

**LECTURE 3**  
**DIRECT PRODUCTS AND SPECTROSCOPIC SELECTION RULES**

### 3.1 Direct products and many electron states

Consider the problem of deciding upon the symmetry of functions formed as the product of two or more functions. This issue is of importance in determining the symmetry of many electron states from configurations when we know the symmetry of the individual one electron wavefunctions; and in formulating spectroscopic selection rules between orbitals or electronic states of known symmetry or between vibrational states.

By convention small letters such as  $a_1$ ,  $t_2$  etc. are used to specify configurations e.g.  $a_1^2$ ,  $t_2^4, e^3$ ; and large letters are used to label the many electron states e.g.  $^3A_2$ ,  $^2T_1$  etc. The notation for the many electron states also introduces the spin degeneracy  $(2S+1)$  as a superscript. These conventions are reminiscent of those used in atomic theory and indeed the derivation of Russell-Saunders term symbols for a specified configuration can be considered as a group theoretical problem analogous to that being treated here.

### 3.2 Non-degenerate representations

Suppose we multiply a function belonging to the irreducible representation  $\Gamma_1$  by another function belonging to  $\Gamma_2$ . The characters of the product function  $\Gamma_{12}$  must be given by:

$$\chi_{12}(R) = \chi_1(R)\chi_2(R)$$

We can thus assign the product function to one of the irreducible representations of the relevant point group by simply multiplying out the characters and inspecting the character table.

Consider for example the point group  $C_{2v}$ .

$C_{2v}$	$E$	$C_2$	$\sigma_v(xz)$	$\sigma'_v(yz)$
$A_1$	1	1	1	1
$A_2$	1	1	-1	-1
$B_1$	1	-1	1	-1
$B_2$	1	-1	-1	1

Trivially multiplying a function of any symmetry by a function of  $A_1$  symmetry does not alter the symmetry of the original function. In addition if we multiply together any two functions of the same symmetry we produce a function of  $A_1$  symmetry. We also have:

$C_{2v}$	$E$	$C_2$	$\sigma_v(xz)$	$\sigma'_v(yz)$	
$A_2 \times B_1$	1	-1	-1	1	$= B_2$
$A_2 \times B_2$	1	-1	1	-1	$= B_1$
$B_1 \times B_2$	1	1	-1	-1	$= A_2$

We can thus set up a table of *direct products*.

$C_{2v}$	$A_1$	$A_2$	$B_1$	$B_2$
$A_1$	$A_1$	$A_2$	$B_1$	$B_2$
$A_2$		$A_1$	$B_2$	$B_1$
$B_1$			$A_1$	$A_2$
$B_2$				$A_1$

One simple use of this table is to demonstrate that closed shell configurations such as  $a_1^2$ ,  $a_2^2$ ,  $b_1^2$  etc. must give rise to a totally symmetric  $A_1$  state. This must be  $^1A_1$  because the electrons are spin paired in a non-degenerate level.

### 3.3 Groups with degenerate irreducible representations

Consider the point group  $C_{3v}$ . The same ideas as developed for the point group  $C_{2v}$  apply to the non-degenerate  $A_1$  and  $A_2$  irreducible representations. In addition  $A_1 \times E$  or  $A_2 \times E$  is simply  $E$ . The interesting case is  $E \times E$ , which gives a set of characters that do not correspond to one of the irreducible representations of the group. However, application of the reduction formula allows us to deduce that this representation is reducible to  $A_1 + A_2 + E$ .

$C_{3v}$	$E$	$2C_3$	$3\sigma_v$
$A_1$	1	1	1
$A_2$	1	1	-1
$E$	2	-1	0
$E \times E$	4	1	0

Thus the direct product table has the form shown below.

$C_{3v}$	$A_1$	$A_2$	$E$
$A_1$	$A_1$	$A_2$	$E$
$A_2$		$A_1$	$E$
$E$			$A_1 + [A_2] + E$

There is a problem in deciding upon the electronic states that are supported by the  $e^2$  configuration. There are only 6 ways of arranging 2 electrons in a pair of degenerate orbitals so as not to violate the Pauli exclusion principle. Thus we cannot freely associate

singlet and triplet spin wave functions with each of the  $A_1$ ,  $A_2$  and  $E$  spatial wavefunctions. The required 6 microstates are produced either by the states  ${}^3A_1 + {}^1A_2 + {}^1E$  or by  ${}^1A_1 + {}^3A_2 + {}^1E$ . If we use the symbols  $\alpha$  and  $\beta$  to denote spin up and spin down and distinguish between electron 1 and 2 with parentheses, then the possible spin wavefunctions are:

$$\begin{array}{ll} \alpha(1)\beta(2) - \alpha(2)\beta(1) & \text{Singlet spin wavefunction} \\ \alpha(1)\alpha(2) & \\ \beta(1)\beta(2) & \text{Triplet spin wavefunctions.} \\ \alpha(1)\beta(2) + \alpha(2)\beta(1) & \end{array}$$

The triplet spin wavefunctions are thus symmetric with respect to particle interchange, whereas the singlet spin wavefunctions are antisymmetric. Electrons are *Fermions* and therefore the overall wavefunction should be antisymmetric with respect to particle interchange. Thus the triplet spin wavefunctions must be associated with that part of the direct product which is antisymmetric with respect to particle interchange. Special procedures exist for deciding which part is antisymmetric under interchange, but it suffices here to note that square brackets in the direct product tables are used to identify the antisymmetric part. Thus in the present case we see that the triplet spin wavefunction is associated with the  $A_2$  spatial wavefunction. Hence the configuration  $e^2$  gives terms  ${}^1A_1 + {}^3A_2 + {}^1E$ .

Extending these ideas to the point group  $T_d$  where we have both 2-fold and 3-fold degenerate irreducible representations, we must reduce the representations associated with the direct product  $E \times E$ ,  $E \times T_1$ ,  $E \times T_2$ ,  $T_1 \times T_1$ ,  $T_1 \times T_2$  and  $T_2 \times T_2$  to give the direct product table shown below.

$T_d$	$A_1$	$A_2$	$E$	$T_1$	$T_2$
$A_1$	$A_1$	$A_2$	$E$	$T_1$	$T_2$
$A_2$		$A_1$	$E$	$T_2$	$T_1$
$E$			$A_1 + [A_2] + E$	$T_1 + T_2$	$T_1 + T_2$
$T_1$				$A_1 + E + [T_1] + T_2$	$A_2 + E + T_1 + T_2$
$T_2$					$A_1 + E + [T_1] + T_2$

Where a two-electron configuration involves occupation of two different subshells, both singlet and triplet states are allowed without restriction:

$$\begin{array}{lll} f_1^1 e^1 & \rightarrow & {}^3T_1 + {}^1T_1 + {}^3T_2 + {}^1T_2 \\ f_2^1 e^1 & \rightarrow & {}^3T_1 + {}^1T_1 + {}^3T_2 + {}^1T_2 \\ f_1^1 f_2^1 & \rightarrow & {}^3A_2 + {}^1A_2 + {}^3E + {}^1E + {}^3T_1 + {}^1T_1 + {}^3T_2 + {}^1T_2 \end{array}$$

Again problems arise in dealing with the states arising from configurations with two electrons in the same subshell. Of course the character tables give us the final answer, but in the particular case of the  $e^2$  and  $t_2^2$  configuration we can use a correlation approach to decide which irreducible representations support triplet states.

We know that the  $d^2$  electron configuration gives rise to the following Russell-Saunders terms:

$$d^2 \rightarrow {}^1S + {}^3P + {}^1D + {}^3F + {}^1G$$

But tables in descent of symmetry tell us that the triplet atomic terms behave as follows in a tetrahedral field:

$$\begin{array}{ll} {}^3P & \rightarrow {}^3T_1 \\ {}^3F & \rightarrow {}^3A_2 + {}^3T_1 + {}^3T_2 \end{array}$$

The molecular terms derived from the atomic terms by descent of symmetry must correspond to the terms derived from direct products in the three possible  $d$  electron configurations in a tetrahedral field, namely  $e^2$ ,  $t_2^1e^1$  and  $t_2^2$ . The  $t_2^1e^1$  configuration accounts for  ${}^3T_1 + {}^3T_2$  so that the triplet term for  $e^2$  must be  ${}^3A_2$  and the triplet term for  $t_2^2$  must be  ${}^3T_1$ . Hence we have:

$$\begin{array}{ll} e^2 \rightarrow {}^1A_1 + {}^3A_2 + {}^1E & \text{(gives 6 microstates in total)} \\ t_2^2 \rightarrow {}^1A_1 + {}^1E + {}^3T_1 + {}^1T_2 & \text{(gives 15 microstates in total)} \end{array}$$

### 3.4 General features of tables of direct products

Tables of direct products are supplied in finals. They do not deal explicitly with all groups and the basic tables need to be supplemented with the additional rules:

$g \times g = g$	$' \times ' = '$
$u \times u = g$ for groups with an $i$ centre.	$'' \times '' = ' \quad \text{for groups with a } \sigma_h \text{ plane}$
$g \times u = u$	$' \times '' = '' \quad \text{but no } i \text{ centre.}$

A general feature of **all** of the tables (illustrated by the specific examples above) is that the totally symmetrical irreducible representation only occurs on the diagonal in the tables, where we are multiplying together two functions belonging to the same irreducible representation.

### 3.5 Quantum mechanical integrals

Very often in quantum mechanics we need to evaluate integrals of the sort:

$$I = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} f(x, y, z) dx dy dz$$

which is often abbreviated as:

$$I = \int f(x, y, z) d\tau$$

where the symbol  $d\tau$  indicates integration over all space.

In one dimension we know that when we integrate a function between  $+\infty$  and  $-\infty$ , the integral is zero for odd functions:

$$\text{if } f_1(x) = -f_1(-x), \quad \text{then } \int_{-\infty}^{+\infty} f_1(x) dx = 0$$

by contrast for even functions the integral is not necessarily zero:

$$\text{if } f_1(x) = f_1(-x), \quad \text{then } \int_{-\infty}^{+\infty} f_1(x) dx \neq 0$$

By extending these ideas to three dimensions, a general rule emerges which is that in a particular point group an integral over all space can only non zero if the function being integrated belongs to the totally symmetric irreducible representation. If this condition is not satisfied the "odd" nature of the function under one or more symmetry operations always give rise to negative volume elements which cancel positive volume elements. Note however that even if a function is totally symmetric, this does not guarantee that the integral will be non zero. For example a  $p_z$  orbital on oxygen in  $\text{H}_2\text{O}$ , but the integral over all space is zero.

### 3.6 Spectroscopic selection rules

In spectroscopy we are concerned with transitions between states each characterised by wavefunctions. Let ground and excited state wavefunctions be  $\Psi_1$  and  $\Psi_2$ . In general a transition is mediated by an operator  $\hat{O}$  and the intensity of the transition is such that:

$$I \propto \left| \int \Psi_1 \hat{O} \Psi_2 \right|^2$$

Hence for non-zero intensity the direct product  $\Gamma_1 \times \Gamma_O \times \Gamma_2$  must contain the totally symmetric irreducible representation.

For both **infrared and visible/UV** spectroscopy the operator responsible for transitions driven by the oscillating electric fields associated with the incident electromagnetic radiation is the *electric dipole moment operator*. This has components which transform like the translations  $x$ ,  $y$  and  $z$ . The irreducible representations corresponding to the three vectors always appear in character tables. Much weaker *magnetic dipole transitions* are mediated by oscillating magnetic fields. Here the operator transforms like the rotations  $R_x$ ,  $R_y$  and  $R_z$ .

When dealing with closed shell molecules in their ground vibrational state, the ground state wavefunction is totally symmetric and does not therefore affect the direct product  $\Gamma_0 \times \Gamma_2$ . It thus follows that the only transitions that can be observed in IR involve vibrations of same symmetry as the dipole moment operator (because only on the diagonal of the direct product table do we find totally symmetric irreducible representations), and we can deduce IR activity by simple inspection of the character table.

In **Raman spectroscopy** incident electric fields produce an oscillating polarisation of the molecule, which then emits radiation at the incident frequency minus a vibrational frequency (Stokes scattering). Raman activity is governed by the **polarisability tensor**, which relates the dipole induced in x, y and z directions to electric fields  $E_x$ ,  $E_y$  and  $E_z$ .

$$\begin{pmatrix} \mu_x \\ \mu_y \\ \mu_z \end{pmatrix} = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix}$$

The components of the polarisability tensor transform like  $x^2$ ,  $y^2$ ,  $xy$ ,  $xz$  etc. or linear combinations of them. Since  $xy$  and  $yx$ ,  $xz$  and  $zx$  and  $yz$  and  $zy$  have the same transformation properties, there are 6 components of the polarisability tensor to worry about. One component is always totally symmetrical, whilst the other 5 components behave like the d orbitals. Again for closed shell molecules one can deduce the pattern of Raman activity by simple inspection of the character table which always spells out explicitly the irreducible representations corresponding to the 6 components of the polarisability tensor.

### 3.7 Some examples of electronic transitions from transition metal spectroscopy

#### 3.7.1 $d^1$ in a tetrahedral environment.

The ground state  $e^1$  configuration gives a term  $^2E$  ground term and the  $t_2^1$  excited state gives a term  $^2T_2$ . The dipole operator is  $T_2$ . The direct product  $E \times T_2 \times T_2$  may be evaluated step by step as  $(E \times T_2) \times T_2 = (T_1 + T_2) \times T_2$ . The term  $T_2 \times T_2$  obviously contains  $A_1$  so that the transition  $^2E \rightarrow ^2T_2$  is allowed.

#### 3.7.2 $d^2$ in a tetrahedral environment.

The  $e^2$  ground configuration gives a  $^3A_2$  ground state, whilst the excited configuration  $e^1 t_2^1$  gives triplet terms  $^3T_1$  and  $^3T_2$ .

$$A_2 \times T_2 \times T_1 = (A_2 \times T_2) \times T_1 = T_1 \times T_1 = A_1 + E + T_1 + T_2$$

This triple direct product contains  $A_1$  and so the transition  $^3A_2 \rightarrow ^3T_1$  is allowed.

$$A_2 \times T_2 \times T_2 = (A_2 \times T_2) \times T_2 = T_1 \times T_2 = A_2 + E + T_1 + T_2$$

This triple direct product does not contain  $A_1$  and so the transition  $^3A_2 \rightarrow ^3T_2$  is not allowed.

### 3.7.3 *d* electron configurations in octahedral ( $O_h$ ) symmetry.

All *d* electron configurations necessarily give rise to gerade (*g*) terms because the *d* orbitals are *g*. The dipole moment operator is  $T_{1u}$ . Any direct product of the sort  $g \times u \times g = u$  and so cannot contain  $A_{1g}$ . Hence *d* to *d* transitions are dipole forbidden in octahedral symmetry.

## 3.8 Combination and overtone bands

For purely harmonic potential functions, only one vibrational quantum can be excited by absorption of one photon. However, anharmonicity allows simultaneous excitation of two or more quanta of one vibration in *overtone bands* or one quantum each of two or more different vibrations in combination bands. Where two quanta are involved the selection rule is that the quadruple direct product  $\Gamma_1 \times \Gamma_0 \times (\Gamma_2 \times \Gamma_3)$  must contain the totally symmetric irreducible representation. For closed shell molecules this effectively means that the direct product between the two vibrations involved  $\Gamma_2 \times \Gamma_3$  must contain  $\Gamma_0$ . A special point is that because vibrations are Bosons, only the symmetric part of the direct product (*i.e.* that part **not** appearing in brackets in multiplication tables) is relevant.

## 3.9 Vibronic transitions

These involve a simultaneous change in electronic and vibrational state. The vibronic mechanism may allow appearance of an otherwise forbidden electronic transition by involvement of a *promoting* vibrational mode. Again we must consider a quadruple product, but here the ground wavefunction  $\Gamma_1$  may not be totally symmetric if we are dealing with transition metal compounds.  $\Gamma_2$  represents the excited state electronic wavefunction and  $\Gamma_3$  the promoting vibration.

A very important set of transitions involving a vibronic mechanism are *d* to *d* transitions in octahedral complexes. An octahedron has stretching vibrations  $a_{1g} + e_g + t_{1u}$  and bends  $t_{1u} + t_{2u} + t_{2g}$ . Consider excitation of a *d*<sup>1</sup> complex from the  $T_{2g}$  ground state to the  $E_g$  excited state. This is electronically forbidden but the quadruple product:

$$t_{2g} \times t_{1u} \times (e_g \times t_{1u}) = (t_{2g} \times t_{1u}) \times (t_{1u} + t_{2u}) = (a_{2u} + e_u + \mathbf{t_{1u}} + \mathbf{t_{2u}}) \times (\mathbf{t_{1u}} + \mathbf{t_{2u}})$$

contains two diagonal products (and therefore  $a_{1g}$  twice) and so the transition vibronically promoted by the  $t_{1u}$  modes is allowed.

## PROBLEMS

1. The sequence of electronic states for *d*<sup>7</sup> Co(II) ions in a tetrahedral environment is  ${}^4A_2 < {}^4T_2 < {}^4T_1 < {}^4T_1$ . Show that in absorption from the  ${}^4A_2$  ground state, only 2 of the possible 3 transitions are electronically allowed by an electric dipole mechanism, but that in emission from the highest  ${}^4T_1$  state, all 3 transitions are allowed.

**2.** Show that the transition  ${}^2T_{2g} \rightarrow {}^2E_g$  in an octahedral  $d^1$  compound is magnetic dipole allowed.