Chapter 4

Before reading this chapter, read Appendix I (p. 417). It reviews matrix math.

4.1 Prefactory Comments about Matrices and Vectors

We'll begin with a brief review of matrix math here as well. A matrix is a regular array of numbers written within a set of square brackets. Matrices are equal if they are identical. Matrices can be added only if they have equal numbers of rows and columns.

$$\begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \end{bmatrix} + \begin{bmatrix} b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \end{bmatrix} = \begin{bmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \end{bmatrix} \quad \text{where } c_{\mathrm{ij}} = a_{\mathrm{ij}} + b_{\mathrm{ij}}$$

Multiplying a matrix by a scalar (a non-matrix component) is also straightforward.

$$\mathrm{x}\begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \end{bmatrix} = \begin{bmatrix} \mathrm{x}a_{11} & \mathrm{x}a_{12} & \mathrm{x}a_{13} \\ \mathrm{x}a_{21} & \mathrm{xi}_{22} & \mathrm{x}a_{23} \end{bmatrix}$$

Multiplying two matrices is less obvious. One condition required for matrix multiplication is that the number of columns in the first matrix must equal the number of rows on the second.

$$\begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \end{bmatrix} \mathrm{x} \begin{bmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \\ b_{31} & b_{32} \end{bmatrix} = \begin{bmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \end{bmatrix}$$

where $c_{11} = a_{11}b_{11} + a_{12}b_{21} + a_{13}b_{31}$ $\qquad$ $c_{21} = a_{21}b_{11} + a_{22}b_{21} + a_{23}b_{31}$

$c_{12} = a_{11}b_{12} + a_{12}b_{22} + a_{13}b_{32}$ $\qquad$ $c_{22} = a_{21}b_{12} + a_{22}b_{22} + a_{23}b_{32}$

or more generally: $c_{\mathrm{ij}} = \Sigma a_{\mathrm{ik}}b_{\mathrm{kl}}$

Read "A Special Case of Matrix Multiplication" (p. 68) on your own. We'll make use of block matrices later in the chapter.

Characters of Conjugate Matrices

The character, χ, of a matrix is equal to the sum of its diagonal elements. $\chi = \sum_j a_{\mathrm{jj}}$. If there are 4 matrices: $\mathcal{A}$, $\mathcal{B}$, $\mathcal{C}$, and $\mathcal{D}$, then if $\mathcal{AB} = \mathcal{C}$ and $\mathcal{BA} = \mathcal{D}$, then $\chi_c = \chi_d$. Note this matrix multiplication can only occur for square matrices. Conjugate matrices have identical characters and are related by $\mathcal{A}^{-1}\mathcal{B}\mathcal{A} = \mathcal{C}$, where $\mathcal{B}$ and $\mathcal{C}$ are conjugate and

$$\mathcal{A}^{-1}\mathcal{A} = \mathcal{E} = \begin{bmatrix} 1 & 0 & 0 & \dots & 0 \\ 0 & 1 & 0 & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \dots & 1 \end{bmatrix}$$

Matrix Notation for Geometric Transformations

A point in space or a vector is given by the 3x0 matrix $\begin{bmatrix} x \\ y \\ z \end{bmatrix}$. This means that any 3 dimensional transformation (i.e. one of the symmetry operations) must be a 3x3 matrix, so that the two may be multiplied. We'll begin with the simplest, the identity transformation, *E*.

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

Thus, we see that the 3x3 matrix with all ones on the diagonal and zeros elsewhere does not change any value on the vector.

From here on out, it is easiest (at least to me) to consider an operation that you can see in your mind's eye. Constructing the transforming matrix is then less difficult. Inversion is also not difficult, recall that it moves a point (x, y, z) to (-x, -y, -z). If the *E* matrix changes nothing, then a matrix with all -1's on the diagonal affects this change so …

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ -y \\ -z \end{bmatrix}$$

[NB: I'll continue to use the traditional "-" sign to indicate negatives, rather than the "bar" symbolism the book uses.] When one uses a reflection plane some, all, or no items may move, depending on whether or not they lie in the plane under consideration. Let's consider an *xz* plane placed on a set of Cartesian coordinate axes (i.e. the 'normal' way). In this case, any point on the *x* or *z* axes will not change position, but one on the *y* axis, will move to –*y*. The matrix that will accomplish this is:

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ -y \\ z \end{bmatrix}$$

The *xy* and *yz* planes are similarly constructed. See the book for details. It should be noted that not all planes will lie along these axes (e.g. the planes in a D_{3h} molecule); nonetheless this gives you a feel for how the transformative matrices for reflection planes are constructed. Still, the large majority of point groups have planes that are perpendicular, so the planes may be aligned along a set of Cartesian axes.

Initially, proper rotation axes seem to present a more challenging situation, but there is a generally applicable simplification. While there are a range of C_n axes possible, except for the high symmetry groups, all other axes either lie along the principal axis or are C_2 and lie perpendicular to it. Thus, we begin by always aligning the principal axis along the Cartesian *z* axis. In this case, *z* coordinates do not change. The *x* and *y* coordinates then change as follows:

$$\begin{bmatrix} \cos\phi & \sin\phi & 0 \\ -\sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x\cos\phi + y\sin\phi \\ -x\sin\phi + y\cos\phi \\ 1 \end{bmatrix}$$

We can use the *x*-axis for an example of a perpendicular C_2 rotational matrix, in this case:

$$C_2(x) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

Recall that an improper rotation, S_n, is given by $C_n\sigma_h = \sigma_h C_n$ or in matrix notation:

$$\begin{bmatrix} \cos\phi & \sin\phi & 0 \\ -\sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} \cos\phi & \sin\phi & 0 \\ -\sin\phi & \cos\phi & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

This also demonstrates how 2 symmetry operations are carried out mathematically: the matrices are multiplied.

All of the previous matrices are orthogonal. From this observation, their inverses may be generated by transposing the rows and columns. i.e. row 1 $\rightarrow$ column 1 and column 1 $\rightarrow$ row 1, etc. For example:

$$\mathcal{A} = \begin{bmatrix} a & b \\ c & d \end{bmatrix} \rightarrow \mathcal{A}^{-1} = \begin{bmatrix} a & c \\ b & d \end{bmatrix}$$

A real example is shown on pp. 73-74. The book then looks at the C_3 axes of a tetrahedron.

Vectors and Their Scalar Products

The scalar (or dot) product of 2 vectors can be given by either of 2 methods:

For the vectors **A** and **B**:

$\mathbf{A}\bullet\mathbf{B} = A'B'\cos\theta$ = where A', B' = lengths of vectors, $\cos\theta$ = angle between them

or $\mathbf{A}\bullet\mathbf{B} = A_xB_x + A_yB_y$ where A_x, A_y, B_x, B_y are the coordinates of the vectors in two space.

4.2 Representations of Groups

It was noted earlier that all point groups are closed groups. We begin this section by demonstrating that this is true by working an example. We'll go with the book example because it works nicely. Start by creating, the outline, then filling in the first row & column of the matrix because that multiplication is unambiguous. The diagonals are all *E*s because each operation is followed by itself and regenerates the original position. The others result from performing the sequence of operations described. Show the following GMT is correct using a set of models.

C_{2v}	E	C_2	σ_v	σ_v'
E				
C_2				
σ_v				
σ_v'				

$\longrightarrow$

C_{2v}	E	C_2	σ_v	σ_v'
E	E	C_2	σ_v	σ_v'
C_2	C_2			
σ_v	σ_v			
σ_v'	σ_v'			

$\longrightarrow$

C_{2v}	E	C_2	σ_v	σ_v'
E	E	C_2	σ_v	σ_v'
C_2	C_2	E	σ_v'	σ_v
σ_v	σ_v	σ_v'	E	C_2
σ_v'	σ_v'	σ_v	C_2	E

You can see the group is indeed closed. The same GMT can be developed using matrix multiplication. The book works $\sigma_v C_2 = \sigma_v'$ on p. 78, $\sigma_v\sigma_v'$ appears below.

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \text{ which is } C_2.$$

A <u>representation of a group</u> is a collection of matrices that can be combined in a manner corresponding to the combination of real physical operations in a molecule. Each matrix corresponds to one of the physical operations.

The 4 matrices shown in the middle of p. 78 for C_{2v} make up a representation.

There are 4 representations in the middle of p. 79 (the table with all 1's & -1's. We will see how those numbers were chosen shortly, but these are the 4 simplest representations possible for C_{2v}. The purpose of this exercise is to show that as you move from a theoretical minimum to a molecule as a whole, then to individual parts, (e.g. bonds, atoms) the number of factors you will have to consider expands.

The following properties we will discuss represent very important practical considerations.

Assume that a set of matrices, $\mathcal{E}$, $\mathcal{A}$, $\mathcal{B}$, $\mathcal{C}$, … form a representation of a group. Making the same similarity transformation on each matrix yields a new set of matrices.

$\mathcal{Q}^{-1}\,\mathcal{E}\mathcal{Q} = \mathcal{E}'$

$\mathcal{Q}^{-1}\,\mathcal{A}\mathcal{Q} = \mathcal{A}'$

On p. 80 the books provides a proof of the following: if $\mathcal{A}\mathcal{B} = \mathcal{D}$, then $\mathcal{A}'\mathcal{B}' = \mathcal{D}'$. What this means is that for each matrix in the original set there will be one in the new set that behaves similarly. Thus, the sets are said to run in a parallel fashion. If this is true, the second set of matrices must be second representation of the group.

Now assume when $\mathcal{A}$ is transformed into $\mathcal{A}'$ by $\mathcal{Q}$, it is found that $\mathcal{A}'$ is a block factored matrix.

$$\text{e.g.} \quad \mathcal{A}' = \begin{bmatrix} \mathcal{A}_1' & & \\ & \mathcal{A}_2' & \\ & & \mathcal{A}_3' \end{bmatrix}$$

This happens with some frequency. If this pattern is found for all matrices in the set: $\mathcal{E}'$, $\mathcal{A}'$, $\mathcal{B}'$…, then

$\mathcal{A}_1'\mathcal{B}_1' = \mathcal{D}_1'$

$\mathcal{A}_2'\mathcal{B}_2' = \mathcal{D}_2'$

A result is that each matrix will be subdivided into a series of smaller matrices.

$\mathcal{E}_1'$, $\mathcal{A}_1'$, $\mathcal{B}_2'$, $\mathcal{C}_1'$, …

$\mathcal{E}_2'$, $\mathcal{A}_2'$, $\mathcal{B}_2'$, $\mathcal{C}_2'$,…

Following the parallel matrices argument each of these sets of matrices are representations of a group. If a set of matrices $\mathcal{E}$, $\mathcal{A}$, $\mathcal{B}$, $\mathcal{C}$, … can be transformed as just described into a set of blocked matrices, $\mathcal{E}'$, $\mathcal{A}'$, $\mathcal{B}'$, $\mathcal{C}'$ they form a reducible representation. If not, they are an <u>irreducible representation</u>.

4.3 The Great Orthogonality Theorem

Nomenclature

h = order of a group

ℓ_i = the dimension ith representation, in our case this will be the value of E for any irreducible representation

R = operations in the group

$\Gamma_i(\mathrm{R})_{mn}$ = element in row m, column n of the ith irreducible representation

* = conjugate (takes into account complex numbers).

Theorem: $\sum_{\mathrm{R}} \left[\Gamma_i(\mathrm{R})_{mn}\right]\left[\Gamma_i(\mathrm{R})_{m'n'}\right]^* = \frac{h}{\sqrt{\ell_i \ell_j}}\delta_{ij}\delta_{mm'}\delta_{nn'}$

This equation simply states that for an irreducible representation made up of matrices, one set of elements from each matrix will yield a set of normalized, mutually orthogonal vectors in h-space.

Five Important Rules

The Great Orthogonality Theorem leads to the following rules. We'll use C_{3v} as an example to illustrate the rules. Recall that χ_i is the character of a group and in this case is the coefficient preceding the operations on the top line of the character table.

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

Γ

ℓ = dimension of Γ

1. $\sum_i \ell_i^2 = h$ For the previous example, h = 1 + 2 + 3 = 6 and $\sum_i \ell_i^2 = 1^2 + 1^2 + 2^2 = 6$.

2. $\sum_{\mathrm{R}} \left[\chi_i(\mathrm{R})\right]^2 = h$. For the 3 irreducible representations of C_2v, we see

$$\sum_{\mathrm{R}}[\chi_{\mathrm{i}}(\mathrm{R})]^2 = 1(1)^2 + 2(1)^2 + 3(1)^2 = 6$$

$$\sum_{\mathrm{R}}[\chi_{\mathrm{i}}(\mathrm{R})]^2 = 1(1)^2 + 2(1)^2 + 3(-1)^2 = 6$$

$$\sum_{\mathrm{R}}[\chi_{\mathrm{i}}(\mathrm{R})]^2 = 1(2)^2 + 2(-1)^2 + 3(0)^2 = 6$$

3. $\sum_{\mathrm{R}}\chi_i(\mathrm{R})\chi_j(\mathrm{R}) = 0$ when $i \neq j$. Again, for C_{3v}:

$$\Sigma = 1(1)(1) + 2(1)(1) + 3(1)(-1) = 0$$

$$\Sigma = 1(1)(2) + 2(1)(-1) + 3(1)(0) = 0$$

$$\Sigma = 1(1)(2) + 2(1)(-1) + 3(-1)(0) = 0$$

This shows that each irreducible representation is orthogonal to the others. As we shall soon see, a very similar calculation involving an irreducible representation and a reducible one, will yield a non-zero total.

4. In a given representation (reducible or irreducible), the characters of all matrices belonging to operations in the same class are identical. We have seen this above and it allows the multiplication we've done.

5. The number of irreducible representations of a group is equal to the number of classes in a group. For C_{3v} there are 3 classes and 3 irreducible representations.

<u>An important practical relationship</u>

On pages 87-88 the book derives a key relationship that I'll just give you.

$$a_i = \frac{1}{h}\sum_{\mathrm{R}}\chi(\mathrm{R})\chi_i(\mathrm{R})$$

Where a_i = the number of times the block constituting the ith irreducible representation will appear when the reducible representation is completely reduced by the necessary similarity transformation.

The best way to understand this equation is to see it used. Let's go over the book example on pp 88-89.

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
Γ_a	5	2	-1

$h = 6$ (i.e. $1E + 2C_3 + 3\sigma_v$)

In the following arithmetic, first of the 3 numbers multiplied is the character for the class, the second comes from the irreducible representation (e.g. A_1), and the third from the reducible representation (Γ_a).

$$A_1 = \left(\frac{1}{6}\right)[(1)(1)(5) + (2)(1)(2) + (3)(1)(-1)] = \left(\frac{1}{6}\right)(5 + 4 - 3) = 1$$

$$A_2 = \left(\frac{1}{6}\right)[(1)(1)(5) + (2)(1)(2) + (3)(-1)(-1)] = \left(\frac{1}{6}\right)(5 + 4 + 3) = 2$$

$$E = \left(\frac{1}{6}\right)[(1)(2)(5) + (2)(-1)(2) + (3)(0)(-1)] = \left(\frac{1}{6}\right)(10 - 4 + 0) = 1$$

Thus, Γ_a is composed of 1 A_1, 2 A_2, and 1 E irreducible representations. On page 89 the book shows that if these 4 irreducible representation are added the original reducible representation is obtained as you would expect.

4.4 Character Tables

A detailed description of the character tables is provided in this section. Some of this is interesting, but not required. You are not required memorize material from this section that does not appear in the notes.

The horizontal lines are the irreducible representations of the group. One dimensional representations are “A” or “B,” 2 dimensional representations are “E,” and 3 dimensional representations are “T.” “A” representations are symmetric with respect to rotation about the principle rotation axis while “B” representations are antisymmetric.

Every table will have a section with the symbols: x, y, z, R_x, R_y, and R_z. x, y, and z Represent Cartesian coordinates, while the “R” terms denote clockwise rotation about the x, y, and z axes, respectively. Later, we’ll see the x, y, and z terms represent movement (translation) in the indicated direction. The book also shows how the irreducible representations are generated from matrices. Even though you won’t be tested on this, it is a nice exercise to see how each term in an irreducible representation is generated.

The fourth area is not important now, but will become so later on. Until then, you can ignore this area of the character table.

<u>The Character Table for D_4</u>

This is an exercise in constructing a character table from scratch. We begin by determining that D_4 contains the following operations: E, C_4, C_4^2, C_4^3, C_2(x), C_2(y), C_2(xy), $C_2(x\bar{y})$ These can be collected as: E, $2C_4$, C_2(z), $2C_2$, $2C_2'$. We saw earlier that the number of classes (in this case 5) must equal the number of irreducible representations, so there are 5 of these.

Applying the first of the “5 important rules” (p. 7), we see that:
$\Sigma\ell^2 = h = 8 = (1)^2 + (1)^2 + (1)^2 + (1)^2 + (2)^2 = 8$. This result is the only one possible. Thus, D_4 has 4 “A” or “B” irreducible representations and one “E.” These are the integers for the E column. Also there will always be a totally symmetric representation (all 1s). See the figure in the middle of p. 93.

Applying the second rule, we see that for the one dimensional irreducible representations, all of the characters must be 1 or -1.

$\Sigma = 1(1)(1) + 2(1)(1) + 1(1)(1) + 2(1)(-1) + 2(1)(-1) = 0$

As you can see, the result will be zero if, and only if, the character for E and C_2(z) are both 1. In this situation, then if 2 of the operations $2C_4$, $2C_2$, and $2C_2'$ have -1 characters, the summation equals zero. There are 3 combinations of 1's and -1's that work here and they represent the remaining 3 one-dimensional irreducible representations. I leave it to you to read how the two-dimensional representation is generated.

4.5 Representations for Cyclic Groups;

You may skip this section.