

## Chapter 5

### 5.1 Wave Functions as Bases for Irreducible Representations

Remember that  $\mathcal{H}\Psi = E\Psi$  where  $H$  = Hamiltonian operator,  $\Psi$  = wave function,  $E$  = eigenvalue (the system energy). Thus,  $\mathcal{H}\Psi$  means that an operation ( $\mathcal{H}$ ) acts on a function ( $\Psi$ ) to yield a constant ( $E$ ) times the same function. When a wave function obeys this equation it is called an eigenfunction. In the text below, the terms will be used interchangeably.

An important property of the Hamiltonian is that it must not change if an applicable symmetry operation is performed on the molecule. This is reasonable since the molecule after the operation is indistinguishable from it before and so its energy should not change either.

If this is true, then operations must commute with the Hamiltonian:

$$\mathcal{H}R\Psi = R\mathcal{H}\Psi = ER\Psi = RE\Psi$$

All this says is that, since the energy doesn't change, it doesn't matter if one performs the symmetry operation before or after applying the Hamiltonian to the wave function.

Now each electron is associated with a particular wave function and it's possible for them to lie in degenerate orbitals. This means it's possible for different wave functions to yield the same eigenvalues. e.g.

$$\mathcal{H}\Psi_{i1} = E_i\Psi_{i1} \quad \text{and} \quad \mathcal{H}\Psi_{i2} = E_i\Psi_{i2}$$

In this case it's important to remember that  $\Psi_{i1}$  and  $\Psi_{i2}$  are not identical because the orbitals exist in different regions of space (e.g.  $p_x$  &  $p_y$ ), but yield orbitals of equal energy. Furthermore, a linear combination of the eigenfunctions will yield the same eigenvalue. (i.e.  $\mathcal{H}\sum_j a_{ij}\Psi_{ij} =$

$E_i\sum_j a_{ij}\Psi_{ij}$  where  $a_{ij}$  is the relative weighting of each eigenfunction)

Eigenfunctions are also orthonormal. These are functions that are both orthogonal ( $\int\Psi_i\Psi_j d\tau$

= 0 where  $i \neq j$ ) and normalized (total probability equals 1).

Recall from earlier that symmetry operations must commute with the Hamiltonian. Using the book's notation " $R$ " for a generic symmetry operation, we find for a non-degenerate eigenfunction

$$\mathcal{H}R\Psi_i = E_i R\Psi_i$$

Since the eigenfunction must be normalized, then  $R$  must equal  $\pm 1$ . This will be true of each operation in a point group so that one will generate a representation  $\Gamma$  for the group with values of  $\pm 1$  for each element (class). Since the element  $E$  is  $+1$ , this must be an irreducible representation.

The situation for degenerate eigenfunctions is more complex. The book works through the general math, then a specific example on pp. 102 – 105. I'll provide an alternative narrative to go with the math. From equations 5.1-9 – 5.1-13, the object is to show that for degenerate orbitals, you start by plugging in a linear combination of eigenfunctions and then, because the "multiplication" of any two operators within a point group gives rise to a third operator within the same point group, you can generate another irreducible representation that incorporates the degeneracy. This is, perhaps, not obvious from the abstract math on pp. 102 & 103 and so the example on the next 2 pages serves to illustrate that this is true.

The example, the  $p$  orbitals in ammonia, involves intrinsically linked orbitals. The eigenfunctions for the orbitals ( $\Psi_1 \sin\theta \cos\phi$  and  $\Psi_1 \sin\theta \sin\phi$ ) differ somewhat from what you have seen in the past because, I think, they take into account the 3 dimensional shape of the orbital. The book refers you to Figure 8.1 (p. 205) which is worth looking at if you've never worked with polar coordinates. The 4 lines following "and hence" are a mathematical relationship you may have forgotten:  $\cos(\alpha + \beta) = \cos\alpha \cos\beta - \sin\alpha \sin\beta$  &  $\sin(\alpha + \beta) = \sin\alpha \cos\beta + \cos\alpha \sin\beta$

This, then, lays the groundwork for operating each of the symmetry elements on the eigenfunction to illustrate the creation of a 2-dimensional irreducible representation.

## 5.2 The Direct Product

From the perspective of point groups, a direct product of two eigenfunctions, each transforming as an irreducible representation, results in multiplying each pair of characters for a given class to give either a reducible or irreducible representation. (This is the first theorem and is proved in the book.) For example, consider the totally symmetric irreducible representation for any group, multiplying it by any other irreducible representation of that point group, returns the second irreducible representation. For example, for  $C_{3v}$   $A_1A_2 = A_2$ .

$C_{3v}$	E	$2C_3$	$3\sigma_v$
$A_1$	1	1	1
$A_2$	1	1	-1
E	2	-1	0
$A_1A_2$	1	1	-1

However, as we'll see later, the product may be reducible, depending on which irreducible representations are multiplied. If so, the resulting reducible representation is a linear combination of irreducible representations (p. 106) and can be deconstructed (see pp. 87 – 88). Direct products are important because they describe the interaction of eigenfunctions. Finally, higher order direct products are possible. These involve multiplying more than 2 irreducible representations, but otherwise they work exactly the same as just described.

Consider 2 functions  $f_A$  and  $f_B$ . For the integral  $\int f_A f_B d\tau$ , the result will be zero unless the integrand  $f_A f_B$  is invariant to all symmetry operations in the point group in question. (Remember that the integrand is the function to be integrated and that invariant means that the integrand does

not change sign or magnitude.) In general, the integrand will be invariant only if  $\Gamma_{AB}$  (reducible representation of the direct product  $A \cdot B$ ) includes the total symmetric irreducible representation. If it does, the totally symmetric irreducible representation will appear only once.

### Illustrative Example – Point Group $D_4$

In brief, this section shows that, for at least one point group  $D_4$ , the product of at least one pair of irreducible representations produces a reducible representation that includes the  $A_1$  representation. Also, for the integration of higher order integrals the same is true. One of the irreducible representations must be  $A_1$  for the integral to be non-zero. You can show yourself this is generally true by working an example on another point group.

### 5.3 Identifying Non-Zero Matrix Elements

The interaction energy between any 2 states is given by the equation:

$$\mathcal{H}\psi_i = E\psi_j \rightarrow \frac{\int \psi_i \mathcal{H} \psi_j d\tau}{\int \psi_i \psi_j d\tau} = E$$

Since the Hamiltonian must contain all of the symmetry elements of the molecule, the symmetry of the integrands depends on  $\psi_i$  and  $\psi_j$ . If their product includes the totally symmetric representation the integral will have a non-zero value. This will happen if their irreducible representations are the same.

Another application of the material from Section 5.2 concerns the selection rules for spectral transitions. The frequency of light associated with a spectral transition is given by  $h\nu = E_i - E_j$ .

The intensity of this transition is given by:

$$I \propto \int \psi_i \mu \psi_j d\tau$$

where  $\mu$  is the transition moment operator. When  $\mu$  is the electric dipole operator, then

$$\mu = \sum_i e_i x_i + \sum_i e_i y_i + \sum_i e_i z_i$$

where  $e_i$  is the charge on a particle and  $x$ ,  $y$ , and  $z$  are its Cartesian coordinates. This operator couples the electric vector of a molecule with electromagnetic radiation to allow its transfer to or from the molecule.

Because the coordinate axes are orthogonal, equation 5.3-3 expands to:

$$I_x \propto \int \psi_i x \psi_j d\tau$$

$$I_y \propto \int \psi_i y \psi_j d\tau$$

$$I_z \propto \int \psi_i z \psi_j d\tau$$

The symmetry of the molecule directly affects how the light interacts with it. First, the electric dipole will have one irreducible representation associated with it in each direction. Thus, the direct product of the irreducible representations of  $\psi_i$ ,  $\psi_j$ , and the electric dipole must contain the totally symmetric irreducible representation for an absorption or emission to occur. In most cases, molecules are very low symmetry and only light polarized in a single direction will be absorbed. It is certainly possible for none of the transitions to be symmetry allowed. It is also possible for 2 or 3 of the transitions to combine, but this requires the molecules to have E and T irreducible representations.

Illustrative Example:  $\text{Mo}_2\text{X}_8^{4-}$

This molecule belongs to the  $D_{4h}$  point group. If the  $\delta$  and  $\delta^*$  molecular orbitals are subjected to each of the operations in  $D_{4h}$  the table at the bottom of p. 112 is generated (make sure you can do this). Thus,  $\delta$  has  $B_{1g}$  symmetry, while  $\delta^*$  has  $B_{2u}$  symmetry. So, for the transition  $\delta \rightarrow \delta^*$ , what is  $\int \psi_\delta(x,y,z) \psi_{\delta^*} d\tau$ ?

From the character tables, we see that  $z = A_{2u}$  and  $x = y = E_u$ . Now

$$\int \psi_{\delta u} \mu \psi_{\delta^*} = B_{1g} \times A_{2u} \times B_{2u} \text{ or } B_{1g} \times E_u \times B_{2u}$$

$D_{4h}$	$E$	$2C_4$	$C_2$	$2C_2'$	$2C_2''$	$i$	$2S_4$	$\sigma_h$	$2\sigma_v$	$2\sigma_d$	
$B_{1g} \times A_{2u} \times B_{2u}$	1	1	1	1	1	1	1	1	1	1	$= A_{1g}$
$B_{1g} \times E_u \times B_{2u}$	2	0	-2	0	0	2	0	-2	0	0	$= E_g$

Thus, from our previous discussion, absorption or emission is allowed only with z-polarization.

This is what is meant by the statement that a transition is “symmetry allowed” or “symmetry forbidden.” Those that are forbidden must decay by non-radiative pathways and generally have long lifetimes.