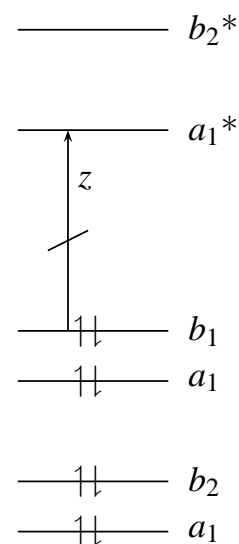
## 7. Direct product representations

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Consider first the case of non-degenerate representations. Suppose that we want to know whether the electronic transition from the HOMO of  $\text{H}_2\text{O}$  ( $b_1$  symmetry) to the LUMO ( $a_1$ ) is allowed in  $z$  polarization. The integral is  $\int \psi_{a_1}^* \hat{\mu}_z \psi_{b_1} d\tau$ . A symmetry operator  $R$  affects each factor in the integrand individually, so

$$\begin{aligned} R(\psi_{a_1}^* \hat{\mu}_z \psi_{b_1}) &= (R\psi_{a_1})^* (R\hat{\mu}_z) (R\psi_{b_1}) \\ &= \psi_{a_1}^* \chi^{A_1}(R) \hat{\mu}_z \chi^{A_1}(R) \psi_{b_1} \chi^{B_1}(R) \\ &= \psi_{a_1}^* \hat{\mu}_z \psi_{b_1} (\chi^{A_1}(R))^2 \chi^{B_1}(R). \end{aligned}$$

We get the character for the whole integrand just by multiplying together the characters of the individual factors. In this case the result is  $\chi^{B_1}(R)$ , so the integrand transforms according to  $B_1$ , which is not symmetric. Consequently the integral is zero and the transition is forbidden.



For non-degenerate representations, we find the character of a product of functions by simply multiplying together the characters of the factors. If the functions belong to degenerate representations, it turns out that this is still true, but the proof is a little more complicated.

Suppose that we have two sets of functions:  $\{\xi_1, \xi_2, \dots, \xi_m\}$ , a basis for representation  $\Gamma_a$ , and  $\{\eta_1, \eta_2, \dots, \eta_n\}$ , a basis for  $\Gamma_b$ , and consider the set of products  $\xi_i \eta_j$ . Operating with  $R$  gives

$$R(\xi_i \eta_j) = \sum_k \xi_k D_{ki}^{\Gamma_a}(R) \sum_l \eta_l D_{lj}^{\Gamma_b}(R) = \sum_{kl} (\xi_k \eta_l) D_{ki}^{\Gamma_a}(R) D_{lj}^{\Gamma_b}(R) \quad (7.1)$$

We can also view the  $mn$  product functions, labelled by the double index  $ij$ , as a basis for a new representation of dimension  $mn$ :

$$R(\xi_i \eta_j) = \sum_{kl} (\xi_k \eta_l) D_{kl,ij}^{\Gamma_a \otimes \Gamma_b}(R). \quad (7.2)$$

This is the *direct product representation*  $\Gamma_a \otimes \Gamma_b$ .

## The character of the direct product

For the direct product, we have

$$R(\xi_i \eta_j) = \sum_{kl} (\xi_k \eta_l) D_{kl,ij}^{\Gamma_a \otimes \Gamma_b}(R) = \sum_{kl} (\xi_k \eta_l) D_{ki}^{\Gamma_a}(R) D_{lj}^{\Gamma_b}(R),$$

so the representation matrices for the direct product are

$$D_{kl,ij}^{\Gamma_a \otimes \Gamma_b} = D_{ki}^{\Gamma_a}(R) D_{lj}^{\Gamma_b}(R). \quad (7.3)$$

To find the character  $\chi^{\Gamma_a \otimes \Gamma_b}$  we set  $kl$  equal to  $ij$  and sum over  $i$  and  $j$ :

$$\chi^{\Gamma_a \otimes \Gamma_b}(R) = \sum_{ij} D_{ii}^{\Gamma_a}(R) D_{jj}^{\Gamma_b}(R) = \chi^{\Gamma_a}(R) \chi^{\Gamma_b}(R). \quad (7.4)$$

So the character is very easily determined, and the standard reduction procedure gives the irreducible components.

## How many symmetric components in a direct product? 67

It is often important to know how many times the symmetric representation occurs in a direct product, for example to determine whether an integral is non-zero.

If  $\Gamma_a$  and  $\Gamma_b$  are both irreducible, then the direct product  $\Gamma_a^* \otimes \Gamma_b$  (for which the basis functions are  $\xi_i^* \eta_j$ ) contains the symmetric representation *once* if  $\Gamma_a \sim \Gamma_b$ , and otherwise not at all.

To prove this, we use eq. (4.5) to find the number of occurrences of  $\Gamma_1$ :

$$\begin{aligned}
 m_1 &= \frac{1}{h} \sum_c h_c \chi^{\Gamma_1}(c) * \chi^{\Gamma_a^* \otimes \Gamma_b} = \frac{1}{h} \sum_c h_c \chi^{\Gamma_1}(c) * (\chi^{\Gamma_a}(c) * \chi^{\Gamma_b}(c)) \\
 &= \frac{1}{h} \sum_c h_c \chi^{\Gamma_a}(c) * \chi^{\Gamma_b}(c) \\
 &= \delta_{\Gamma_a \Gamma_b}.
 \end{aligned} \tag{7.5}$$

## The symmetric component of a direct product 68

In the case where the representations forming the direct product are identical (not just equivalent) so that  $\Gamma_a = \Gamma_b = \Gamma$ , the totally symmetric component is given by the projection formula, eq. (4.10):

$$\begin{aligned}
 (\xi_i^* \eta_j)^{\Gamma_1} &= \frac{1}{h} \sum_R D_{11}^{\Gamma_1}(R) R(\xi_i^* \eta_j) \\
 &= \frac{1}{h} \sum_R \sum_{kl} \xi_k^* \eta_l D_{ki}^{\Gamma}(R) * D_{lj}^{\Gamma}(R) \\
 &= \sum_{kl} (\xi_k^* \eta_l) \frac{1}{n_{\Gamma}} \delta_{kl} \delta_{ij}
 \end{aligned}$$

so finally

$$\boxed{(\xi_i^* \eta_j)^{\Gamma_1} = \delta_{ij} \frac{1}{n_{\Gamma}} \sum_k \xi_k^* \eta_k.} \tag{7.6}$$

The  $\delta_{ij}$  in this equation means that  $\xi_i^* \eta_j$  contains no totally symmetric component unless  $i = j$ .

## Calculation of integrals

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Now we can find general rules for determining whether integrals are zero or not. One common type of integral is the overlap integral  $\int (\xi_i^a)^* \eta_j^b d\tau$ , where  $\xi_i^a$  transforms according to component  $i$  of irreducible representation  $\Gamma_a$  and  $\eta_j^b$  according to component  $j$  of representation  $\Gamma_b$ . The integrand here is a component of the direct product  $\Gamma_a^* \otimes \Gamma_b$ , which contains  $\Gamma_1$  only if  $\Gamma_a \sim \Gamma_b$ . Therefore

$$\int (\xi_i^a)^* \eta_j^b d\tau = 0 \quad \text{unless } \Gamma_a \sim \Gamma_b. \quad (7.7)$$

If  $\Gamma_a = \Gamma_b = \Gamma$  (identical representations, not just equivalent) then from eq. (7.6) we see that

$$\int (\xi_i^\Gamma)^* \eta_j^\Gamma d\tau = 0 \quad \text{unless } i = j. \quad (7.8)$$

Eq. (7.6) also shows that if  $i = j$  then

$$\int (\xi_i^\Gamma)^* \eta_i^\Gamma d\tau = \frac{1}{n_\Gamma} \int \sum_k (\xi_k^\Gamma)^* \eta_k^\Gamma d\tau \quad (7.9)$$

and is the same for all  $i$ .

## Calculation of integrals *contd.*

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Next we consider integrals such as  $\int (\xi_i^a)^* \hat{Q}_k^c \eta_j^b d\tau$ , which involve an operator. Here  $\hat{Q}_k^c$  is one of a set of operators transforming according to the irreducible representation  $\Gamma_c$ . The functions  $\hat{Q}_k^c \eta_j^b$  form a basis for the direct product representation  $\Gamma_c \otimes \Gamma_b$ , so

$$\int (\xi_i^a)^* \hat{Q}_k^c \eta_j^b d\tau = 0 \quad \text{unless } \Gamma_c \otimes \Gamma_b \ni \Gamma_a. \quad (7.10)$$

A special case of eq. (7.10) arises when  $\Gamma_c = \Gamma_1$ —that is, the operator is totally symmetric.

Then  $\Gamma_c \otimes \Gamma_b = \Gamma_1 \otimes \Gamma_b = \Gamma_b$ , and (7.10) reduces to a formula like (7.7):

$$\int (\xi_i^a)^* \hat{Q}^{\Gamma_1} \eta_j^b d\tau = 0 \quad \text{unless } \Gamma_a \sim \Gamma_b, \quad (7.11)$$

and if  $\Gamma_a = \Gamma_b = \Gamma$  (identical representations) then

$$\int (\xi_i^\Gamma)^* \hat{Q}^{\Gamma_1} \eta_j^\Gamma d\tau = 0 \quad \text{unless } i = j. \quad (7.12)$$

Here again we see that  $\int (\xi_i^\Gamma)^* \hat{Q}^{\Gamma_1} \eta_i^\Gamma d\tau$  is independent of  $i$ .

## Integrals for M.O. theory

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The application of these results to M.O. theory is now clear. The Hamiltonian, by definition, is unaffected by any symmetry operator and so is totally symmetric. Therefore:

- Overlap integrals and Hamiltonian integrals between symmetry orbitals of different symmetries are zero. That is, orbitals of different symmetry don't mix.
- If symmetry orbitals of the same symmetry are constructed so that their components match (the representations are identical, not just equivalent) then integrals involving different components of the same representation are also zero.
- Moreover for different components  $i$  and  $j$ , we have

$$\int (\xi_i^a)^* \hat{H} \eta_i^a d\tau = \int (\xi_j^a)^* \hat{H} \eta_j^a d\tau,$$

and similarly for the overlap integrals, so that the secular equations for components  $i$  and  $j$  are identical.

## The symmetrized and antisymmetrized square

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When the two bases  $\{\xi_1, \xi_2, \dots, \xi_n\}$  and  $\{\eta_1, \eta_2, \dots, \eta_n\}$  in a direct product span the *same* representation  $\Gamma$ , it is often convenient to consider as basis functions for the direct product the symmetrized products  $\xi_i \eta_j + \eta_i \xi_j$  (symmetric with respect to exchange of  $\xi$  and  $\eta$ ) and the antisymmetrized products  $\xi_i \eta_j - \eta_i \xi_j$ , rather than the simple products  $\xi_i \eta_j$ .

The symmetrized products transform only among themselves, and they therefore form a basis for a representation, of dimension  $\frac{1}{2}n(n+1)$ , which is called the *symmetrized square* of  $\Gamma$  and denoted  $(\Gamma \otimes \Gamma)_+$ . Similarly the antisymmetrized products form a basis for the *antisymmetrized square*  $(\Gamma \otimes \Gamma)_-$ , with dimension  $\frac{1}{2}n(n-1)$ . The characters of these two representations are given by the formula

$$\chi^{\Gamma \otimes \Gamma_{\pm}}(R) = \frac{1}{2} [(\chi^{\Gamma}(R))^2 \pm \chi^{\Gamma}(R^2)]. \quad (7.13)$$

If the two bases are the same, so that  $\xi_i = \eta_i$ , then evidently the antisymmetrized products vanish.

## The direct product $E \otimes E$

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If we have two sets of basis functions,  $\{\xi_x, \xi_y\}$  and  $\{\eta_x, \eta_y\}$ , both transforming according to  $E$ , the direct product basis is  $\{\xi_x\eta_x, \xi_x\eta_y, \xi_y\eta_x, \xi_y\eta_y\}$ .

$\xi_x\eta_x$  and  $\xi_y\eta_y$  are already symmetric. From the other two products we can construct  $\xi_x\eta_y + \eta_x\xi_y$  (symmetric) and  $\xi_x\eta_y - \eta_x\xi_y$  (antisymmetric).

The direct product transforms as  $A_1 \oplus A_2 \oplus E$ , and the symmetry-adapted functions are

$$\begin{aligned} A_1 : & \quad \xi_x\eta_x + \xi_y\eta_y && \text{symmetric} \\ A_2 : & \quad \xi_x\eta_y - \eta_x\xi_y && \text{antisymmetric} \\ E : & \quad \xi_x\eta_y + \eta_x\xi_y && \text{symmetric} \\ & \quad \xi_x\eta_x - \xi_y\eta_y && \text{symmetric} \end{aligned}$$

The symmetrized square is  $(E \otimes E)_+ = A_1 \oplus E$ , and the antisymmetrized square is  $(E \otimes E)_- = A_2$ .

## Electronic terms

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If we have two electrons in the same degenerate set of orbitals, then we can take  $\xi_i = \psi_i(1)$  and  $\eta_i = \psi_i(2)$ . We can construct orbitally-symmetric functions

$$\xi_i\eta_j + \eta_i\xi_j = \psi_i(1)\psi_j(2) + \psi_i(2)\psi_j(1), \quad (7.14)$$

and orbitally-antisymmetric ones

$$\xi_i\eta_j - \eta_i\xi_j = \psi_i(1)\psi_j(2) - \psi_i(2)\psi_j(1). \quad (7.15)$$

The orbitally-symmetric functions, i.e. the components of the symmetrized square, have to be combined with antisymmetric (singlet) spin functions, and the orbitally-antisymmetric ones with symmetric (triplet) spin functions, in order that the overall wavefunction shall be antisymmetric.

Thus the configuration  $e^2$  for a molecule, with two electrons in an  $E$  set of orbitals, leads to  ${}^1A_1$ ,  ${}^3A_2$  and  ${}^1E$  molecular terms.

In octahedral symmetry, the symmetrized square  $(T_{2g} \otimes T_{2g})_+ = A_{1g} \oplus E_g \oplus T_{2g}$ , while the antisymmetrized square  $(T_{2g} \otimes T_{2g})_- = T_{1g}$ . Therefore the configuration  $t_{2g}^2$  leads to the molecular terms  ${}^1A_{1g}$ ,  ${}^1E_g$ ,  ${}^1T_{2g}$  and  ${}^3T_{1g}$ .

In the Full Rotation Group, the direct product  $\Gamma^{(J_1)} \otimes \Gamma^{(J_2)}$  reduces as follows (see ex. 6.2.):

$$\Gamma^{(J_1)} \otimes \Gamma^{(J_2)} = \Gamma^{(J_1+J_2)} \oplus \Gamma^{(J_1+J_2-1)} \oplus \dots \oplus \Gamma^{|J_1-J_2|}.$$

In the language of angular momentum, this means that a system having two components, one with angular momentum  $J_1$  and one with angular momentum  $J_2$ , has states with total angular momentum  $J_1 + J_2, J_1 + J_2 - 1, \dots, |J_1 - J_2|$ . (This is called the Clebsch–Gordan series.)

With  $J_1 = J_2$  this becomes

$$\Gamma^{(J)} \otimes \Gamma^{(J)} = \Gamma^{(2J)} \oplus \Gamma^{(2J-1)} \oplus \dots \oplus \Gamma^{(0)}.$$

It can be shown that the terms in this direct sum are alternately symmetric and antisymmetric, so that

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

## Atomic terms

To find the allowed terms for the  $p^2$  configuration, we need

$$(P \otimes P)_+ = \Gamma^{(2)} \oplus \Gamma^{(0)} = D \oplus S, \quad (P \otimes P)_- = \Gamma^{(1)} = P.$$

To construct antisymmetric states to satisfy the Pauli principle, the symmetric space functions have to be combined with the antisymmetric, i.e. singlet, spin functions, and *vice versa*, so the allowed terms are  $^1D$ ,  $^3P$  and  $^1S$ .

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

## 8. The Jahn–Teller theorem

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We consider a molecule in an orbitally degenerate state of symmetry  $\Gamma$ , so that there are  $n$  degenerate many-electron wavefunctions  $\{\psi_1, \psi_2, \dots, \psi_n\}$ .

The Jahn–Teller theorem states that a non-symmetric distortion of symmetry  $\Gamma_Q$  will lower the energy of at least one of the states, provided that  $(\Gamma \otimes \Gamma)_+ \ni \Gamma_Q$ .

If the molecule is distorted away from the symmetrical geometry, the electronic Hamiltonian will change, introducing a perturbation  $V_Q$  of the same symmetry  $\Gamma_Q$  as the distortion itself. Perturbation theory shows that the energy changes are, to first order in the distortion, the eigenvalues  $\varepsilon_i$  of the matrix  $V$  with elements  $V_{ij} = \int \psi_i^* V_Q \psi_j d\tau$ . We assume that the functions  $\psi_i$  are all real (which can always be arranged in the case of an orbital degeneracy) and note that the perturbation  $V_Q$  is just a change in potential—the kinetic energy terms in the electronic Hamiltonian do not change—and that it too is real. Consequently we can write

$$V_{ij} = \int (\psi_i \psi_j) V_Q d\tau,$$

and we see that all the  $V_{ij}$  vanish unless the representation spanned by the  $(\psi_i \psi_j)$  (that is, the symmetrized square  $(\Gamma \otimes \Gamma)_+$ ) contains  $\Gamma_Q$ .

## The Jahn–Teller theorem *contd.*

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We can now prove the following results:

1. The sum of the energy changes is zero unless the distortion is totally symmetric.

To see that this is so, remember that the sum of the eigenvalues of the matrix  $V$  is equal to its trace. That is,

$$\sum_i \varepsilon_i = \sum_i V_{ii} = \int \left( \sum_i \psi_i^2 \right) V_Q d\tau \quad (8.1)$$

which vanishes unless  $\Gamma_Q = \Gamma_1$ , because  $\sum_i \psi_i^2$  is symmetric (eq. (7.6)).

However we are interested only in unsymmetrical distortions, because a symmetric distortion does not change the symmetry of the electronic Hamiltonian and so cannot lift the degeneracy.



## The Jahn–Teller theorem *contd.*

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1. The sum of the energy changes is zero unless the distortion is totally symmetric.
2. The sum of the squares of the energy changes is non-zero provided that  $(\Gamma \otimes \Gamma)_+ \ni \Gamma_Q$ .

If  $V$  has eigenvalues  $\varepsilon_i$ , then the matrix  $V^2$  has eigenvalues  $\varepsilon_i^2$ . So the sum of squares of the energy changes is

$$\sum_i \varepsilon_i^2 = \text{trace}(V^2) = \sum_{ij} V_{ij}V_{ji} = \sum_{ij} |V_{ij}|^2, \quad (8.2)$$

and this will be non-zero if any of the elements of  $V$  is non-zero. The requirement for this is that  $(\Gamma \otimes \Gamma)_+ \ni \Gamma_Q$ , as noted above.

## The Jahn–Teller theorem *contd.*

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1. The sum of the energy changes is zero unless the distortion is totally symmetric.
2. The sum of the squares of the energy changes is non-zero provided that  $(\Gamma \otimes \Gamma)_+ \ni \Gamma_Q$ .

If the sum of the energy changes is zero, but the sum of their squares is non-zero, then at least one must be negative, and the Jahn–Teller theorem follows.

It can be shown that for non-linear molecules there is always a distortion satisfying the Jahn–Teller condition. Proving it is much more difficult, and was not achieved until 20 years after Jahn & Teller proved their theorem. For a discussion, see Landau & Lifshitz, *Quantum Mechanics (Non-relativistic Theory)*, 3rd edn., pp. 405–410.

It is much easier to show that for *linear* molecules there is *never* a distortion satisfying the Jahn–Teller condition.

## Jahn–Teller distortion in octahedral $d^9$ complexes

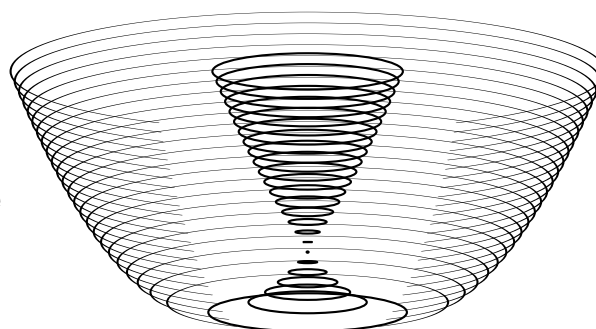
81

The classical example of Jahn–Teller distortion is the octahedral  $d^9$  complex. Here the electronic state is  $E_g$ , with symmetrized square  $A_{1g} \oplus E_g$ , so the distortion has to be  $E_g$ .

The mode in which the  $z$  ligands move out and the  $x$  and  $y$  ones move in is one component of an  $E_g$  vibration; the other component has the  $x$  ligands moving out and the  $y$  ligands moving in, with the  $z$  ligands not moving at all. (Compare  $d_{z^2}$  and  $d_{x^2-y^2}$  orbitals, also of  $E_g$  symmetry.)

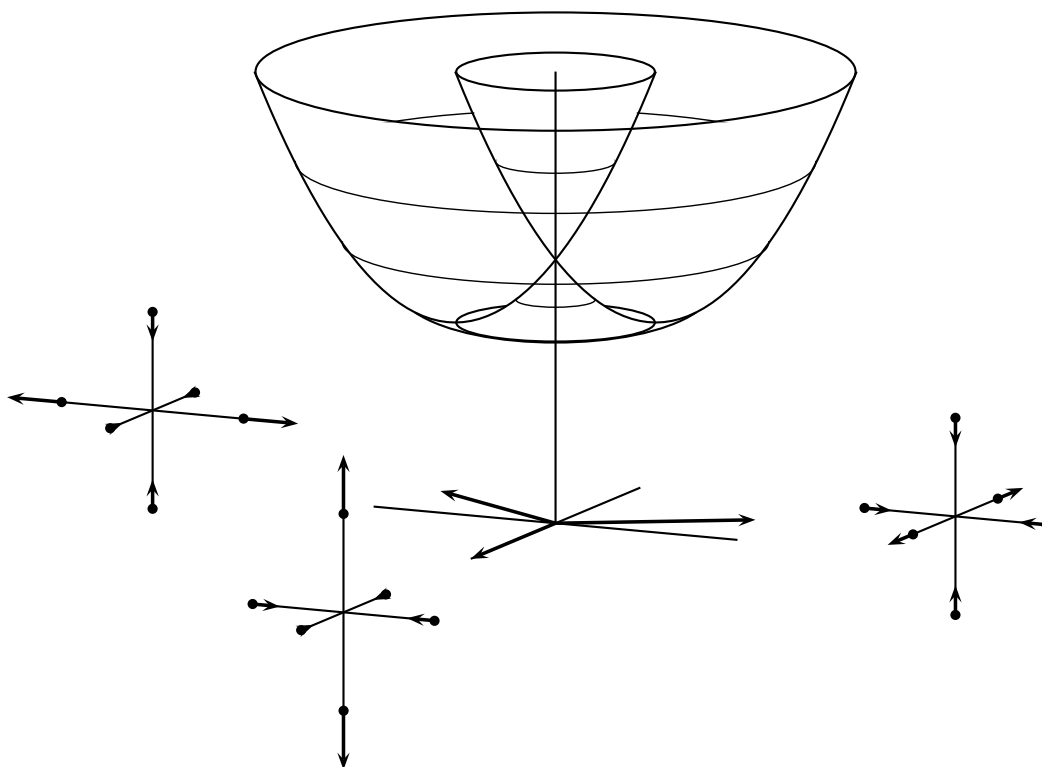
In fact any linear combination of these modes leads to a splitting of the  $e_g$  orbitals in first order, with one orbital lowered in energy and the other raised. For large distortions of this type the repulsion between the ligands and the central ion causes the energy to rise.

The potential energy surface is approximately a parabola rotated around an axis parallel to its own axis, and has a ring-shaped well. There are normally three minima on this ring, corresponding to the geometries in which two ligands move out and the others in.



## Jahn–Teller distortion in octahedral $d^9$ complexes

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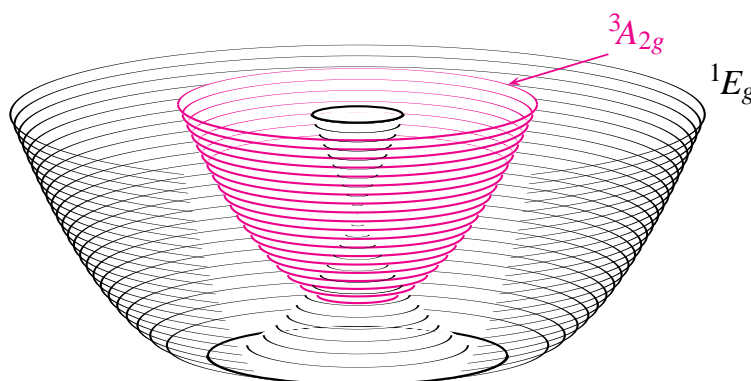


## Jahn–Teller distortion in octahedral $d^8$ complexes

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In  $d^8$  complexes, the electron configuration is  $e_g^2$  and the allowed terms are  $^1E_g$ ,  $^1A_{1g}$  and  $^3A_{2g}$ . The lowest-energy state in the octahedral geometry is  $^3A_{2g}$ , according to Hund's first rule, with the  $^1E_g$  above it and the  $^1A_{1g}$  above that, but the  $^1E_g$  state is subject to Jahn–Teller distortion, which may reduce the energy below that of the triplet.

Consequently in  $d^8$  we expect either a symmetrical triplet state or a distorted singlet.



## The dynamical Jahn–Teller effect

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In some Jahn–Teller molecules the energy associated with the Jahn–Teller distortion is quite small compared with  $kT$ , and then the distortion is not static but dynamic.

This does not occur in 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.

## 9. Vibrational coordinates

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Vibrational coordinates can be symmetry-adapted in much the same way as atomic orbitals. Each atom has 3 cartesian displacement coordinates, and together they provide  $3N$  symmetry coordinates. 3 of these correspond to translational motions, and 3 to rotations (or 2 in the case of linear molecules). Subtracting these off, we are left with  $3N - 6$  (or  $3N - 5$ ) true vibrations.

In the case of  $\text{BF}_3$ , the  $3N$  cartesian displacement coordinates transform as  $A'_1 \oplus A'_2 \oplus 2A''_2 \oplus 3E' \oplus E''$ . The translations transform as  $A''_2 \oplus E'$  and the rotations as  $A'_2 \oplus E''$ , leaving the true vibrations  $A'_1 \oplus A'_2 \oplus 2E'$ .

Of these, the  $A'_1$  mode is the symmetric combination  $\sqrt{\frac{1}{3}}(r_1 + r_2 + r_3)$  of the fluorine radial displacement coordinates.

The  $A''_2$  mode is a linear combination of  $z_B$  and the symmetric combination of the fluorine  $z$  coordinates  $\sqrt{\frac{1}{3}}(z_1 + z_2 + z_3)$ :

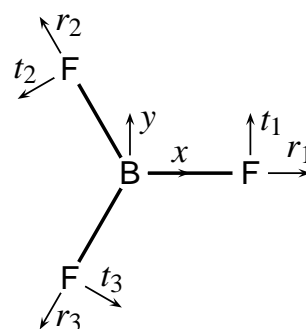
$$Q_{A''_2} = c_1 z_B + c_2 \sqrt{\frac{1}{3}}(z_1 + z_2 + z_3). \quad (9.1)$$

The coefficients have to be chosen so that the motion leaves the centre of mass stationary.

## Vibrational coordinates for $\text{BF}_3$

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$D_{3h}$	$E$	$2C_3$	$3C_2$	$\sigma_h$	$2S_3$	$3\sigma_v$	
$A'_1$	1	1	1	1	1	1	
$A'_2$	1	1	-1	1	1	-1	$R_z$
$E'$	2	-1	0	2	-1	0	$(x, y)$
$A''_1$	1	1	1	-1	-1	-1	
$A''_2$	1	1	-1	-1	-1	1	$z$
$E''$	2	-1	0	-2	1	0	$(R_x, R_y)$
$B(x, y)$	2	-1	0	2	-1	0	$E'$
$Bz$	1	1	-1	-1	-1	1	$A''_2$
$F(z_1, z_2, z_3)$	3	0	-1	-3	0	1	$A''_2 \oplus E''$
$F(r_1, r_2, r_3)$	3	0	1	3	0	1	$A'_1 \oplus E'$
$F(t_1, t_2, t_3)$	3	0	-1	3	0	-1	$A'_2 \oplus E'$

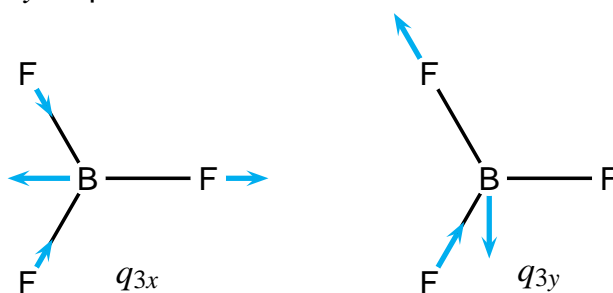


Cartesian:	$A'_1$	$A'_2$	$2A''_2$	$3E'$	$E''$
Translations:			$A''_2$	$E'$	
Rotations:		$A'_2$			$E''$
Vibrations:	$A'_1$		$A''_2$	$2E'$	

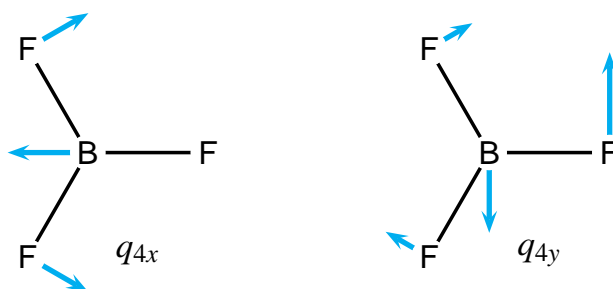
## $E'$ modes for $\text{BF}_3$

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The  $E'$  symmetry coordinate constructed from the  $r_i$  is essentially a stretching mode. We need to add an  $x$  or  $y$  displacement of the B atom so that the centre of mass does not move.



Similarly the  $E'$  symmetry coordinate constructed from the  $t_i$  is a bending mode.



These diagrams are schematic only. See Herzberg, *Infrared and Raman Spectra*, p. 179, for a diagram of the calculated modes, allowing also for mixing between  $q_3$  and  $q_4$ .

## Allowed harmonic terms in the vibrational potential

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Normally the potential energy for nuclear motion is expanded in a Taylor series about the equilibrium geometry. The linear terms are zero, so the first terms to consider are the quadratic (harmonic) terms. However the Hamiltonian is totally symmetric, so only symmetric terms can appear.

If we have a set of vibrational coordinates  $(q_{a1}, q_{a2}, \dots)$  belonging to irreducible representation  $\Gamma_a$ , and another set  $(q_{b1}, q_{b2}, \dots)$  belonging to  $\Gamma_b$ , possible quadratic terms are the elements  $q_{ai}q_{bj}$  of the direct product. This set of elements includes a single symmetric component if and only if  $\Gamma_a \sim \Gamma_b$ . If  $\Gamma_a = \Gamma_b$ , the symmetric component is proportional to  $\sum_i q_{ai}q_{bi}$ . (Eq. (7.6).)

Thus the only quadratic terms that may appear in the vibrational potential of  $\text{BF}_3$  are

$$q_1^2, \quad q_2^2, \quad q_{3x}^2 + q_{3y}^2, \quad q_{4x}^2 + q_{4y}^2 \quad \text{and} \quad q_{3x}q_{4x} + q_{3y}q_{4y}. \quad (9.2)$$

Here  $q_1$  is the  $A_1'$  mode and  $q_2$  the  $A_2''$  one. Note that the components  $(q_{3x}, q_{3y})$  and  $(q_{4x}, q_{4y})$  have been defined so that they match — the representations are identical, not just equivalent, so that we can use eq. (7.6) to find the symmetric component of the direct product  $(q_{3x}, q_{3y}) \otimes (q_{4x}, q_{4y})$ .

There are more possibilities for anharmonic terms.

- (i) Any of the harmonic terms can be multiplied by  $q_1$ , which is symmetric, to obtain an allowed cubic term.
- (ii) If we could construct a quadratic term of  $A_2''$  symmetry, we could multiply it by  $q_2$  to obtain a symmetric term. However the only such combination is  $q_1q_2$ , which would give  $q_1q_2^2$ , and this has been included under (i) above.
- (iii) We can construct a quadratic  $E'$  term from  $(q_{3x}, q_{3y})$ . It has the components  $(q_{3x}^2 - q_{3y}^2, -2q_{3x}q_{3y})$ . (They have to be defined like this so that they transform in the standard way, i.e. like  $(x, y)$ .) The  $A_1'$  component of the direct product of this with  $(q_{3x}, q_{3y})$  is  $q_{3x}^3 - 3q_{3x}q_{3y}^2$ , which may therefore appear as a cubic anharmonic term. Other terms of similar form may be constructed from mixtures of  $q_3$  and  $q_4$  components.

No other cubic terms may appear in the Hamiltonian.

Anharmonic terms can lead to coupling between vibrational states, and hence to perturbations of their energies. Because the anharmonic terms must be symmetric, they can only couple states of the same symmetry.

## Scaling the harmonic oscillator

The harmonic oscillator Hamiltonian is

$$\mathcal{H} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial q^2} + \frac{1}{2}kq^2. \quad (9.3)$$

Define  $x = q/s$ , where  $s$  is some length, to be determined. We get

$$\mathcal{H} = -\frac{\hbar^2}{2ms^2} \frac{\partial^2}{\partial x^2} + \frac{1}{2}ks^2x^2, \quad (9.4)$$

or

$$\frac{\mathcal{H}}{ks^2} = -\frac{\hbar^2}{2mks^4} \frac{\partial^2}{\partial x^2} + \frac{1}{2}x^2. \quad (9.5)$$

Choose  $s = (\hbar^2/mk)^{1/4}$ , and we get  $ks^2 = \hbar\sqrt{k/m} = \hbar\omega$  and

$$\frac{\mathcal{H}}{\hbar\omega} = -\frac{1}{2} \frac{\partial^2}{\partial x^2} + \frac{1}{2}x^2. \quad (9.6)$$

## Vibrational ladder operators

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To deal with the symmetries of excited vibrational states it is helpful to introduce some new operators.

If we use the scaled units, with the energy unit as  $\hbar\omega$ , the harmonic oscillator Hamiltonian is

$$\mathcal{H} = -\frac{1}{2}\frac{\partial^2}{\partial x^2} + \frac{1}{2}x^2.$$

Define the operators

$$\hat{Q} = \sqrt{\frac{1}{2}}\left(x + \frac{\partial}{\partial x}\right), \quad \hat{Q}^\dagger = \sqrt{\frac{1}{2}}\left(x - \frac{\partial}{\partial x}\right). \quad (9.7)$$

For any  $\psi$ ,

$$\hat{Q}\hat{Q}^\dagger\psi = \frac{1}{2}\left(x + \frac{\partial}{\partial x}\right)\left(x - \frac{\partial}{\partial x}\right)\psi = \frac{1}{2}\left(x^2 - \frac{\partial^2}{\partial x^2} + 1\right)\psi = (\mathcal{H} + \frac{1}{2})\psi. \quad (9.8)$$

Therefore  $\hat{Q}\hat{Q}^\dagger = \mathcal{H} + \frac{1}{2}$ . Similarly  $\hat{Q}^\dagger\hat{Q} = \mathcal{H} - \frac{1}{2}$ .

## Vibrational ladder operators

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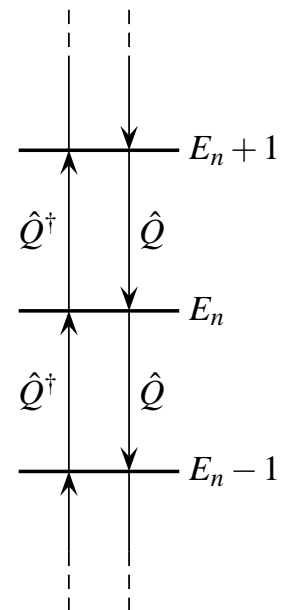
Now suppose that there is a wavefunction  $\psi_n$  that is an eigenfunction of  $\mathcal{H}$ :  $\mathcal{H}\psi_n = E_n\psi_n$ . Consider the new function  $\hat{Q}^\dagger\psi_n$ . We find

$$\begin{aligned} \mathcal{H}(\hat{Q}^\dagger\psi_n) &= (\hat{Q}^\dagger\hat{Q} + \frac{1}{2})\hat{Q}^\dagger\psi_n = \hat{Q}^\dagger(\hat{Q}\hat{Q}^\dagger + \frac{1}{2})\psi_n \\ &= \hat{Q}^\dagger(\mathcal{H} + 1)\psi_n = (E_n + 1)(\hat{Q}^\dagger\psi_n). \end{aligned} \quad (9.9)$$

So  $\hat{Q}^\dagger\psi_n$  is an eigenfunction of  $\mathcal{H}$  with eigenvalue  $E_n + 1$ . (Remember that the energy unit is  $\hbar\omega$ .)

In the same way, we can show that  $\hat{Q}\psi_n$  is an eigenfunction with energy  $E_n - 1$ .

$\hat{Q}$  and  $\hat{Q}^\dagger$  are called *ladder operators* or *raising and lowering operators*, because they move up and down a ladder of vibrational states.



## Vibrational ladder operators

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The energy of a harmonic oscillator can't be negative, so there must be some state  $\psi_0$  for which  $\hat{Q}\psi_0 = 0$ . The energy of that state is given by

$$\mathcal{H}\psi_0 = (\hat{Q}^\dagger \hat{Q} + \frac{1}{2})\psi_0 = \frac{1}{2} \quad (9.10)$$

(in units of  $\hbar\omega$ ). To find the wavefunction  $\psi_0$  we solve  $\hat{Q}\psi_0 = 0$ :

$$\sqrt{\frac{1}{2}} \left( x + \frac{\partial}{\partial x} \right) \psi_0 = 0, \quad (9.11)$$

with the solution

$$\psi_0 = \exp(-\frac{1}{2}x^2) = \exp\left(-\sqrt{\frac{km}{\hbar^2}} q^2\right). \quad (9.12)$$

Now we can get all the other vibrational wavefunctions using  $\hat{Q}^\dagger$ :

$$\psi_n = (\hat{Q}^\dagger)^n \psi_0, \quad (9.13)$$

and  $\psi_n$  has energy  $(n + \frac{1}{2})\hbar\omega$ .

## State symmetries for non-degenerate vibrations

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The ground state vibrational wavefunction is  $\exp(-\frac{1}{2}x^2)$ , and if  $x$  is a non-degenerate vibrational coordinate then  $x^2$  is symmetric, so  $\psi_0$  is symmetric.

$\psi_1 = \hat{Q}^\dagger \psi_0$ , and  $\hat{Q}^\dagger$  has the same symmetry as  $x$ , so  $\psi_1$  also has the same symmetry as  $x$ .

$\psi_2 = (\hat{Q}^\dagger)^2 \psi_0$ , which is symmetric because  $(\hat{Q}^\dagger)^2$  is symmetric.

Thus for non-degenerate vibrations, the vibrational states  $\psi_n$  alternate between symmetric (even  $n$ ) and the same symmetry as the vibrational coordinate (odd  $n$ ).



For a degenerate vibration, with coordinates  $x_1, x_2, \dots$ , there is a pair of ladder operators  $\hat{Q}_i$  and  $\hat{Q}_i^\dagger$  for each  $x_i$ . The ground state has zero quanta in each mode; it is  $\Psi_{00\dots} = \exp(-\frac{1}{2}(x_1^2 + x_2^2 + \dots))$ . The exponent is symmetric (see eq. (7.6)) so  $\Psi_{00\dots}$  is symmetric.

There is a set of singly-excited states  $\hat{Q}_i^\dagger \Psi_{00\dots}$ . These transform like the  $Q_i^\dagger$  and therefore like the  $x_i$ .

The doubly-excited states are  $Q_i^\dagger Q_j^\dagger \Psi_{00\dots}$ . These transform like the products  $Q_i^\dagger Q_j^\dagger$ , but  $Q_i^\dagger Q_j^\dagger = Q_j^\dagger Q_i^\dagger$ , so we only get the components of the symmetrized square.

Thus for an  $E$  vibration in  $\mathcal{D}_3$ , the ground state has symmetry  $A_1$ , the first excited state is doubly degenerate, with symmetry  $E$ , and the second excited state has symmetry  $(E \otimes E)_+ = A_1 + E$ . The  $A_1$  and  $E$  components will have different energies (no accidental degeneracy!) due to anharmonic interactions involving other vibrational states.

## Fermi resonance in CO<sub>2</sub>

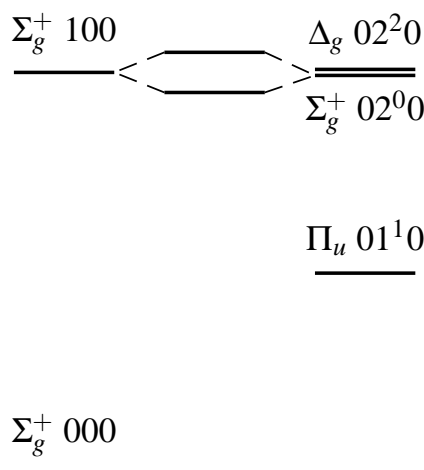
The bending vibration,  $\nu_2$ , in CO<sub>2</sub> has symmetry  $\Pi_u$ . The first excited state  $01^10$  has the same symmetry.

(The notation here indicates that there is one quantum of excitation in  $\nu_2$  and that the resulting angular momentum about the molecular axis is  $\pm 1$ .)

The doubly-excited state of this vibration has symmetry  $(\Pi_u \otimes \Pi_u)_+ = \Sigma_g^+ \oplus \Delta_g$ .

These states are denoted by  $02^00$  and  $02^20$  respectively: 2 quanta in  $\nu_2$ , leading to angular momentum 0 or  $\pm 2$ .

The  $\Sigma_g^+ 02^00$  state has the same symmetry, and very nearly the same energy, as the state  $100$  with a single excitation in the  $\nu_1$  symmetric stretch. There is an anharmonic term in the Hamiltonian proportional to  $Q_1(Q_{2x}^2 + Q_{2y}^2)$ , and this is responsible for the mixing between the two  $\Sigma_g^+$  states and the resulting splitting.



## 10. More on symmetry operations

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In ammonia, there are six possible permutations of the three protons, namely  $E$ ,  $(abc)$ ,  $(acb)$ ,  $(ab)$ ,  $(ac)$  and  $(bc)$ , each of which can be combined with the inversion  $E^*$  to give six permutation–inversions. Thus there are twelve operations altogether. However the usual symmetry group,  $C_{3v}$ , has only six elements. Which of the twelve do these correspond to, and what do the other six do?

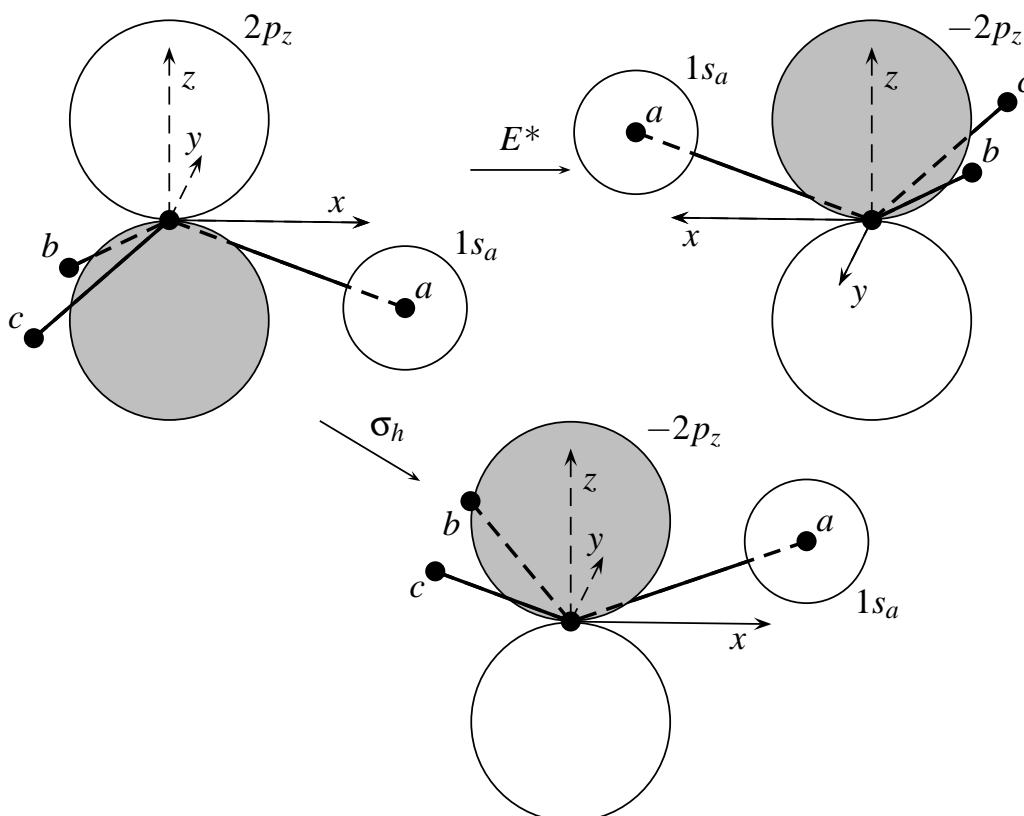
Permutation–inversions correspond to improper operations, and true permutations to proper ones, and it is not difficult to establish the mapping of  $(abc)$  and  $(acb)$  to  $C_3$  and  $C_3^{-1}$ , and of  $(ab)^*$ ,  $(bc)^*$  and  $(ac)^*$  to the three reflections. What does  $E^*$  do?

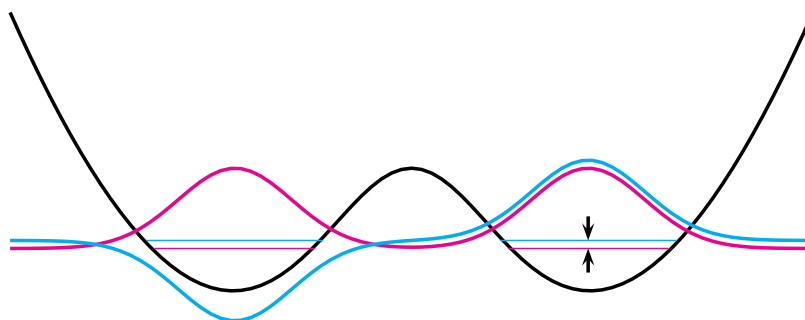
We define axes with  $z$  perpendicular to the plane of the H atoms,  $x$  so that the  $xz$  plane contains atom  $a$ , and  $y$  in the direction from  $c$  to  $b$ . The direction of the  $z$  axis is chosen to complete a right-handed frame.

Then the effect of  $E^*$  is to reflect everything, including the nuclear configuration, in the plane of the H atoms. We can regard it as a  $\sigma_h$  operation.

### Symmetry operations for $\text{NH}_3$ : $E^*$

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The new configuration of ammonia generated by the  $E^*$  operation is not superimposable on the original one — it is a mirror image. It is a second *version* of the equilibrium geometry, distinguishable from the first if we take nuclear labels into account. Moreover it is accessible from the original configuration via a planar configuration, with a low barrier of about  $25 \text{ kJ mol}^{-1}$ .

Vibrational wavefunctions of the two versions can mix by tunnelling through the barrier, and this leads to a small but observable splitting of the energy levels. The wavefunctions are either symmetric or antisymmetric with respect to the  $E^*$  operation, so we need it to get a complete symmetry classification.

## Feasibility

In ammonia, the two versions of the equilibrium geometry are easily accessible from each other via a low barrier. The operations that convert one version into the other are said to be *feasible*, and we need them for a complete classification of the energy levels.

In the methane molecule, there are  $4! = 24$  permutations of the four H atoms, and 24 permutation–inversions.

However some of these (in fact exactly half of them) lead to an inverted configuration of methane that can only be reached by crossing a very high energy barrier. There is no mixing between wavefunctions of these two versions of methane, and the symmetry operations that convert one into the other do not add any useful information. Such *non-feasible* operations can be ignored.

The *Molecular Symmetry Group* is the set of feasible permutations and permutation–inversions.

Ammonia is an example of a *non-rigid molecule*. Such molecules have more than one version of the minimum-energy geometry, distinguished from one another by nuclear labels, and connected to each other by low-energy pathways on the potential energy surface.

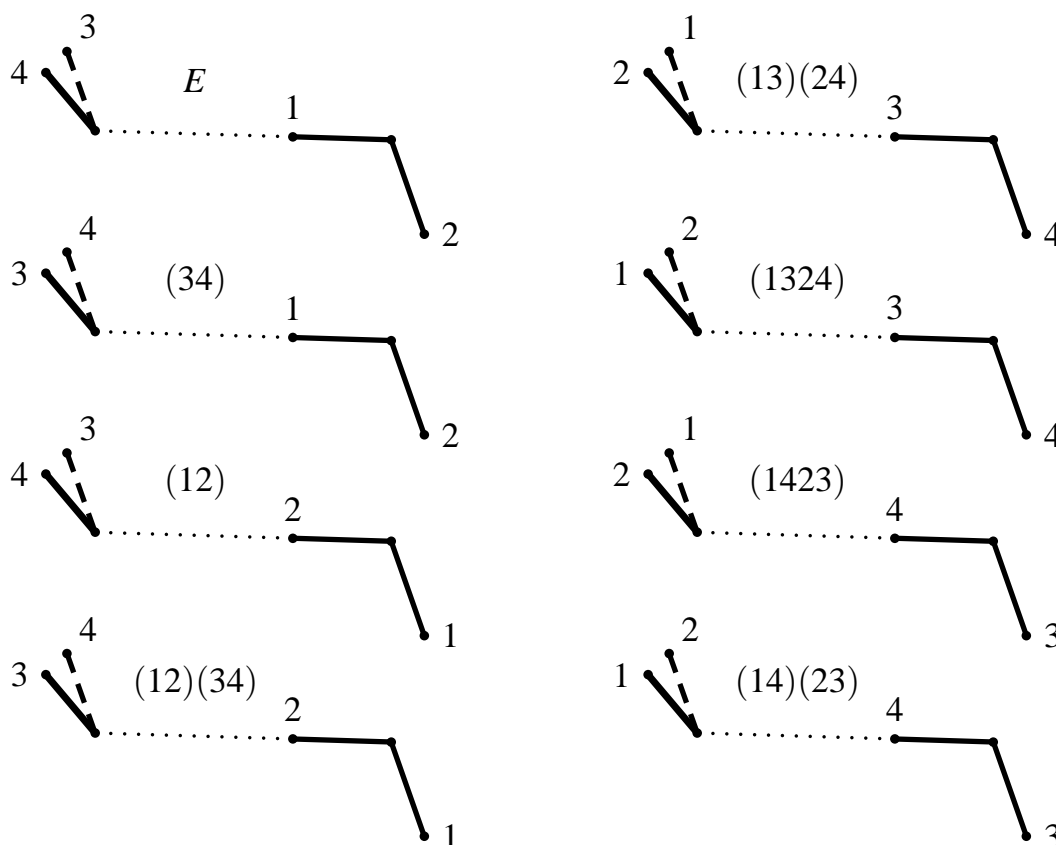
An important class of such non-rigid molecules comprises weakly-bound 'Van der Waals molecules'.

In the water dimer, for example, one molecule acts as a proton donor to the other to form a hydrogen bond. The resulting structure has  $C_s$  symmetry. The H atom in the hydrogen bond can be any of the four; moreover the two H atoms in the acceptor molecule can change places by a feasible motion.

Consequently there are eight versions of the equilibrium structure, each having  $C_s$  symmetry, so there are sixteen symmetry operations in the molecular symmetry group. All of these must be included in order to classify the vibrational states.

Often the symmetry groups for molecular clusters like this do not correspond to any of the standard tabulated symmetry groups.

## Water dimer



In the complex  $[\text{Ni}(\text{en})_3]^{2+}$  (en = ethylene diamine) the six N atoms act as ligands to the metal ion. Formally, the complex has  $\mathcal{D}_3$  symmetry only, and the metal  $d$  orbitals are classified in this group as  $A_1 \oplus E \oplus E$ .

This information does not in itself tell us much about the relative energies of the  $d$  orbitals. However the immediate environment of the metal ion is approximately octahedral. In  $O_h$  symmetry we know that the  $d$  orbitals split into  $E_g \oplus T_{2g}$ , with the  $E_g$  orbitals higher in energy by the crystal-field splitting  $\Delta$ , which we can estimate reasonably reliably from our knowledge of true octahedral complexes.

To determine what happens in  $[\text{Ni}(\text{en})_3]^{2+}$  we use *descent in symmetry*.

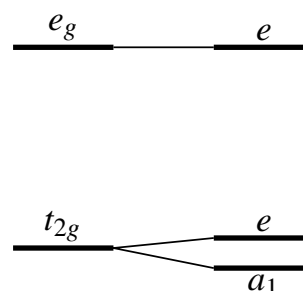
We start by classifying the orbitals according to the approximate symmetry  $O_h$ . Then we investigate the behaviour of the  $O_h$  symmetry orbitals under the symmetry operations that remain in  $\mathcal{D}_3$ .

## Descent in symmetry

Of the 48 symmetry elements in  $O_h$ , only six survive in  $\mathcal{D}_3$ : the identity, one of the  $C_3$  operations and its inverse, and three of the six dihedral  $C_2$  operations. In the  $O_h$  character table, we delete all the columns referring to the other symmetry operations, leaving three columns only. For each representation  $\Gamma$  of  $O_h$ , these three columns give the character for the surviving elements in  $\mathcal{D}_3$ . We have to reduce this character to determine the corresponding symmetry species in  $\mathcal{D}_3$ .

For  $[\text{Ni}(\text{en})_3]^{2+}$  we see that the  $E_g$  orbitals remain degenerate ( $E$  in  $\mathcal{D}_3$ ) while the  $T_{2g}$  orbitals split into  $A_1 \oplus E$ . We expect this splitting to be small. Group theory alone cannot predict the magnitude of the splitting or even its sign, but often the application of perturbation theory can answer such questions.

$O_h$	$E$	$C_3$	$C_2$	$\mathcal{D}_3$
$A_{1g}$	1	1	1	$A_1$
$A_{2g}$	1	1	-1	$A_2$
$E_g$	2	-1	0	$E$
$T_{1g}$	3	0	-1	$A_2 \oplus E$
$T_{2g}$	3	0	1	$A_1 \oplus E$



Time-dependent perturbation theory tells us that the transition probability between states  $|\Psi'\rangle$  and  $|\Psi''\rangle$  when a perturbation  $V \cos \omega t$  is applied is proportional to  $|\langle \Psi' | V | \Psi'' \rangle|^2$ , provided that  $\hbar\omega = |E' - E''|$ .

Usually  $V$  is proportional to the electric dipole moment operator (electric dipole transitions) but it can be the magnetic dipole operator (in magnetic resonance), the polarizability (in Raman scattering) or various other quantities. We consider only the electric dipole case, where the perturbation is the scalar product  $-\boldsymbol{\mu} \cdot \mathbf{E} \cos \omega t$  of the electric dipole operator and the electric vector of the radiation field.

The fundamental selection rule is then simply that if  $|\Psi'\rangle$ ,  $|\Psi''\rangle$  and  $\boldsymbol{\mu}$  transform according to  $\Gamma'$ ,  $\Gamma''$  and  $\Gamma_\mu$  respectively, then the transition probability is zero (the transition is *forbidden*) unless  $\Gamma_\mu \otimes \Gamma'' \ni \Gamma'$ .

## Selection rules for molecular spectroscopy

The general derivation of selection rules for molecular spectroscopy is summarized very briefly as follows. Write the wavefunction for the molecule as  $\Psi = \psi_{\text{rot}} \psi_{\text{int}}$ , where  $\psi_{\text{rot}}$  is the rotational function and  $\psi_{\text{int}}$  is the internal, i.e. vibrational-electronic or *vibronic*, function. Suppose that the light is polarized in the  $Z$  direction (fixed in space) so that  $V = -\mu_Z E_Z$  is proportional to the component  $\mu_Z$  of the dipole operator. We have  $\mu_Z = \sum_\alpha l_{\alpha Z} \mu_\alpha$ , where the  $l_{\alpha Z}$  are direction cosines depending on the orientation  $\Omega$  of the molecule, and the  $\mu_\alpha$  are components of  $\boldsymbol{\mu}$  referred to axes fixed in the molecule.

Then we can factorise the golden rule integral into a part that depends only on the molecular orientation, and a part that depends only on the internal coordinates:

$$\begin{aligned} \langle \Psi' | \mu_Z | \Psi'' \rangle &= \int \psi'_{\text{rot}}{}^* \psi'_{\text{int}}{}^* \mu_Z \psi''_{\text{rot}} \psi''_{\text{int}} d\tau \\ &= \sum_\alpha \int \psi'_{\text{rot}}{}^* l_{\alpha Z} \psi''_{\text{rot}} d\Omega \int \psi'_{\text{int}}{}^* \mu_\alpha \psi''_{\text{int}} dQ dq, \end{aligned} \quad (11.1)$$

where  $Q$  refers to vibrational coordinates and  $q$  to electronic.

Here the transition is between rotational levels of the same vibronic state, usually the ground state, so  $\Psi'_{\text{int}} = \Psi''_{\text{int}} = \Psi_{\text{int}}^0$  and the second integral in (11.1) is the expectation value of the dipole moment in the ground state  $\Psi_{\text{int}}^0$ . At least one component must be non-zero for pure rotational transitions to occur. The first factor of (11.1) then gives the detailed selection rules  $\Delta J = 0, \pm 1$  etc.

For example, consider a linear molecule. Here  $\mu_x = \mu_y = 0$ , so the only non-zero term in (11.1) has  $\alpha = z$ . If the molecular axis  $z$  lies in the direction  $(\theta, \varphi)$ , then  $l_{zZ} = \cos \theta$ , which is proportional to the spherical harmonic  $Y_{10}$ , while the rotational wavefunctions are also spherical harmonics.

Consequently the rotational factor has the form

$$\int Y_{J'M'}^* Y_{10} Y_{J''M''} d\Omega, \quad (11.2)$$

which is zero unless  $\Gamma^{(J'')} \otimes \Gamma^{(1)} \ni \Gamma^{(J')}$ , i.e. unless  $J'' = J'$  or  $J' \pm 1$ . However we must also take parity into account:  $Y_{JM}$  changes sign under the parity operation if  $J$  is odd but not if  $J$  is even, so the integral vanishes if  $J' + J'' + 1$  is odd, which it is if  $J' = J''$ . Consequently the selection rule is  $J' = J'' \pm 1$ .

## Vibration-rotation spectroscopy

Write  $\Psi_{\text{int}} = \Psi_{\text{elec}}(q, Q) \Psi_{\text{vib}}(Q)$  and integrate over the electronic coordinates  $q$ . The transition is between vibration-rotation levels of the same electronic state, so  $\Psi'_{\text{elec}} = \Psi''_{\text{elec}} = \Psi_{\text{elec}}^n$  and the second factor in (11.1) becomes

$$\int \Psi'_{\text{vib}}^* \mu_{\alpha}^n(Q) \Psi''_{\text{vib}} dQ, \quad (11.3)$$

where  $\mu_{\alpha}^n(Q)$  is the dipole moment in state  $\Psi_{\text{elec}}^n$ :

$$\mu_{\alpha}^n(Q) = \int \Psi_{\text{elec}}^n(q, Q)^* \mu_{\alpha}(q, Q) \Psi_{\text{elec}}^n(q, Q) dq. \quad (11.4)$$

$\mu_{\alpha}^n$  remains a function of  $Q$ ; expand it in a Taylor series about the equilibrium geometry:

$$\mu_{\alpha}^n(Q) = (\mu_{\alpha}^n)_{\text{eq}} + \sum_k Q_k \left( \frac{\partial \mu_{\alpha}^n}{\partial Q_k} \right)_{\text{eq}} + \dots \quad (11.5)$$

$$\mu_{\alpha}^n(Q) = (\mu_{\alpha}^n)_{\text{eq}} + \sum_k Q_k \left( \frac{\partial \mu_{\alpha}^n}{\partial Q_k} \right)_{\text{eq}} + \dots \quad (11.5)$$

Now the terms in this equation must all transform in the same way.  $\mu_{\alpha}^n$  is a vector component and transforms as such; the normal mode  $Q_k$  transforms according to some irreducible representation  $\Gamma_k$ ; while the coefficients  $(\mu_{\alpha}^n)_{\text{eq}}$  and  $(\partial \mu_{\alpha}^n / \partial Q_k)_{\text{eq}}$  are just numbers and so are totally symmetric.

Thus  $(\mu_{\alpha}^n)_{\text{eq}}$  must be zero unless  $\mu_{\alpha}$  is symmetric, and similarly  $(\partial \mu_{\alpha}^n / \partial Q_k)_{\text{eq}}$  must be zero unless  $Q_k$  has the same symmetry as  $\mu_{\alpha}$ .

The first factor of (11.1) gives the rotational selection rules in the same way as before, but we may now have *parallel* vibrations in which  $\mu_z$  varies, and *perpendicular* vibrations in which  $\mu_x$  or  $\mu_y$  vary. For the former, the rotational selection rules are as for pure rotational spectroscopy, so that the spectrum shows *P* and *R* branches but no *Q*; for the latter, it turns out that the *Q* branch is allowed as well. For details, see Hollas 'High Resolution Spectroscopy' or Bernath 'Spectra of Atoms and Molecules'.

The second term in (11.5) is responsible for vibrational transitions...

## Vibrational selection rule

The vibrational integral is now

$$\begin{aligned} \int \psi'_{\text{vib}} * \mu_{\alpha}^n(Q) \psi''_{\text{vib}} dQ &= \int \psi'_{\text{vib}} * \left( (\mu_{\alpha}^n)_{\text{eq}} + \sum_k Q_k \left( \frac{\partial \mu_{\alpha}^n}{\partial Q_k} \right)_{\text{eq}} + \dots \right) \psi''_{\text{vib}} dQ \\ &= (\mu_{\alpha}^n)_{\text{eq}} \int \psi'_{\text{vib}} * \psi''_{\text{vib}} dQ \\ &\quad + \sum_k \left( \frac{\partial \mu_{\alpha}^n}{\partial Q_k} \right)_{\text{eq}} \int \psi'_{\text{vib}} * Q_k \psi''_{\text{vib}} dQ + \dots \end{aligned} \quad (11.6)$$

The first term is an overlap integral between vibrational eigenfunctions, and is zero unless  $\psi'_{\text{vib}} = \psi''_{\text{vib}}$ , in which case we're back to pure rotational spectroscopy.

In the second term, we can write  $Q_k$  in terms of the ladder operators:

$$Q_k = \sqrt{\frac{1}{2}} (\hat{Q}_k + \hat{Q}_k^{\dagger}). \quad (11.7)$$

Operating on  $\psi''_{\text{vib}}$  this increases or reduces the vibrational quantum number in mode  $k$  by 1 (for harmonic oscillator functions), so we obtain the vibrational selection rule  $\Delta v_k = \pm 1$ .



## Electronic spectroscopy

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Here  $\psi'_{\text{elec}} \neq \psi''_{\text{elec}}$ , but we can still follow the same procedure to get an expansion of the transition dipole between the electronic states ( $m$  and  $n$ , say)

$$\begin{aligned} \mu_{\alpha}^{mn}(Q) &= \int \psi_{\text{elec}}^m(q, Q)^* \mu_{\alpha}(q, Q) \psi_{\text{elec}}^n(q, Q) dq \\ &= (\mu_{\alpha}^{mn})_{\text{eq}} + \sum_k Q_k \left( \frac{\partial \mu_{\alpha}^{mn}}{\partial Q_k} \right)_{\text{eq}} + \dots \end{aligned} \quad (11.8)$$

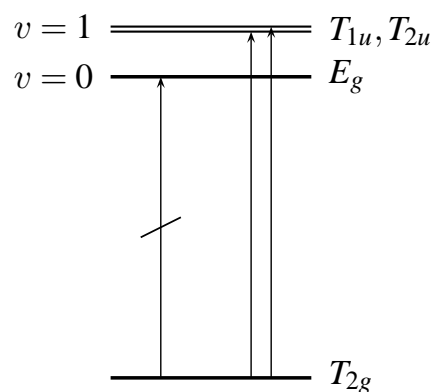
If  $(\mu_{\alpha}^{mn})_{\text{eq}} \neq 0$ , the transition is allowed; if  $(\mu_{\alpha}^{mn})_{\text{eq}} = 0$ , so that the transition is electronically forbidden, the second term may still be non-zero (so that the transition dipole becomes non-zero when the molecule is distorted) and we get a simultaneous vibrational–electronic transition. Such transitions are substantially weaker than normal allowed transitions.

## Vibrationally allowed electronic transitions

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In octahedral transition-metal complexes, the low-lying excited states arise from  $d-d$  transitions between the  $t_{2g}$  and  $e_g$  levels. Being  $g \leftrightarrow g$  transitions they are forbidden by the Laporte (parity) selection rule.

Consider however a transition in a  $d^1$  complex from the  ${}^2T_{2g}$  electronic ground state in its ground vibrational state to the  ${}^2E_g$  electronic excited state with (say) a  $T_{1u}$  vibration excited. The upper state has symmetry  $E_g \otimes T_{1u} = T_{1u} \oplus T_{2u}$ .



The dipole operator transforms according to  $T_{1u}$ , so transitions are allowed to excited states that transform like some component of  $T_{2g} \otimes T_{1u} = A_{2u} \oplus E_u \oplus T_{1u} \oplus T_{2u}$ . Consequently transitions to both the  $T_{1u}$  and  $T_{2u}$  components of the excited state are allowed.