# Chapter 7.    Symmetry Labeling of Molecular Energies

## Notes:

- *Most of the material presented in this chapter is taken from Bunker and Jensen (1998), Chap. 6, and Bunker and Jensen (2005), Chap. 7.*

## 7.1   Hamiltonian Symmetry Operations

We have seen in section 6.1.4 of the previous chapter that any elements of the CNPI group, and therefore any elements of the MS group, associated with a given molecule commute with the corresponding molecular Hamiltonian. That is, given a symmetry operator $R$ we have

$$\left[ \hat{H}^0, R \right] = 0. \tag{7.1}$$

We also saw that this implies that if a wave function $\psi$ of the Hamiltonian is transformed by $R$ such that $\psi^R = R\psi$, then this transformed function is also a wave function of the Hamiltonian with the same energy level as the original function, since

$$\hat{H}^0 \psi_n^R = \hat{H}^0 R\psi_n = R\hat{H}^0 \psi_n = RE_n^0 \psi_n = E_n^0 \psi_n^R, \tag{7.2}$$

where $E_n^0$ is the energy associated with the wave function $\psi_n$. For a non-degenerate energy level, this in turn implies that

$$\psi_n^R = c\psi_n, \tag{7.3}$$

with $c$ some constant. As we will now see, the determination of the different values that this constant can take is central to the use of symmetry labels, associated with each irreducible representation of the MS group, for identifying the energy levels of a molecule.

### 7.1.1   Non-degenerate Energy Levels

Consider again the case of a MS group operator $R$ acting on a wave function $\psi_n$ of non-degenerate energy level $E_n^0$. However, because of the group axioms that states that both $R^q$, with $q$ and integer, and the identity $E$ must be part of the group, it follows that for some integer $m$ we must have

$$R^m = E. \tag{7.4}$$

We therefore find from equation (7.3) that

$$R^m \psi_n = c^m \psi_n = E\psi_n = \psi_n, \tag{7.5}$$

or alternatively

$$c = \sqrt[m]{1}. \tag{7.6}$$

For example, for the permutation $(12)$ we find that $c = \pm 1$.

**Example**

Consider the following three fictitious wave functions for the water molecule (the protons are labeled 1 and 2)

$$\begin{aligned}
\psi_1 &= \sin(X_1 - X_2) \\
\psi_2 &= \cos(X_1 - X_2) \\
\psi_3 &= \sin(X_1 + X_2).
\end{aligned} \tag{7.7}$$

Determine the constants associated with each operator of the MS group for this molecule, and use the corresponding character table to determine the irreducible representation generated by the wave functions.

**Solution**

The MS group for this molecule is $C_{2v}(M)$ and its character table is given in Table 7-1. Applying the different operators to the wave functions we have

$$\begin{aligned}
\psi_1^E &= \sin(X_1 - X_2) = \psi_1 \\
\psi_1^{(12)} &= \sin(X_2 - X_1) = -\psi_1 \\
\psi_1^{E^*} &= \sin(X_2 - X_1) = -\psi_1 \\
\psi_1^{(12)^*} &= \sin(X_1 - X_2) = \psi_1,
\end{aligned} \tag{7.8}$$

and similarly

$$\begin{aligned}
\psi_2^E &= \psi_2^{(12)} = \psi_2^{E^*} = \psi_2^{(12)^*} = \psi_2 \\
\psi_3^E &= \psi_3^{(12)} = -\psi_3^{E^*} = -\psi_3^{(12)^*} = \psi_3.
\end{aligned} \tag{7.9}$$

**Table 7-1** – The character table of the $C_{2v}(M)$ group.

| $C_{2v}(M):$ | $E$ | $(12)$ | $E^*$ | $(12)^*$ |
|---|---|---|---|---|
| $A_1:$ | 1 | 1 | 1 | 1 |
| $A_2:$ | 1 | 1 | −1 | −1 |
| $B_1:$ | 1 | −1 | −1 | 1 |
| $B_2:$ | 1 | −1 | 1 | −1 |

It is therefore apparent that the characters of the different wave functions when acted upon with the MS group operators are such that if we collect the different constants $c_i^R$, with $i = 1, 2, 3$ for the wave functions, we have

| | $c_i^E$ | $c_i^{(12)}$ | $c_i^{E^*}$ | $c_i^{(12)^*}$ | |
|---|---|---|---|---|---|
| $\psi_1:$ | 1 | $-1$ | $-1$ | 1 | $= B_1$ |
| $\psi_2:$ | 1 | 1 | 1 | 1 | $= A_1$ |
| $\psi_3:$ | 1 | 1 | $-1$ | $-1$ | $= A_2$ |

And, as indicated in the last column, $\psi_1, \psi_2,$ and $\psi_3$ have the symmetry of $B_1, A_1,$ and $A_2$, respectively. Because the energy levels are different for the three wave functions (they are non-degenerate), then we find that *we can label the energy levels using the different irreducible representations of the MS group*.

### 7.1.2 Degenerate Energy Levels

When an energy level $E_n^0$ is $l$-fold degenerate, there are $l$ wave functions $\psi_{n1}, \ldots, \psi_{nl}$ that transform into linear combinations of themselves when acted upon by an operator $R$ of the MS group. This is expressed mathematically as follows

$$R\psi_{ni} = \sum_{j=1}^{l} D[R]_{ij}\, \psi_{nj}, \qquad (7.10)$$

where $D[R]$ is the representation matrix associated to $R$. Now imagine that we are forming another set of $l$-fold degenerate functions $\Phi_{nk}$ using an orthogonal matrix $A$ with

$$\Phi_{nk} = \sum_{i=1}^{l} A_{ki}\psi_{ni}. \qquad (7.11)$$

Evidently these new functions are also wave functions of the Hamiltonian with the same energy $E_n^0$ as the original wave functions $\psi_{ni}$. We would like to find out what representation of the MS group the wave functions $\Phi_{nk}$ generate. If we denote the new representation matrix associated to $R$ with $\bar{D}[R]$, then

$$R\Phi_{nk} = \sum_{r=1}^{l} \bar{D}[R]_{kr}\, \Phi_{nr}. \qquad (7.12)$$

But using equations (7.11) and (7.10) we can also write

$$R\Phi_{nk} = \sum_{i=1}^{l} A_{ki} R\psi_{ni}$$

$$= \sum_{i=1}^{l} A_{ki} \sum_{j=1}^{l} D[R]_{ij}\, \psi_{nj},$$

(7.13)

and we substitute for $\psi_{nj}$ using the inverse of equation (7.11) to get

$$R\Phi_{nk} = \sum_{i=1}^{l} A_{ki} \sum_{j=1}^{l} D[R]_{ij} \sum_{r=1}^{l} A_{jr}^{-1}\Phi_{nr}$$

$$= \sum_{r} \sum_{i,j} \left( A_{ki} D[R]_{ij} A_{jr}^{-1} \right) \Phi_{nr}$$

(7.14)

$$= \sum_{r=1}^{l} \left( AD[R]A^{-1} \right)_{kr} \Phi_{nr}.$$

Comparing this result with equation (7.12) reveals that the new representation $\bar{D}[R]$ is related to the original representation $D[R]$ via a similarity transformation. That is,

$$\bar{D}[R] = AD[R]A^{-1}.$$

(7.15)

Since we already know that the character of a matrix is invariant under a similarity transformation (see equation (6.50) of the previous chapter), then we find the important result that *the character of a representation generated by a set of degenerated wave functions of the Hamiltonian is unique and can be used to reduce it to its irreducible components (see equations (6.59) and (6.60) of Chapter 6). The corresponding degenerated energy level can thus be labeled with the irreducible representations of the MS group.* This result is an extension of what was previously found for non-degenerate energy levels.

## 7.2  Projection Operators

Let us again consider a set of wave functions $\psi_{js}$ that generate the irreducible representations $\Gamma^j$ of dimension (i.e., degeneracy) $l_j$, with $s = 1, \ldots, l_j$. Any other set (of similar size) of functions $\Phi_n$ generating a reducible representation $\Gamma$ can expressed as a linear combination of the $\psi_{js}$ (because they form a basis) with

$$\Phi_n = \sum_{j} \sum_{k=1}^{l_j} A_{n,jk} \psi_{jk}.$$

(7.16)

(**Note:** The notation of equation (7.16) is potentially confusing, but it is understood that $A_{n,jk}$ is the element of a matrix $A$ belonging to row $n$ and column $jk$. That is, the indices $j$ and $k$ taken together form a single index. The implication is that the column

vector representation of $\psi_{jk}$ is such that its first $l_1$ elements belong to $j=1$ and $k=1,\ldots,l_1$, the next $l_2$ elements belong to $j=2$ and $k=1,\ldots,l_2$, and so on.) Equation (7.16) can also be inverted to give

$$\psi_{jk} = \sum_n A_{jk,n}^{-1} \Phi_n. \tag{7.17}$$

Now consider the following operator

$$\boxed{P_{mm}^{\Gamma_i} = \frac{l_i}{h} \sum_R D^{\Gamma_i}[R]_{mm}^* R} \tag{7.18}$$

where $D^{\Gamma_i}[R]$ is the matrix associated to the operator $R$ in the $\Gamma_i$ irreducible representation of the corresponding symmetry group of order $h$. We now apply this operator to a function of the $\Phi_n$ set

$$
\begin{aligned}
P_{mm}^{\Gamma_i} \Phi_n &= \frac{l_i}{h} \sum_R D^{\Gamma_i}[R]_{mm}^* R \Phi_n \\
&= \frac{l_i}{h} \sum_R D^{\Gamma_i}[R]_{mm}^* R \left( \sum_j \sum_{k=1}^{l_j} A_{n,jk} \psi_{jk} \right) \\
&= \sum_j \sum_{k=1}^{l_j} A_{n,jk} \frac{l_i}{h} \sum_R D^{\Gamma_i}[R]_{mm}^* \left( R \psi_{jk} \right) \\
&= \sum_j \sum_{k=1}^{l_j} A_{n,jk} \frac{l_i}{h} \sum_R D^{\Gamma_i}[R]_{mm}^* \left( \sum_{s=1}^{l_j} D^{\Gamma_j}[R]_{ks} \psi_{js} \right) \\
&= \sum_j \sum_{k=1}^{l_j} A_{n,jk} \sum_{s=1}^{l_j} \psi_{js} \left( \frac{l_i}{h} \sum_R D^{\Gamma_i}[R]_{mm}^* D^{\Gamma_j}[R]_{ks} \right),
\end{aligned}
\tag{7.19}
$$

where equations (7.16) and (7.10) (suitably rewritten) were used. We can now make use of the GOT (i.e., equation (6.54) of Chapter 6) to find that

$$
\begin{aligned}
P_{mm}^{\Gamma_i} \Phi_n &= \sum_j \sum_{k=1}^{l_j} A_{n,jk} \sum_{s=1}^{l_j} \psi_{js} \left( \delta_{ij} \delta_{mk} \delta_{ms} \right) \\
&= A_{n,im} \psi_{im}.
\end{aligned}
\tag{7.20}
$$

We therefore find that the **projection operator** $P_{mm}^{\Gamma_i}$ when applied to $\Phi_n$ produces the part of $\Phi_n$ that belongs to the $m$th row of the $\Gamma_i$ irreducible representation. In other words, given the matrix irreducible representations $D^{\Gamma_i}[R]$ of a group we can use the projection operator to break down an arbitrary set of functions $\Phi_n$ into the irreducible

representations-generating wave functions $\psi_{im}$ that compose it. For example, if the functions $\Phi_n$ do not contain the $\Gamma_i$ irreducible representation, then equation (7.20) will yield

$$P_{mm}^{\Gamma_i}\Phi_n = 0. \tag{7.21}$$

It is important to emphasize the fact we need to know the matrices $D^{\Gamma_i}[R]$ in order to use this projection operator. On the other hand, is possible to define a simpler (and less powerful) projection operator from equation (7.18) with

$$\boxed{P^{\Gamma_i} = \sum_m P_{mm}^{\Gamma_i} = \frac{l_i}{h}\sum_R \chi^{\Gamma_i}[R]^* R} \tag{7.22}$$

For example, we can calculate from equation (7.20) that

$$P^{\Gamma_i}\Phi_n = \sum_m A_{n,im}\psi_{im}. \tag{7.23}$$

So, when applied to $\Phi_n$ this projection operator will yield a function that belongs to $\Gamma_i$, but not belonging to any particular row $m$. However, it will still be able to tell us if $\Phi_n$ does not contain any functions belonging to $\Gamma_i$, since in this case

$$P^{\Gamma_i}\Phi_n = 0, \tag{7.24}$$

from equation (7.21). It is important to note that for a one-dimensional irreducible representation the operators of equations (7.18) and (7.22) are one and the same.

**Example**

Let us return to our previous example of the water molecule, but this time with three new wave functions defined as

$$\begin{aligned}
\Phi_a &= \sin(X_1 - X_2) + \sin(X_1 + X_2) \\
\Phi_b &= \sin(X_1 - X_2) + \cos(X_1 - X_2) \\
\Phi_c &= \sin(X_1 + X_2) - \sin(X_1 - X_2),
\end{aligned} \tag{7.25}$$

which we assume to be degenerate (i.e., we now specify that $\psi_1, \psi_2$, and $\psi_3$ are also degenerate) and spanning a reducible representation $\Gamma$. We seek to determine the combinations of $\Phi_a, \Phi_b$, and $\Phi_c$ that belong to the different irreducible representations of the MS group of the water molecule (i.e., $C_{2v}(M)$).

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**Solution**

Using the character table for $C_{2v}(M)$ (i.e., Table 7-1) we can calculate the $3 \times 3$ matrices $D^\Gamma[R]$ corresponding to the transformation brought by the operators of the group on $\Phi_a$, $\Phi_b$, and $\Phi_c$. For example, we can verify from equations (7.25) that

$$E\begin{bmatrix}\Phi_a\\\Phi_b\\\Phi_c\end{bmatrix} = \begin{bmatrix}\Phi_a\\\Phi_b\\\Phi_c\end{bmatrix} = \underbrace{\begin{bmatrix}1&0&0\\0&1&0\\0&0&1\end{bmatrix}}_{D^\Gamma[E]}\begin{bmatrix}\Phi_a\\\Phi_b\\\Phi_c\end{bmatrix}.$$

$$(12)\begin{bmatrix}\Phi_a\\\Phi_b\\\Phi_c\end{bmatrix} = \begin{bmatrix}\Phi_c\\\Phi_b+\Phi_c-\Phi_a\\\Phi_a\end{bmatrix} = \underbrace{\begin{bmatrix}0&0&1\\-1&1&1\\1&0&0\end{bmatrix}}_{D^\Gamma[(12)]}\begin{bmatrix}\Phi_a\\\Phi_b\\\Phi_c\end{bmatrix} \qquad (7.26)$$

$$E^*\begin{bmatrix}\Phi_a\\\Phi_b\\\Phi_c\end{bmatrix} = \begin{bmatrix}-\Phi_a\\\Phi_b+\Phi_c-\Phi_a\\-\Phi_c\end{bmatrix} = \underbrace{\begin{bmatrix}-1&0&0\\-1&1&1\\0&0&-1\end{bmatrix}}_{D^\Gamma[E^*]}\begin{bmatrix}\Phi_a\\\Phi_b\\\Phi_c\end{bmatrix},$$

and

$$D^\Gamma\left[(12)^*\right] = D^\Gamma\left[(12)\right]D^\Gamma\left[E^*\right]$$

$$= \begin{bmatrix}0&0&1\\-1&1&1\\1&0&0\end{bmatrix}\begin{bmatrix}-1&0&0\\-1&1&1\\0&0&-1\end{bmatrix} = \begin{bmatrix}0&0&-1\\0&1&0\\-1&0&0\end{bmatrix}. \qquad (7.27)$$

The characters of these matrices are easily determined to be

$$\chi[E]=3, \quad \chi[(12)]=1, \quad \chi[E^*]=-1, \quad \chi\left[(12)^*\right]=1. \qquad (7.28)$$

Using equation (6.60) of Chapter 6 and Table 7-1, we find that

$$a_{A_1} = \frac{1}{4}\sum_R \chi^\Gamma[R]\chi^{A_1}[R]^*$$

$$= \frac{1}{4}(3+1-1+1)=1 \qquad (7.29)$$

$$a_{A_2} = \frac{1}{4}\sum_R \chi^\Gamma[R]\chi^{A_2}[R]^*$$

$$= \frac{1}{4}(3+1+1-1) = 1$$

$$a_{B_1} = \frac{1}{4}\sum_R \chi^\Gamma[R]\chi^{B_1}[R]^*$$

$$= \frac{1}{4}(3-1+1+1) = 1$$

$$a_{B_2} = \frac{1}{4}\sum_R \chi^\Gamma[R]\chi^{B_2}[R]^*$$

$$= \frac{1}{4}(3-1-1-1) = 0.$$

(7.30)

We can therefore write

$$\Gamma = A_1 \oplus A_2 \oplus B_1, \tag{7.31}$$

the $B_2$ representation is not generated by $\Gamma$. The functions belonging to the three realized irreducible representation are determined through equation (7.22) and the character table of the MS group. For example, using $\Phi_a$ we have

$$P^{A_1}\Phi_a = \left\{\frac{1}{4}\sum_R \chi^{A_1}[R]^* R\right\}\Phi_a = \frac{1}{4}\left\{E+(12)+E^*+(12)^*\right\}\Phi_a$$

$$= \frac{1}{4}(\Phi_a + \Phi_c - \Phi_a - \Phi_c) = 0$$

$$P^{A_2}\Phi_a = \left\{\frac{1}{4}\sum_R \chi^{A_2}[R]^* R\right\}\Phi_a = \frac{1}{4}\left\{E+(12)-E^*-(12)^*\right\}\Phi_a$$

$$= \frac{1}{4}(\Phi_a + \Phi_c + \Phi_a + \Phi_c) = \frac{1}{2}(\Phi_a + \Phi_c)$$

$$P^{B_1}\Phi_a = \left\{\frac{1}{4}\sum_R \chi^{B_1}[R]^* R\right\}\Phi_a = \frac{1}{4}\left\{E-(12)-E^*+(12)^*\right\}\Phi_a$$

$$= \frac{1}{4}(\Phi_a - \Phi_c + \Phi_a - \Phi_c) = \frac{1}{2}(\Phi_a - \Phi_c)$$

$$P^{B_2}\Phi_a = \left\{\frac{1}{4}\sum_R \chi^{B_2}[R]^* R\right\}\Phi_a = \frac{1}{4}\left\{E-(12)+E^*-(12)^*\right\}\Phi_a$$

$$= \frac{1}{4}(\Phi_a - \Phi_c - \Phi_a + \Phi_c) = 0.$$

(7.32)

Applying $P^{\Gamma_i}$ to $\Phi_c$ would yields the same results. Finally, projecting $\Phi_b$ onto each irreducible representation gives

$$
\begin{aligned}
P^{A_1}\Phi_b &= \left\{\frac{1}{4}\sum_R \chi^{A_1}[R]^* R\right\}\Phi_b = \frac{1}{4}\left\{E+(12)+E^*+(12)^*\right\}\Phi_b \\
&= \frac{1}{4}\left[\Phi_b+(\Phi_b+\Phi_c-\Phi_a)+(\Phi_b+\Phi_c-\Phi_a)+\Phi_b\right]=\Phi_b+\frac{1}{2}(\Phi_c-\Phi_a) \\
P^{A_2}\Phi_b &= \left\{\frac{1}{4}\sum_R \chi^{A_2}[R]^* R\right\}\Phi_b = \frac{1}{4}\left\{E+(12)-E^*-(12)^*\right\}\Phi_b \\
&= \frac{1}{4}\left[\Phi_b+(\Phi_b+\Phi_c-\Phi_a)-(\Phi_b+\Phi_c-\Phi_a)-\Phi_b\right]=0 \\
P^{B_1}\Phi_b &= \left\{\frac{1}{4}\sum_R \chi^{B_1}[R]^* R\right\}\Phi_b = \frac{1}{4}\left\{E-(12)-E^*+(12)^*\right\}\Phi_b \\
&= \frac{1}{4}\left[\Phi_b-(\Phi_b+\Phi_c-\Phi_a)-(\Phi_b+\Phi_c-\Phi_a)+\Phi_b\right]=\frac{1}{2}(\Phi_a-\Phi_c) \\
P^{B_2}\Phi_b &= \left\{\frac{1}{4}\sum_R \chi^{B_2}[R]^* R\right\}\Phi_b = \frac{1}{4}\left\{E-(12)+E^*-(12)^*\right\}\Phi_b \\
&= \frac{1}{4}\left[\Phi_b-(\Phi_b+\Phi_c-\Phi_a)+(\Phi_b+\Phi_c-\Phi_a)-\Phi_b\right]=0.
\end{aligned}
\tag{7.33}
$$

Summarize these results, we find three functions

$$
\begin{aligned}
\psi(A_1) &= \Phi_b+\frac{1}{2}(\Phi_c-\Phi_a)=\cos(X_1-X_2) \\
\psi(A_2) &= \frac{1}{2}(\Phi_a+\Phi_c)=\sin(X_1+X_2) \\
\psi(B_1) &= \frac{1}{2}(\Phi_a-\Phi_c)=\sin(X_1-X_2),
\end{aligned}
\tag{7.34}
$$

which respectively transform as the $A_1$, $A_2$, and $B_1$ representations. A careful look at these functions reveals them to be equaled to our previous $\psi_2$, $\psi_3$, and $\psi_1$, respectively, which we also previously determined to be transforming as the $A_1$, $A_2$, and $B_1$ representations. This is an example of the power of the projection operator for identifying underlying symmetries in otherwise arbitrary functions.

### 7.2.1 The Symmetry of a Product of Functions

As we saw earlier when dealing with the molecular Hamiltonian and its simplifications (e.g., the Born-Oppenheimer approximation), the complete wave functions corresponding to the rovibronic states of a molecule can be approximated by the product of electronic,

vibration, and rotational wave functions. It is therefore important to determine the symmetry and character of a product of functions.

Let us consider two representations $\Gamma^m$ and $\Gamma^n$ of $r$-fold and $s$-fold degeneracy, respectively. We also assume them to be generated by corresponding sets of wave functions $\Phi_{mi}$ and $\Phi_{nj}$ (i.e., $i = 1, \ldots, r$ and $j = 1, \ldots, s$) of energy levels $E_m$ and $E_n$, respectively. We already know from equation (7.10) that under an element $R$ of the MS group functions from these sets will transform as follows

$$R\Phi_{mi} = \sum_{k=1}^{r} D^{\Gamma^m}[R]_{ik} \Phi_{mk}$$

$$R\Phi_{nj} = \sum_{l=1}^{s} D^{\Gamma^n}[R]_{jl} \Phi_{nl}.$$

(7.35)

If we denote the representation generated by all possible $r \times s$ products of pairs of functions $\left( \Phi_{mi}, \Phi_{nj} \right)$ by $\Gamma^{mn}$

$$R\left[ \Phi_{mi} \Phi_{nj} \right] = \sum_{k=1}^{r} \sum_{l=1}^{s} D^{\Gamma^m}[R]_{ik} D^{\Gamma^n}[R]_{jl} \Phi_{mk} \Phi_{nl},$$

(7.36)

but if we further define

$$\psi_{ij} = \Phi_{mi} \Phi_{nj},$$

(7.37)

then we can write

$$R\psi_{ij} = \sum_{k=1}^{r} \sum_{l=1}^{s} D^{\Gamma^{mn}}[R]_{ij,kl} \psi_{kl}.$$

(7.38)

We identify (and define) the matrix $D^{\Gamma^{mn}}[R]$ by the **direct product**

$$D^{\Gamma^{mn}}[R] = D^{\Gamma^m}[R] \otimes D^{\Gamma^n}[R],$$

(7.39)

or

$$D^{\Gamma^{mn}}[R]_{ij,kl} = D^{\Gamma^m}[R]_{ik} D^{\Gamma^n}[R]_{jl}.$$

(7.40)

For example, we represent the direct product of two $2 \times 2$ matrices $A$ and $B$ with

$$A \otimes B = \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} \otimes \begin{bmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{bmatrix} = \left[ \begin{array}{cc:cc} a_{11}b_{11} & a_{11}b_{12} & a_{12}b_{11} & a_{12}b_{12} \\ a_{11}b_{21} & a_{11}b_{22} & a_{12}b_{21} & a_{12}b_{22} \\ \hdashline a_{21}b_{11} & a_{21}b_{12} & a_{22}b_{11} & a_{22}b_{12} \\ a_{21}b_{21} & a_{21}b_{22} & a_{22}b_{21} & a_{22}b_{22} \end{array} \right]. \tag{7.41}$$

We see that the first and third indices of $D^{\Gamma^{mn}}[R]_{ij,kl}$ specify the quadrant of the resulting matrix, while the second and forth indices specify which element of the quadrant is selected. From this definition we can easily proceed to calculate the character of the direct-product matrix with

$$\chi^{\Gamma^{mn}}[R] = \sum_{k=1}^{r} \sum_{l=1}^{s} D^{\Gamma^{mn}}[R]_{ij,ij} = \sum_{i=1}^{r} \sum_{j=1}^{s} D^{\Gamma^{m}}[R]_{ii} D^{\Gamma^{n}}[R]_{jj}$$

$$= \chi^{\Gamma^{m}}[R] \chi^{\Gamma^{n}}[R]. \tag{7.42}$$

The character of a direct product matrix is thus simply the product of the characters of the two matrices involved. We also write symbolically

$$\Gamma^{mn} = \Gamma^{m} \otimes \Gamma^{n}. \tag{7.43}$$

**Example**

Consider the two pairs of degenerate functions

$$\Phi_{1} = X_{1} - X_{2}$$
$$\Phi_{2} = \frac{1}{\sqrt{3}}(2X_{3} - X_{1} - X_{2}), \tag{7.44}$$

and

$$\theta_{a} = Y_{1} - Y_{2}$$
$$\theta_{b} = \frac{1}{\sqrt{3}}(2Y_{3} - Y_{1} - Y_{2}). \tag{7.45}$$

**a)** Show that $(\Phi_{1}, \Phi_{2})$ (and therefore $(\theta_{a}, \theta_{b})$) generates the $E$ representation of the $C_{3v}(\mathrm{M})$ group (see Table 7-2).

**b)** Determine the representation generated by the products $(\Phi_{1}, \Phi_{2}) \times (\theta_{a}, \theta_{b})$, and decompose it into a sum of the irreducible representations of $C_{3v}(\mathrm{M})$.

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**Table 7-2** – The character table of the $C_{3v}(M)$ group.

| $C_{3v}(M)$: | $E$ | $(123)$ $(132)$ | $(23)^*$ $(13)^*$ $(12)^*$ |
|---|---|---|---|
| $A_1$ : | 1 | 1 | 1 |
| $A_2$ : | 1 | 1 | −1 |
| $E$ : | 2 | −1 | 0 |

**Solution.**

**a)** Applying one element from each of the three classes of operators from the $C_{3v}(M)$ group to the functions $\Phi_1$ and $\Phi_2$ we have

$$E\Phi_1 = \Phi_1$$

$$E\Phi_2 = \Phi_2$$

$$(123)\Phi_1 = X_3 - X_1 = -\frac{1}{2}\left(\Phi_1 - \sqrt{3}\Phi_2\right)$$

$$(123)\Phi_2 = \frac{1}{\sqrt{3}}\left(2X_2 - X_3 - X_1\right) = -\frac{1}{2}\left(\sqrt{3}\Phi_1 + \Phi_2\right) \quad (7.46)$$

$$(23)^*\Phi_1 = -X_1 + X_3 = -\frac{1}{2}\left(\Phi_1 - \sqrt{3}\Phi_2\right)$$

$$(23)^*\Phi_2 = -\frac{1}{\sqrt{3}}\left(2X_2 - X_1 - X_3\right) = \frac{1}{2}\left(\sqrt{3}\Phi_1 + \Phi_2\right).$$

From this, we easily find that

$$\chi^{\Gamma}[E] = 2, \quad \chi^{\Gamma}[(123)] = -1, \quad \chi^{\Gamma}\left[(23)^*\right] = 0, \quad (7.47)$$

which makes it clear, through a comparison with Table 7-2, that $\Gamma = E$. That is, the set $(\Phi_1, \Phi_2)$, and therefore $(\theta_a, \theta_b)$ also, generates the $E$ representation of the $C_{3v}(M)$ group.

**b)** We know from equations (7.42), (7.43), and (7.47) that

$$\chi^{\Gamma^{\Phi\theta}}[E] = 4, \quad \chi^{\Gamma^{\Phi\theta}}[(123)] = 1, \quad \chi^{\Gamma^{\Phi\theta}}\left[(23)^*\right] = 0. \quad (7.48)$$

Using equation (6.60) of the previous chapter

$$a_i = \frac{1}{6}\sum_R \chi^{\Gamma^{\Phi\theta}}[R]\chi^{\Gamma^i}[R]^*, \quad (7.49)$$

we find

$$a_{A_1} = \frac{1}{6}\left[1 \cdot 4 + 2(1 \cdot 1) + 3(1 \cdot 0)\right] = 1$$

$$a_{A_2} = \frac{1}{6}\left[1 \cdot 4 + 2(1 \cdot 1) + 3(-1 \cdot 0)\right] = 1 \qquad (7.50)$$

$$a_E = \frac{1}{6}\left[2 \cdot 4 + 2(-1 \cdot 1) + 3(0 \cdot 0)\right] = 1,$$

or alternatively

$$\Gamma^{\Phi\theta} = A_1 \oplus A_2 \oplus E. \qquad (7.51)$$

If we now apply the projection operators (see equation (7.22)) for the $A_1$ and $A_2$ irreducible representations to some of the product functions $\Phi_i\theta_\alpha$ we could show through some simple mathematics that

$$P^{A_1}\Phi_1\theta_a \propto \left(\Phi_1\theta_a + \Phi_2\theta_b\right)$$

$$P^{A_2}\Phi_1\theta_b \propto \left(\Phi_1\theta_b - \Phi_2\theta_a\right). \qquad (7.52)$$

In a similar manner, if we use equation (7.18) for the projection operator for, and equations (6.44) for the matrices of, the $E$ irreducible representation of $C_{3v}(M)$ it can be shown that

$$P_{11}^E\Phi_1\theta_a \propto \left(\Phi_1\theta_a - \Phi_2\theta_b\right)$$

$$P_{22}^E\Phi_1\theta_b \propto \left(\Phi_1\theta_b + \Phi_2\theta_a\right). \qquad (7.53)$$

That is, the functions $\left(\Phi_1\theta_a + \Phi_2\theta_b\right)$, $\left(\Phi_1\theta_b - \Phi_2\theta_a\right)$, and the pair of functions $\left[\left(\Phi_1\theta_a - \Phi_2\theta_b\right),\left(\Phi_1\theta_b + \Phi_2\theta_a\right)\right]$ respectively generate the $A_1$, $A_2$, and $E$ irreducible representations. In other words, the *symmetric product functions* $\Phi_1\theta_a$, $\Phi_2\theta_b$, and $\left(\Phi_1\theta_b + \Phi_2\theta_a\right)$ generate the representation $A_1 \oplus E$, while the *antisymmetric product functions* $\left(\Phi_1\theta_b - \Phi_2\theta_a\right)$ generate the representation $A_2$.

It is usually written that the symmetric product is

$$[E]^2 = [E \otimes E] = A_1 \oplus E, \qquad (7.54)$$

and that the antisymmetric product is

$$\{E\}^2 = \{E \otimes E\} = A_2. \qquad (7.55)$$

It can be shown[1] that the character of the operators in the symmetric and antisymmetric product representations can be calculated with

$$\chi^{[E \otimes E]}[R] = \frac{1}{2}\left[\left(\chi^{E}[R]\right)^{2} + \chi^{E}\left[R^{2}\right]\right]$$

$$\chi^{\{E \otimes E\}}[R] = \frac{1}{2}\left[\left(\chi^{E}[R]\right)^{2} - \chi^{E}\left[R^{2}\right]\right],$$

(7.56)

as can be verified for the preceding example. In general, the character of the operators in the symmetric $n$th power of the degenerate irreducible representation $E$ is given by

$$\chi^{[E]^{n}}[R] = \frac{1}{2}\left[\chi^{E}[R]\chi^{[E]^{n-1}}[R] + \chi^{E}\left[R^{n}\right]\right].$$

(7.57)

An important question when considering a representation $\Gamma$ resulting from the direct products of functions generating two irreducible representations $\Gamma_{n}^{*}$ and $\Gamma_{m}$ is whether it contains the totally symmetric representation $\Gamma^{(s)}$ ($\Gamma_{n}^{*}$ is the irreducible representation whose matrix representation $D^{\Gamma_{n}}[R]^{*}$ is the complex conjugate of that of $\Gamma_{n}$, i.e., $D^{\Gamma_{n}}[R]$). We know from equation (7.42) that

$$\chi^{\Gamma}[R] = \chi^{\Gamma_{n}}[R]^{*}\chi^{\Gamma_{m}}[R],$$

(7.58)

and the from equation (6.60) that

$$a^{\Gamma^{(s)}} = \frac{1}{h}\sum_{R}\chi^{\Gamma}[R].$$

(7.59)

We now insert equation (7.58) in equation (7.59) to get

$$a^{\Gamma^{(s)}} = \frac{1}{h}\sum_{R}\chi^{\Gamma_{n}}[R]^{*}\chi^{\Gamma_{m}}[R],$$

(7.60)

which implies from the little orthogonality theorem (i.e., equation (6.56)) that

$$a^{\Gamma^{(s)}} = \begin{cases} 1, & \text{if } \Gamma_{m} = \Gamma_{n} \\ 0, & \text{if } \Gamma_{m} \neq \Gamma_{n}, \end{cases}$$

(7.61)

since if $\Gamma_{m}^{*}$ is a realized irreducible representation, then so is $\Gamma_{n}$.

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[1] M. Hamermesh 1964, **Group Theory and its Applications to Physical Problems**, (Reading: Addison-Wesley), pp. 128-134.

## 7.3 The Vanishing Integral Rule

Let us suppose that we have a molecular Hamiltonian $\hat{H}^0$ for which we have previously determined the energy levels $E_n^0$ and corresponding wave functions $\psi_n^0$. We assume that the wave function $\psi_n^0$ generate the representation $\Gamma_n$.

We would like to know which of the molecular states and energy levels will be coupled if a perturbation $\hat{H}'$ is added to the system. In other words, will the perturbation allow the molecule to go from a given state to another? This question will be answered by calculating the matrix elements of the total Hamiltonian $\hat{H} = \hat{H}^0 + H'$ with

$$
\begin{aligned}
H_{mn} &= \int \psi_m^{0\,*} \left( \hat{H}^0 + \hat{H}' \right) \psi_n^0 \, d\tau \\
&= \delta_{mn} E_n^0 + H'_{mn},
\end{aligned}
\tag{7.62}
$$

where

$$
H'_{mn} = \int \psi_m^{0\,*} \hat{H}' \psi_n^0 \, d\tau,
\tag{7.63}
$$

with $d\tau$ the volume element of the relevant space. That is, the matrix element $H'_{mn}$ has to be non-zero for a transition to be possible between two different states $m$ and $n$. It turns out that we can easily find out whether the integral in equation (7.63) vanishes or not by making use of the fact that molecular energies can be labeled with the irreducible representations of the MS group (see Section 7.1). To show how this is done, let us define a function $f$ such that

$$
f(S) = \psi_m^{0\,*} \hat{H}' \psi_n^0,
\tag{7.64}
$$

with $S$ the coordinates of some point in the system's space. If we act on this function with some element $R_i$ of the group $G$ (of order $h$), then we can write (see equation (6.9))

$$
R_i f(S) = f(S') = f^{R_i}(S).
\tag{7.65}
$$

But since the integration in equation (7.63) is performed over all space

$$
\int f(S) \, d\tau = \int f(S') \, d\tau' = \int f^{R_i}(S) \, d\tau = \int \left[ R_i f(S) \right] d\tau,
\tag{7.66}
$$

and therefore

$$
h \int f(S) \, d\tau = \int \left[ \sum_i R_i f(S) \right] d\tau.
\tag{7.67}
$$

We can then rewrite equation (7.63) as

$$H'_{mn} = \int \psi_m^{0*} \hat{H}' \psi_n^0 \, d\tau = \frac{1}{h} \int \left[ \sum_i R_i \left( \psi_m^{0*} \hat{H}' \psi_n^0 \right) \right] d\tau. \tag{7.68}$$

If the perturbation $\hat{H}'$ generates the representation $\Gamma'$, then we know from the previous section that $\psi_m^{0*} \hat{H}' \psi_n^0$ will generate the following representation

$$\Gamma'_{mn} = \Gamma_m^* \otimes \Gamma' \otimes \Gamma_n. \tag{7.69}$$

(Note that $\psi_m^{0*}$ generates $\Gamma_m^*$, which does not necessarily have characters that are complex conjugate of those of $\Gamma_m$.) Let us now apply the projection operator for the totally symmetric representation

$$P^{\Gamma^{(s)}} = \frac{1}{h} \sum_i R_i \tag{7.70}$$

on the integrand of equation (7.63) to find that

$$\int P^{\Gamma^{(s)}} \left( \psi_m^{0*} \hat{H}' \psi_n^0 \right) d\tau = \frac{1}{h} \int \left[ \sum_i R_i \left( \psi_m^{0*} \hat{H}' \psi_n^0 \right) \right] d\tau = H'_{mn} \begin{cases} = 0, & \text{if } \Gamma^{(s)} \not\subset \Gamma'_{mn} \\ \neq 0, & \text{if } \Gamma^{(s)} \subset \Gamma'_{mn} \end{cases} \tag{7.71}$$

(see Section 7.2). We therefore find that

$$H'_{mn} = \int \psi_m^{0*} \hat{H}' \psi_n^0 \, d\tau = 0 \tag{7.72}$$

and *the perturbation $\hat{H}'$ will not couple two states when*

$$\Gamma^{(s)} \not\subset \Gamma_m^* \otimes \Gamma' \otimes \Gamma_n. \tag{7.73}$$

This is the so-called **vanishing integral rule**. In particular, the condition spelled out in equations (7.72) and (7.73) reduces to

$$\Gamma_m \neq \Gamma_n \tag{7.74}$$

when $\hat{H}'$ is totally symmetric (i.e., transforms as $\Gamma^{(s)}$, see below) in the group $G$.

If the energy levels $E_m$ are $r$-fold degenerate with wave functions $\psi_{mi}^0$ (for $i = 1, \ldots, r$) and when $\hat{H}'$ is totally symmetric, then the previous result can be further complemented (with a judicious use of the GOT; see the Second Problem List) with the following rule

$$\int \psi_{mi}^{0*} \hat{H}' \psi_{nj}^0 \, d\tau = 0 \tag{7.75}$$

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unless $\Gamma_m = \Gamma_n$ and $i = j$.

Incidentally, we note that the fact that (from part of equation (7.62))

$$\hat{H}^0_{mn} = \int \psi_m^{0*} \hat{H}^0 \psi_n^0 \, d\tau = \delta_{mn} E_n^0 \tag{7.76}$$

implies that the corresponding element of the unperturbed Hamiltonian matrix will cancel unless $\Gamma_m = \Gamma_n$. This not a surprising result since we built the basis $\{\psi_m^0\}$ from a set of orthogonal wave functions of this Hamiltonian. However, this also means that *the Hamiltonian $\hat{H}^0$ transforms as the totally symmetric representation $\Gamma^{(s)}$ of the MS group*. We could have easily predicted this from the fact that $\hat{H}^0$ commutes with the operators of the MS group (see equation (7.1)), and is therefore invariant under their applications.

**Example**

Consider the two wave functions

$$\psi(A_2) = \sin(X_1 + X_2)$$
$$\psi(B_1) = \sin(X_1 - X_2) \tag{7.77}$$

introduced in an earlier example concerning the $C_{2v}(M)$ group. It is easy to see that the integral of these functions over all space will cancel out. That is,

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \sin(X_1 + X_2) dX_1 dX_2 = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \sin(X_1 - X_2) dX_1 dX_2 = 0, \tag{7.78}$$

since both integrands are odd. We can also explain this result with the vanishing integral rule by saying that these functions are not totally symmetric in the $C_{2v}(M)$ group, where $\Gamma^{(s)} = A_1$, since they transform as $A_2$ and $B_1$, respectively. Likewise, the product of the two functions generates the $A_2 \otimes B_1 = B_2$ irreducible representation (see Table 7-1) and its integral will also cancel out for the same reason. This can also be verified with the following

$$I = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \sin(X_1 + X_2) \sin(X_1 - X_2) dX_1 dX_2$$
$$= \frac{1}{2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left[ \cos(2X_2) - \cos(2X_1) \right] dX_1 dX_2 = 0. \tag{7.79}$$

On the other hand, the integral of the squares of both functions will not cancel out because

$$A_2 \otimes A_2 = B_1 \otimes B_1 = A_1 = \Gamma^{(s)}, \tag{7.80}$$

as can also be verified with

$$I_1 = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \sin^2(X_1 + X_2) dX_1 dX_2$$

$$= \frac{1}{2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left\{1 - \cos\left[2(X_1 + X_2)\right]\right\} dX_1 dX_2 \neq 0$$

$$I_2 = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \sin^2(X_1 - X_2) dX_1 dX_2$$

$$= \frac{1}{2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \left\{1 - \cos\left[2(X_1 - X_2)\right]\right\} dX_1 dX_2 \neq 0.$$

(7.81)

It can be seen that the vanishing integral rule is closely related to the more common concept of the evenness or oddness of the integrand.

In general, the vanishing integral rule cannot tell us what is the value of an integral, but it can tell us when it cancels out. And this is of fundamental importance for determining the selection rules for transitions between different molecular states.