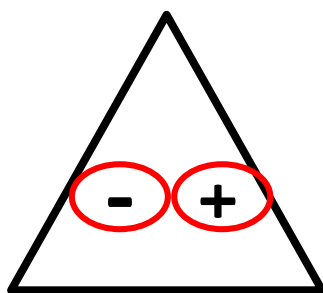
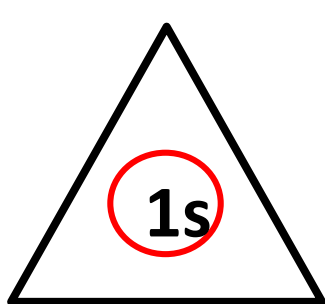
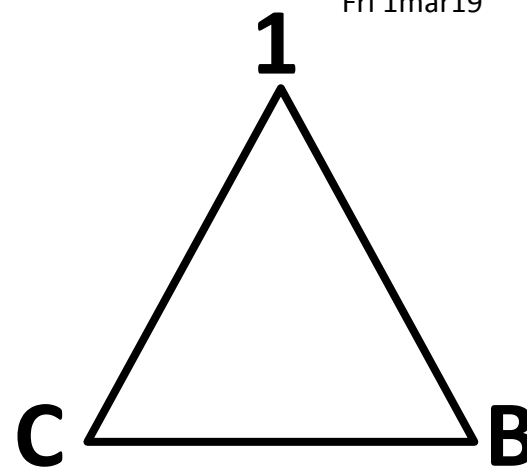
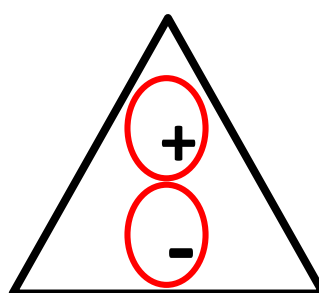


# Group $C_3$ Character Table

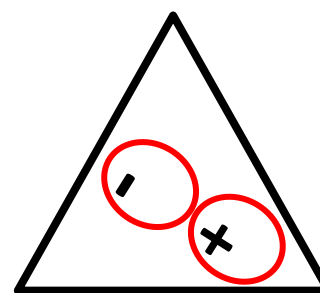
	I	$C_3^+$	$C_3^-$		
A	1	1	1	z	$z^2, x^2+y^2$
E	2	-1	-1	x,y	$x^2-y^2$ xy



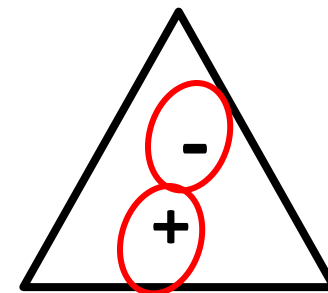
$p_x$



$p_y$



$C_3^+ 2p_y$



$C_3^+ 2p_x$

What is the energy difference for the 3 orientations if there a proton at each corner??? **NONE**

## Creating representations of the member of the Group of symmetry operators

The representatives (representations) are matrices generated by applying the operators to basis functions

Consider the effect of applying the identity,  $I$ , to  $p_x$  and  $p_y$

$$I \begin{pmatrix} p_x \\ p_y \end{pmatrix} = \begin{matrix} 1p_x + & 0p_y \\ 0p_x + & 1p_y \end{matrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} p_x \\ p_y \end{pmatrix} \quad \text{The character = the trace = 2}$$

Consider the effect of applying  $C_3^+$  (120° CW rotation) to  $p_x$  and  $p_y$

$$C_3^+ \begin{pmatrix} p_x \\ p_y \end{pmatrix} = \begin{matrix} -\frac{1}{2}p_x + & \frac{\sqrt{3}}{2}p_y \\ \frac{\sqrt{3}}{2}p_x + & -\frac{1}{2}p_y \end{matrix} = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} p_x \\ p_y \end{pmatrix} \quad \text{The character = the trace = -1}$$

That is exactly what the character table says for x,y which is what  $p_x$  and  $p_y$  are. Thus,  $p_x$  and  $p_y$  belong to the E irreducible representation. (E always indicates dimension = 2

Group  $C_3$  Character Table

	I	$C_3^+$	$C_3^-$		
A	1	1	1	z	$z^2, x^2+y^2$
E	2	-1	-1	x,y	$x^2-y^2, xy$

## The next 6 pages are a more compact and technical statement of the connection between symmetry and quantum chemistry

### Why Study Symmetry and Group Theory ?

This can be summarized by two theorems:

- (I) The energy eigenfunctions (and also molecular orbitals) must be bases\* for the irreducible\* representations\* (I. R. 's) of its symmetry group.

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\* Hang on! These strange words will hopefully be clarified on the next page.

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- (II) (a) If two functions (could be atomic or molecular orbitals, or sums and/or products thereof,)  $\psi_1$  and  $\psi_2$ , "have different symmetry" (which means they are bases for different irreducible representations of the molecule's symmetry group) they will not "interact." That is,

$$\int \psi_1 H \psi_2 dt = 0 \quad \text{where H is the molecule's Hamiltonian operator.}$$

- (b) if  $\psi_1$  and  $\psi_2$  are energy eigenfunctions (or molecular orbitals) they must have different energies (except in rare cases of accidental degeneracy) if they have different symmetry.

If  $\psi_1$  and  $\psi_2$  are a basis set for the same I. R. , they must have the same energy.

Thus, when seeking the eigenfunctions for a molecule having symmetry one need not bother mixing together functions with different symmetry and one can solve several small matrix problems (one for each type of symmetry) instead of one big matrix.

Actually, when dealing with matrix elements of operators other than energy it is also possible to predict when the integral will be zero using group theory. Examples are selection rules for absorption of light, dipole moments, optical rotation, etc.

With respect to theorem II(b) it is important to realize that this is why the Woodward-Hoffman rules work.

## 1. What is a representation of a group?

Simply a set of numbers or matrices which can be substituted for the members of the group so as to have the same multiplication table (~~see p. 95 of text~~). The simplest representation of a group is where each member is represented by the number 1. On page 99 are shown 3 different representations of the  $C_{3v}$  group. Two are 1-dimensional and one is 2-dimensional, i. e., a set of 2 x 2 matrices.

## 2. What is meant by a basis for a representation?

A basis for an n-dimensional representation of a group is simply n different functions from which the representation (set of matrices) can be generated:

Let the basis be  $\varphi_1, \varphi_2, \varphi_3 \dots \varphi_n$ . The representative matrix for a given symmetry operation,  $\sigma_i$ , is generated by operating on each of the n functions.

$$\begin{aligned}\text{Thus, if } \sigma_i \varphi_1 &= a_{11}^i \varphi_1 + a_{12}^i \varphi_2 + \dots + a_{1n}^i \varphi_n \\ \sigma_i \varphi_2 &= a_{21}^i \varphi_1 + a_{22}^i \varphi_2 + \dots + a_{2n}^i \varphi_n \\ &\vdots \\ \sigma_i \varphi_n &= a_{n1}^i \varphi_1 + a_{n2}^i \varphi_2 + \dots + a_{nn}^i \varphi_n\end{aligned}$$

the matrix representing  $\sigma_i$  is

$$R_i = \begin{pmatrix} a_{11}^i & a_{12}^i & \dots & a_{1n}^i \\ a_{21}^i & & & \\ a_{31}^i & & & \\ \vdots & & & \\ a_{n1}^i & a_{n2}^i & \dots & a_{nn}^i \end{pmatrix}$$

Notice that the only requirement is that each operation cause each basis function to go into a function which is a linear combination of the members of the basis set.

### 3. What is meant by irreducible?

Example:

If two functions are a basis for a 2-dimensional irreducible representation, this means there is no way to transform the 2 functions into two new ones which are each basis functions for a one-dimensional representation. *i.e.* are both diagonal.

Example:  $\sigma_i^p x = a_{11}^i p_x + a_{12}^i p_y$

and  $\sigma_i^p y = a_{21}^i p_x + a_{22}^i p_y$  for each operation  $\sigma_i$ .

The representation (i.e. the set of 2 x 2 matrices  $R_i$  is reducible if one can find new linear combinations:

$$p_1 = c_{11}p_x + c_{12}p_y$$

$$p_2 = c_{21}p_x + c_{22}p_y$$

such that

$$\mathcal{O}'_i p_1 = p_1 \quad \text{or} \quad \mathcal{O}'_i p_1 = -p_1$$

and  $\mathcal{O}'_i p_2 = p_2$  or  $\mathcal{O}'_i p_2 = -p_2$  for every  $\mathcal{O}'_i$ .

In other words, if we cannot find linear combinations of  $p_x$  and  $p_y$  which simply go into + or - themselves for each operation of the group then  $p_x$  and  $p_y$  are a basis for a 2-dimensional irreducible representation of the group.

~~(See pages 96-97 in text).~~

#### 4. Character Tables

The various irreducible representations of a group are tabulated and labeled in character tables.

Character = the sum of the diagonal elements of the matrix that represents a particular operation.

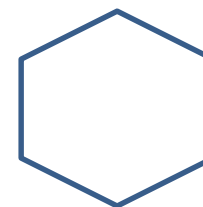
i.e., the TRACE

In a one-dimensional representation the characters are therefore the representation. For n-dimensional representations the character (trace) is tabulated since it is invariant to transformations of the basis set and it is all that is needed to characterize an irreducible representation.

Conventions for labeling:	one dimensional	A & B
	two dimensional	E
	three dimensional	T (or F)
	four dimensional	G
	etc.	



# Example: Character Table for the $D_{6h}$ point group, to which benzene belongs



$D_{6h}$	$E$	$2C_6$	$2C_3$	$C_2$	$3C'_2$	$3C''_2$	$i$	$2S_3$	$2S_6$	$\sigma_h$	$3\sigma_d$	$3\sigma_v$		
$A_g$	1	1	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2, z^2$
$A_{2g}$	1	1	1	1	-1	-1	1	1	1	1	-1	-1	$R_z$	
$B_{1g}$	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1		
$B_{2g}$	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1		
$E_{1g}$	2	1	-1	-2	0	0	2	1	-1	-2	0	0	$(R_x, R_y)$	$(xz, yz)$
$E_{2g}$	2	-1	-1	2	0	0	2	-1	-1	2	0	0		$(x^2 - y^2, xy)$
$A_{1u}$	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1		
$A_{2u}$	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	$z$	
$B_{1u}$	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1		
$B_{2u}$	1	-1	1	-1	-1	1	-1	1	-1	1	1	-1		
$E_{1u}$	2	1	-1	-2	0	0	-2	-1	1	2	0	0	$(x, y)$	
$E_{2u}$	2	-1	-1	2	0	0	-2	1	1	-2	0	0		

The symbols in the two right-hand columns have the following meanings:

The position operators  $x, y, z$ , and the  $p_x, p_y$  orbitals have  $E_{1u}$  symmetry

The  $d_{xy}$  and  $d_{x^2-y^2}$  d orbitals have  $E_{2g}$  symmetry, etc.

$R_x$  means rotation about x, ...

# Direct product

The word *"totally symmetric"* refers to a function that ALWAYS goes into itself upon ALL symmetry operations for the molecule. Typically called  $A_{1g}$  or  $A_g$ , it is the irreducible representation type whose characters are ALL = 1

$D_{6h}$	$E$	$2C_6$	$2C_3$	$C_2$	$3C'_2$	$3C''_2$	$i$	$2S_3$	$2S_6$	$\sigma_h$	$3\sigma_d$	$3\sigma_v$		
$A_g$	1	1	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2, z^2$
$A_{2g}$	1	1	1	1	-1	-1	1	1	1	1	-1	-1	$R_z$	
$B_{1g}$	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1		
$B_{2g}$	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1		
$E_{1g}$	2	1	-1	-2	0	0	2	1	-1	-2	0	0	$(R_x, R_y)$	$(xz, yz)$
$E_{2g}$	2	-1	-1	2	0	0	2	-1	-1	2	0	0		$(x^2 - y^2, xy)$
$A_{1u}$	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1		
$A_{2u}$	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	$z$	
$B_{1u}$	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1		
$B_{2u}$	1	-1	1	-1	-1	1	-1	1	-1	1	1	-1		
$E_{1u}$	2	1	-1	-2	0	0	-2	-1	1	2	0	0	$(x, y)$	
$E_{2u}$	2	-1	-1	2	0	0	-2	1	1	-2	0	0		

The integral,  $\int_{-\infty}^{\infty} \Psi_1 * \bar{A}\Psi_2 d\tau$ , where A is any operator

**MUST** have a *"totally symmetric"* component, or else it will be = 0

because **nodes** in the product  $\Psi_1 * \bar{A}\Psi_2$  ensure that the negative parts of the integral cancel the positive parts

$D_{6h}$	$E$	$2C_6$	$2C_3$	$C_2$	$3C'_2$	$3C''_2$	$i$	$2S_3$	$2S_6$	$\sigma_h$	$3\sigma_d$	$3\sigma_v$		
$A_g$	1	1	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2, z^2$
$A_{2g}$	1	1	1	1	-1	-1	1	1	1	1	-1	-1	$R_z$	
$B_{1g}$	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1		
$B_{2g}$	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1		
$E_{1g}$	2	1	-1	-2	0	0	2	1	-1	-2	0	0	$(R_x, R_y)$	$(xz, yz)$
$E_{2g}$	2	-1	-1	2	0	0	2	-1	-1	2	0	0		$(x^2 - y^2, xy)$
$A_{1u}$	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1		
$A_{2u}$	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	$z$	
$B_{1u}$	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1		
$B_{2u}$	1	-1	1	-1	-1	1	-1	1	-1	1	1	-1		
$E_{1u}$	2	1	-1	-2	0	0	-2	-1	1	2	0	0	$(x, y)$	
$E_{2u}$	2	-1	-1	2	0	0	-2	1	1	-2	0	0		

The x transition dipole integral,  $\int \Psi_1^* \bar{x} \Psi_2 d\tau$

**Example: operator  $x = E_{1u}$ , and  $\psi_1$  is  $A_g$  ground state, then need  $\psi_2 = E_{1u}$  i.e., only transition to  $E_{1u}$  are dipole allowed. x and y are equivalent.**