4.2.3: Character Tables

Introduction to Character Tables, using C_{2v} as example

A character table is the complete set of irreducible representations of a symmetry group. In the previous section, we derived three of the four irreducible representations for the C_{2v} point group. These three irreducible representations are labeled A_1, B_1, and B_2. The fourth irreducible representation, A_2, can be derived using the properties (or "rules") for irreducible representations listed below.

> **Properties of Characters of Irreducible Representations in Point Groups**
>
> 1. There is always a totally symmetric representation in which all the characters are 1.
>   *e.g. In C_{2v}, A_1 is totally symmetric.*
> 2. The order of the group (h) is the total number of symmetry operations in the group.
>   *e.g. In C_{2v}, $h=4$*
> 3. Similar operations are listed as classes (R) and appear as columns in the table.
>   *e.g. In C_{2v}, there are four classes of operations, E, C_2, $\sigma_{v(xz)}$, and $\sigma'_{v(yz)}$*
> 4. The number of irreducible representations (rows) must equal the number of classes (columns). This results in all character tables being square.
>   *e.g. In C_{2v}, there are four classes and four irreducible representations.*
> 5. The sum of squares of all characters under E is equal to the order of the group: $h=\sum[\chi_i]^2$
>   *e.g. In C_{2v}, $h=1^2+1^2+1^2+1^2=4$*
> 6. For any irreducible representation (i), the sum of squares of its characters multiplied by the number of operations in the class is the order of the group: $h=\sum[\chi_i(R)]^2$
>   *e.g. For A_2 in C_{2v}, $h=(1\times 1)^2+(1\times 1)^2+(-1\times 1)^2+(-1\times 1)^2=4$*
> 7. Irreducible representations are orthogonal. For any two representations (i and j): $\sum[\chi_i*(R)\chi_j(R)]=0$
>   *e.g. For B_1 and B_2 of C_{2v}, $[1\times 1]+[-1\times -1]+[1\times -1]+[-1\times 1]=0$*

The complete character table for C_{2v} is given below.

C_{2v}	E	C_2	σ_v	σ'_v	$h=4$	
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

The various sections of the table are as follows:

i. The first element in the table gives the name of the point group, usually in Schoenflies (C_{2v}) notation.
ii. Along the first row are the symmetry operations of the group, E, C_2, σ_v and σ_v ", followed by the order of the group, h.
iii. In the first column are the irreducible representations of the group, represented by Mulliken Labels. In C_{2v} the irreducible representations are A_1, A_2, B_1 and B_2. The Mulliken labels indicate the symmetry of each representation (explained further below).
iv. The characters (χ) of the irreducible representations under each symmetry operation are given in the bulk of the table.
v. The final column(s) of the table lists a number of functions that transform as the various irreducible representations of the group. These are the Cartesian axes (x, y, z), the Cartesian products $(z^2, x^2+y^2, xy, xz, yz)$, and the rotations (R_x, R_y, R_z) (explained further below).

Another example: C_{3v}

Th C_{3v} point group has three classes of operations: E, C_3, and $\sigma_{v(xz)}$. The derivation of transformation matrices for E and $\sigma_{v(xz)}$ is similar to the case for C_{2v}. However, the C_{3v} operation does not give simple 1 or -1 characters. If we carry out a rotation about z by an angle θ, our x and y axes are transformed onto new axes x' and y'. The new axes can each be written as a linear combination of our original x and y axes. The derivation of the rotation matrices will not be covered in this text, but is described elsewhere:

$$
\begin{aligned}
x' &= x\cos\theta + y\sin\theta \\
y' &= -x\sin\theta + y\cos\theta
\end{aligned}
$$

For a C_3 rotation counterclockwise through 120° (or $\frac{2\pi}{3}$):

$$
\begin{aligned}
x' &= x\cos(2\pi/3) + y\sin(2\pi/3) &= -\tfrac{1}{2}x - \tfrac{\sqrt{3}}{2}y \\
y' &= -x\sin(2\pi/3) + y\cos(2\pi/3) &= \tfrac{\sqrt{3}}{2}x - \tfrac{1}{2}y
\end{aligned}
$$

The transformation matrices for symmetry operations of C_{3v} are as follows:

$$
E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad C_3 = \begin{pmatrix} [-\frac{1}{2} & -\frac{\sqrt{3}}{2}] & 0 \\ [\frac{\sqrt{3}}{2} & -\frac{1}{2}] & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \sigma'_{v(xz)} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}
$$

The C_3 transformation matrix contains off-diagonal entries, and therefore it cannot be block diagonalized as 1x1 matrices. However, the first two lines can be diagonalized as a 2x2 and the last line as a 1x1 matrix (Figure $4.2.3.1$):

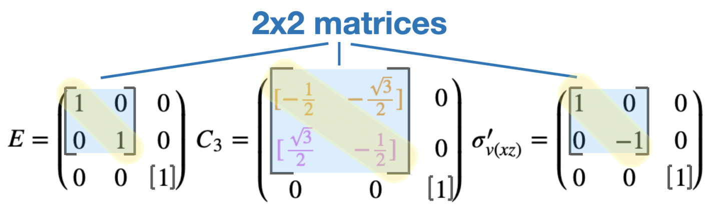

Figure 4.2.3.1: The C_3 transformation matrix contains off-diagonal entries, and therefore it cannot be block diagonalized as 1x1 matrices. However, the first two lines can be diagonalized as a 2x2 and the last line as a 1x1 matrix. (CC-BY-NC-SA; Kathryn Haas)

The character from a 2x2 matrix is the sum of the trace of that matrix. So, for the C_3 operation, the 2x2 matrix gives the character -1 (from $-\frac{1}{2} + -\frac{1}{2}$).

The character table for C_{3v} is shown below.

C_{3v}	E	$2C_3$	$3\sigma_v$	$h = 6$
A_1	1	1	1	z, z^2, x^2+y^2
A_2	1	1	-1	R_z
E	2	-1	0	$(x, y), (xy, x^2+y^2), (xz, yz), (R_x, R_y)$

Additional features of character tables

Additional Features of Character Tables

1. Symmetry operations of the same class are grouped into the same column (class) in the character table and not listed separately.
   e.g. In the C_{3v} point group, there are four operations: E, C_3, C_3^2, and σ_v. The C_3 and C_3^2 operations are listed together in the character table as $2C_3$.
2. IF there are multiple C_2 axes (in a D group), the C_2 axes that are perpendicular to the principle axis are labeled with primes (e.g. C_2' and C_2''); when there are multiple types of perpendicular C_2 axes, one prime (C_2') means that it passes through more atoms, while a double prime (C_2'') means it goes between atoms.
3. Mirror planes that are perpendicular to the principle axis are "horizontal" mirror planes and are designated with an h subscript (σ_h). Mirror planes that are in-plane with the principle axis are "vertical" mirror planes, σ_v. When there are two types of vertical mirror planes, those that run through more atoms are σ_v while those that run between atoms are "dihedral", σ_d.
4. Matching the symmetry operations listed in the character table to the symmetry operations of a molecule can confirm its point group.

5. Irreducible representations are each assigned a Mulliken label, listed in the left-hand column, that indicates the symmetry of that representation as follows:

Mulliken Labels	**meaning**
A	singly degenerate (1x1), symmetric to principle axis
B	singly degenerate (1x1), antisymmetric to principle axis
E	doubly degenerate (2x2)
T	triply degenerate (3x3)
Subscripts and superscripts	**meaning**
1	symmetric to $\sigma_v$or perpendicular to C_2
2	anti-symmetric to $\sigma_v$or perpendicular to C_2
g	symmetric to inversion center
u	anti-symmetric to inversion center
′	symmetric to σ_h
”	anti-symmetric to σ_h

6. The right-hand columns of the character table list a number of functions that transform as the various irreducible representations of the group. These are the Cartesian axes (x, y, z), the Cartesian products $(z^2, x^2+y^2, xy, xz, yz)$, and the rotations (R_x, R_y, R_z). These expressions indicate the properties of orbitals within the symmetry group. The s-orbital, which is totally symmetric, corresponds to the irreducible representation that possesses symmetry of x^2, y^2 and z^2 combined. The p-orbitals each possess the symmetry of the corresponding axis (e.g. p_x corresponds to the x axis). Each of the d-orbitals possess the symmetry of the corresponding binary product (e.g. d_{xy} corresponds to the binary product, xy, in the character table).

The functions listed in the final column of the table are important in many chemical applications of group theory, particularly in spectroscopy. For example, by looking at the transformation properties of x, y and z (sometimes given in character tables as T_x, T_y, T_z) we can discover the symmetry of translations along the x, y, and z axes. Similarly, R_x, R_y and R_z represent rotations about the three Cartesian axes. The transformation properties of x, y, and z can be used to determine whether or not a molecule is IR-active or whether or not it can absorb a photon of x-, y-, or z-polarized light and undergo a spectroscopic transition. The Cartesian products play a similar role in determining selection rules for Raman transitions, which involve two photons.

A visual summary of the sections and their significance is given in Figure 4.2.3.2 Character tables for common point groups are given in the References section of LibreTexts Bookshelves.

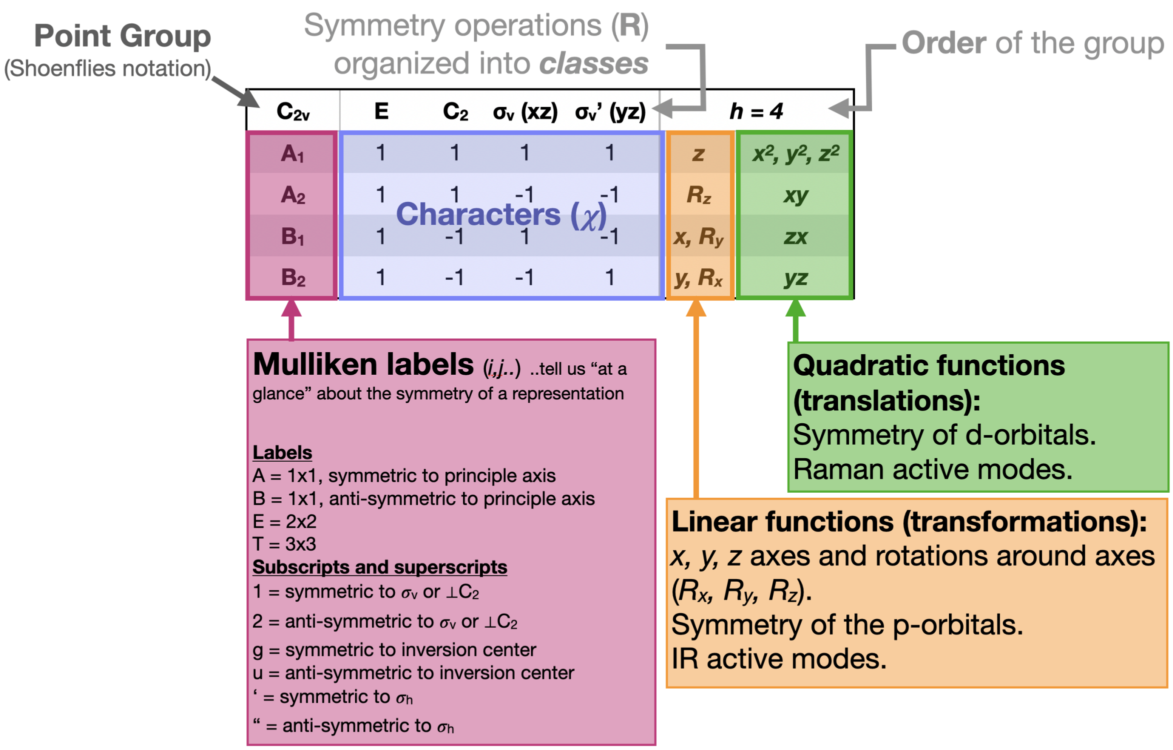

Figure 4.2.3.2: Visual summary of the sections of a character table and their meaning. (CC-BY-NC-SA; Kathryn Haas)

Contributors and Attributions

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  adapted from Character Tables (click here)
