Representations, Character Tables, and One Application of Symmetry

Chapter 4

Friday, October 2, 2015

Matrices and Matrix Multiplication

A matrix is an array of numbers, A_{ij}

columns

rows
$$\begin{pmatrix} -1 & 4 & 3 \\ -8 & -1 & 7 \\ 2 & 14 & 1 \end{pmatrix}$$

column matrix
$$\begin{pmatrix} 1 \\ 2 \\ 3 \end{pmatrix}$$

row matrix
$$\begin{pmatrix} 1 & 2 & 3 & 4 \end{pmatrix}$$

To multiply two matrices, add the products, element by element, of each *row* of the first matrix with each *column* in the second matrix:

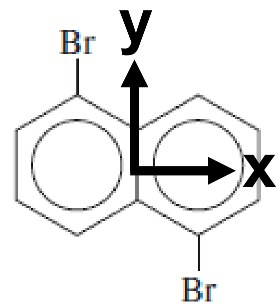
$$\begin{pmatrix} 1 & 2 \\ 3 & 4 \end{pmatrix} \times \begin{pmatrix} 1 & 2 \\ 3 & 4 \end{pmatrix} = \begin{pmatrix} (1\times1)+(2\times3) & (1\times2)+(2\times4) \\ (3\times1)+(4\times3) & (3\times2)+(4\times4) \end{pmatrix} = \begin{pmatrix} 7 & 10 \\ 15 & 22 \end{pmatrix}$$

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \times \begin{pmatrix} 1 \\ 2 \\ 3 \end{pmatrix} = \begin{pmatrix} 1 \\ -2 \\ 6 \end{pmatrix}$$

Transformation Matrices

Each symmetry operation can be represented by a 3×3 matrix that shows how the operation transforms a set of *x*, *y*, and *z* coordinates

Let's consider C_{2h} $\{E, C_2, i, \sigma_h\}$:



1,5-dibromonaphthalene

C_2

x' = -x
y' = -y
z' = z

transformation matrix

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

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

(new coordinates) = (transformation matrix)(old coordinates) = (new in terms of old)

i

x' = -x
y' = -y
z' = -z

transformation matrix

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

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

Representations of Groups

The set of four transformation matrices forms a *matrix representation* of the C_{2h} point group.

$$E: \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad C_2: \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad i: \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad \sigma_h: \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

These matrices combine in the same way as the operations, e.g.,

$$C_2 \times C_2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = E$$

The sum of the numbers along each matrix *diagonal* (the *character*) gives a shorthand version of the matrix representation, called Γ:

C_{2h}	E	C_2	i	σ_h
Γ	3	-1	-3	1

Γ (gamma) is a *reducible representation* b/c it can be further simplified.

Irreducible Representations

The transformation matrices can be reduced to their simplest units (1×1 matrices in this case) by block diagonalization:

x y z

$$E: \begin{pmatrix} [1] & 0 & 0 \\ 0 & [1] & 0 \\ 0 & 0 & [1] \end{pmatrix} \quad C_2: \begin{pmatrix} [-1] & 0 & 0 \\ 0 & [-1] & 0 \\ 0 & 0 & [1] \end{pmatrix} \quad i: \begin{pmatrix} [-1] & 0 & 0 \\ 0 & [-1] & 0 \\ 0 & 0 & [-1] \end{pmatrix} \quad \sigma_h: \begin{pmatrix} [1] & 0 & 0 \\ 0 & [1] & 0 \\ 0 & 0 & [-1] \end{pmatrix}$$

We can now make a table of the characters of each 1×1 matrix for each operation:

symmetry operations

irreducible representations

C_{2h}	E	C_2	i	σ_h	coordinate
B_u	1	-1	-1	1	x
B_u	1	-1	-1	1	y
A_u	1	1	-1	-1	z
Γ	3	-1	-3	1	

The three rows (labeled B_u, B_u, and A_u) are *irreducible representations* of the C_{2h} point group.

They cannot be simplified further. Their characters sum to give Γ.

Irreducible Representations

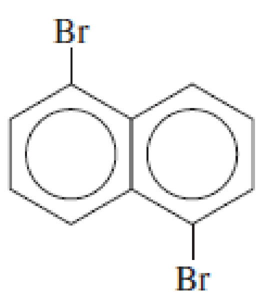
The characters in the table show how each irreducible representation transforms with each operation.

symmetry operations

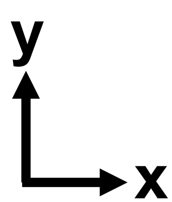
irreducible representations

C_{2h}	E	C_2	i	σ_h	coordinate
B_u	1	-1	-1	1	x
B_u	1	-1	-1	1	y
A_u	1	1	-1	-1	z

1 = symmetric (unchanged); -1 = antisymmetric (inverted); 0 = neither



1,5-dibromonaphthalene



A_u transforms like the *z*-axis: **E → no change**
C_2 → no change
i → inverted
σ_h → inverted

A_u has the same symmetry as z in C_{2h}

Irreducible Representations

The characters in the table show how each irreducible representation transforms with each operation.

symmetry operations

irreducible representations

C_{2h}	E	C_2	i	σ_h	coordinate
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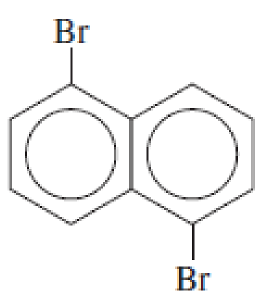

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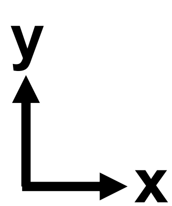


B_u transforms like x and y:

E → no change
C_2 → inverted
i → inverted
σ_h → no change

The two B_u representations are exactly the same. We "merge" them to eliminate redundancy.

Irreducible Representations

The characters in the table show how each irreducible representation transforms with each operation.

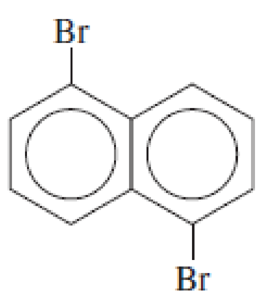
symmetry operations

irreducible representations

C_{2h}	E	C_2	i	σ_h	coordinate
B_u	1	-1	-1	1	x, y
A_u	1	1	-1	-1	z

merged

1 = symmetric (unchanged); -1 = antisymmetric (inverted); 0 = neither



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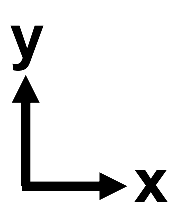

B_u transforms like x and y:

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Character Tables

List of the complete set of irreducible representations (rows) and symmetry classes (columns) of a point group.

symmetry classes

irreducible representations

C_{2h}	E	C_2	i	σ_h	linear	quadratic
A_g	1	1	1	1	R_z	x^2, y^2, z^2, xy
B_g	1	-1	1	-1	R_x, R_y	xz, yz
A_u	1	1	-1	-1	z	
B_u	1	-1	-1	1	x, y	

- **The first column gives the Mulliken label for the representation**
  - *A* or *B* **= 1×1 representation that is symmetric (A) or anti-symmetric (B) to the principal axis.**
  - *E* **= 2×2 representation (character under the identity will be 2)**
  - *T* **= 3×3 representation (character under the identity will be 3)**
  - **For point groups with inversion, the representations are labelled with a subscript** *g* **(gerade) or** *u* **(ungerade) to denote symmetric or anti-symmetric with respect to inversion.**
  - **If present, number subscripts refer to the symmetry of the next operation class after the principle axis. For symmetric use subscript 1 and for anti-symmetric use subscript 2.**

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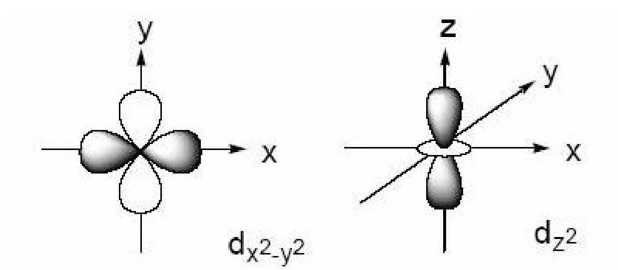
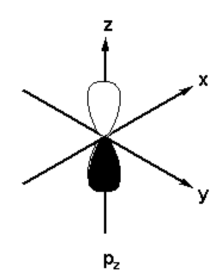
C_{2h}	E	C_2	i	σ_h	linear	quadratic
A_g	1	1	1	1	R_z	x^2, y^2, z^2, xy
B_g	1	-1	1	-1	R_x, R_y	xz, yz
A_u	1	1	-1	-1	z	
B_u	1	-1	-1	1	x, y	

- **The last two columns give functions (*with an origin at the inversion center)* that belong to the given representation (e.g., the d_{x2-y2} and d_{z2} orbitals are A_g, while the p_z orbital is A_u).**





Properties of Character Tables

C_{2h}	E	C_2	i	σ_h	linear	quadratic
A_g	1	1	1	1	R_z	x^2, y^2, z^2, xy
B_g	1	-1	1	-1	R_x, R_y	xz, yz
A_u	1	1	-1	-1	z	
B_u	1	-1	-1	1	x, y	

- **The total number of symmetry operations is the *order* (h). h = 4 in this case.**
- **Operations belong to the same *class* if they are identical within coordinate systems accessible by a symmetry operation. One class is listed per column.**
- **# irreducible representations = # classes (tables are square).**
- **One representation is totally symmetric (all characters = 1).**
- **h is related to the characters (χ) in the following two ways:**

$$h = \sum_i [\chi_i(E)]^2 \qquad h = \sum_R [\chi_i(\boldsymbol{R})]^2$$

where i and *R* are indices for the representations and the symmetry operations.

- **Irreducible representations are *orthogonal*:** $$\sum_R \chi_i(\boldsymbol{R})\,\chi_j(\boldsymbol{R}) = 0 \quad \text{when } i \neq j$$

Example

Let's use the character table properties to finish deriving the C_{2h} table.

From the transformation matrices, we had:

C_{2h}	E	C_2	i	σ_h	coordinate
B_u	1	-1	-1	1	x, y
A_u	1	1	-1	-1	z

There must be four representations and one is totally symmetric, so:

C_{2h}	E	C_2	i	σ_h	coordinate
A_g	1	1	1	1	
?	?	?	?	?	
B_u	1	-1	-1	1	x, y
A_u	1	1	-1	-1	z

The fourth representation must be orthogonal to the other three and have $\chi(E) = 1$.

The only way to achieve this is if $\chi(C_2) = -1$, $\chi(i) = 1$, $\chi(\sigma_h) = -1$, giving a B_g

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There must be four representations and one is totally symmetric, so:

C_{2h}	E	C_2	i	σ_h	coordinate
A_g	1	1	1	1	
B_g	1	-1	1	-1	
B_u	1	-1	-1	1	x, y
A_u	1	1	-1	-1	z

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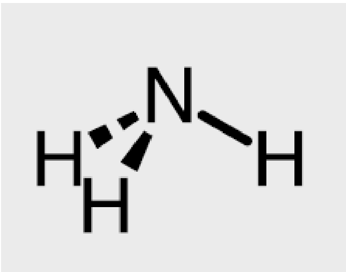
C_{3v} Character Table



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

The characters for A_1 and E come from the transformation matrices:

$$E: \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad C_3: \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} -1/2 & -\sqrt{3}/2 & 0 \\ \sqrt{3}/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \sigma_{v(xz)}: \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

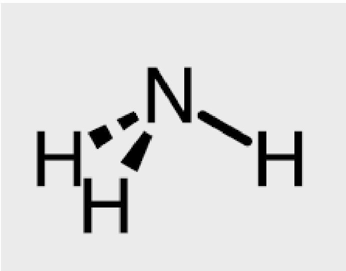
rotation matrix about z-axis
see website and p. 96

In block form:

$$E: \begin{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} & 0 \\ 0 \quad 0 & [1] \end{pmatrix} \quad C_3: \begin{pmatrix} \begin{pmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{pmatrix} & 0 \\ 0 \quad 0 & [1] \end{pmatrix} = \begin{pmatrix} \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix} & 0 \\ 0 \quad 0 & [1] \end{pmatrix} \quad \sigma_{v(xz)}: \begin{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} & 0 \\ 0 \quad 0 & [1] \end{pmatrix}$$

***x* and *y* are not independent in C_{3v} – we get 2×2 (x,y) and 1×1 (z) matrices**

C_{3v} Character Table



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

The third representation can be found from orthogonality and $\chi(E) = 1$.

Note:

- **C_3 and C_3^2 are identical after a C_3 rotation and are thus in the same class ($2C_3$)**
- **The three mirror planes are identical after C_3 rotations → same class ($3\sigma_v$)**
- **The *E* representation is two dimensional ($\chi(E) = 2$), mixing *x,y*. This is a result of C_3.**
- ***x* and *y* considered together have the symmetry of the *E* representation**

Try proving that this character table actually has the properties expected of a character table.

Summary

Each molecule has a point group, the full set of symmetry operations that describes the molecule's overall symmetry

- **You can use the decision tree to assign point groups**

Character tables show how the complete set of irreducible representations of a point group transforms under all of the symmetry classes of that group.

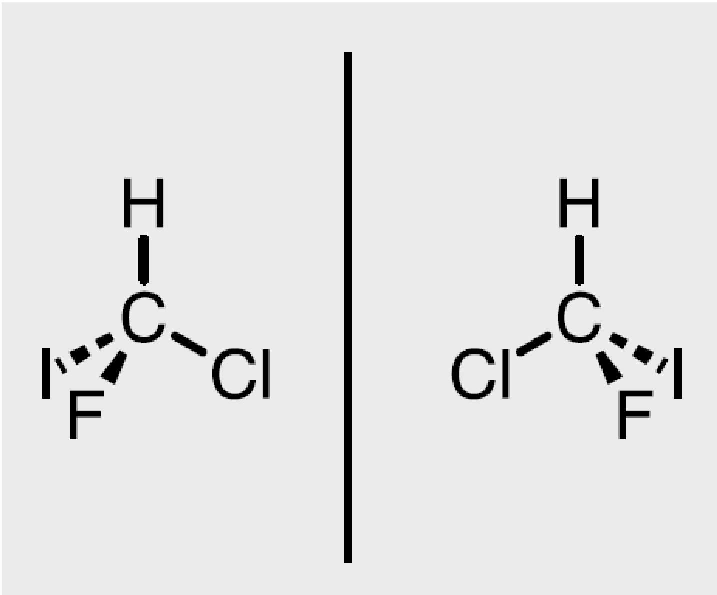
- **The tables contain all of the symmetry information in convenient form**
- **We will use the tables to understand bonding and spectroscopy**

To dig deeper, check out: Cotton, F. A. *Chemical Applications of Group Theory*.

Using Symmetry: Chirality

One use for symmetry is identifying chiral molecules

- **To be chiral, a molecule must lack an improper rotation axis**
- **In other words, for a molecule to be chiral it must be in the C_1, C_n, or D_n point groups (remember that $\sigma = S_1$ and $i = S_2$).**



C_1

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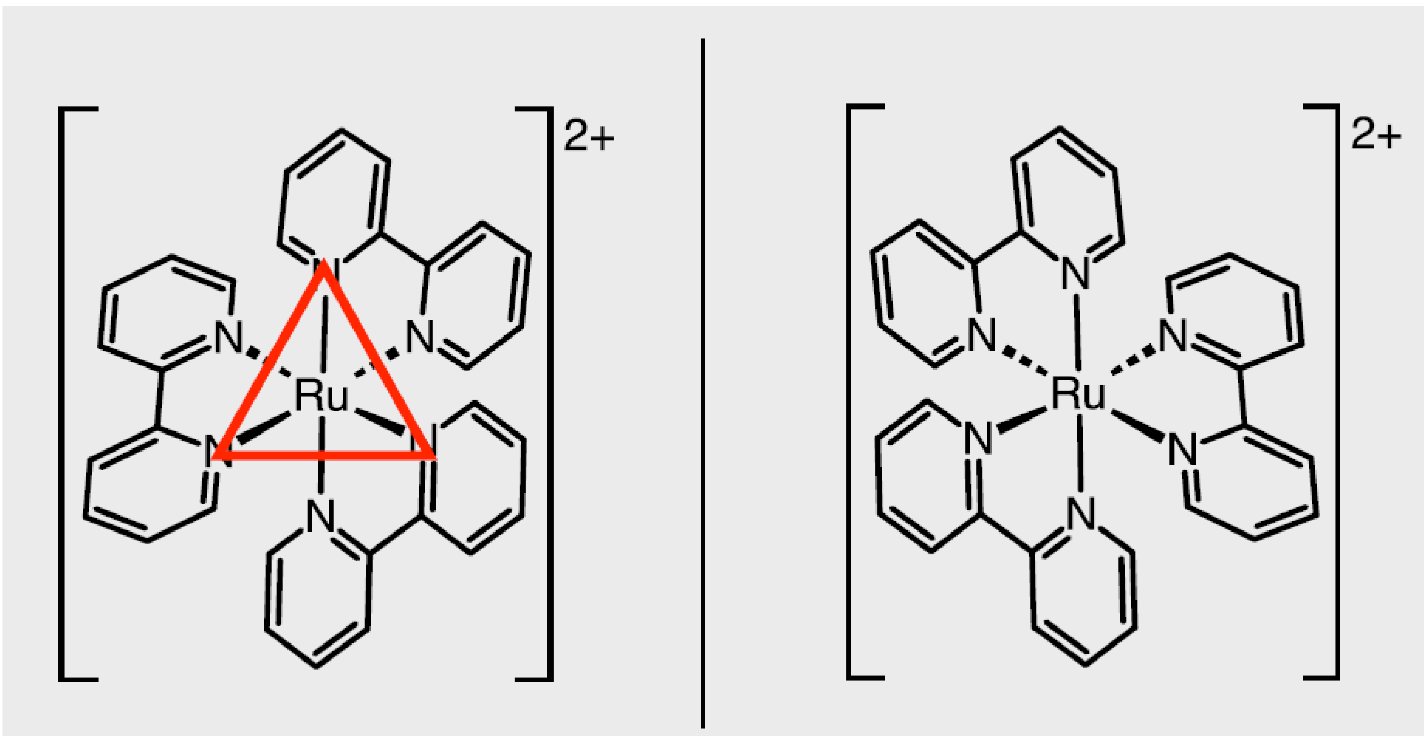

D_3