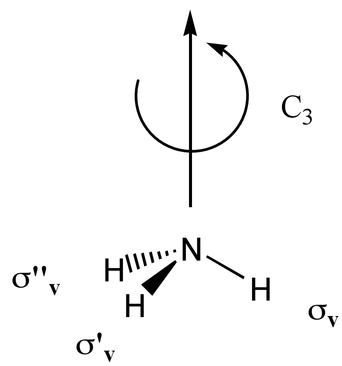
3.4. Characters and Character Tables

3.4.1. Deriving character tables: Where do all the numbers come from?

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

- A general and rigorous method for deriving character tables is based on five theorems which in turn are based on something called *The Great Orthogonality Theorem*. (e.g. F.A. Cotton, "Chemical Applications of Group Theory", QD 461.C65 1990)



The five theorems are:

1) The number of irreducible representations is equal to the number of classes in the group.

e.g. NH_3, point group C_{3v}:

Which C_{3v} symmetry operations are the inverse of which… and which are together in one class?

$E^{-1} = E$ $\quad$ $\sigma_v^{-1} = \sigma_v$ $\quad$ $C_3^{-1} = C^2_3$

$\sigma'_v{}^{-1} = \sigma'_v$ $\quad$ $(C^2_3)^{-1} = C_3$ $\quad$ $\sigma''_v{}^{-1} = \sigma''_v$

Using the above relationships we can set up the following similarity transformations:

$\sigma_v \times C_3 \times \sigma_v = C^2_3$ $\quad$ $C^2_3 \times \sigma_v \times C_3 = \sigma''_v$ $\quad$ $C^2_3 \times E \times C_3 = E$

$\sigma''_v \times C_3 \times \sigma''_v = C^2_3$ $\quad$ $\sigma_v \times \sigma_v \times \sigma_v = \sigma_v$ $\quad$ $\sigma_v \times E \times \sigma_v = E$

$C^2_3 \times C^2_3 \times C_3 = C^2_3$ $\quad$ $C_3 \times \sigma_v \times C^2_3 = \sigma'_v$ $\quad$ $\sigma''_v \times E \times \sigma''_v = E$

$\sigma'_v \times C^2_3 \times \sigma'_v = C_3$ $\quad$ $\sigma''_v \times \sigma'_v \times \sigma''_v = \sigma_v$

$\sigma'_v \times \sigma''_v \times \sigma'_v = \sigma_v$

→ Apparently $\{C_3, C^2_3\}$, $\{\sigma_v, \sigma'_v, \sigma''_v\}$, and $\{E\}$ are each in a class.

→ In C_{3v} there are three classes and hence three irreducible representations.

2) The characters of all operations in the same class are equal in each given irreducible (or reducible) representation.

In above example, all rotations C_3, $C^2{}_3$ will have the same character; all mirror planes σ_v, σ'_v, σ''_v will have the same character, etc.

Def.: The character of a matrix is the sum of all its diagonal elements (also called the trace of a matrix).

Example: Consider the 3x3 matrix that represents the symmetry operation E as performed on a vector (x,y,z) in 3D space:

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \rightarrow \quad \text{trace} = 3$$

THEREFORE: A *reducible* representation for a vector (x,y,z) in 3D space will have a character 3 for the symmetry element E.

Example: Consider the 3x3 matrix that represents the symmetry operation C_3 as performed on a vector (x,y,z) in 3D space:

$$C_3 = \begin{bmatrix} \cos\frac{2\pi}{3} & -\sin\frac{2\pi}{3} & 0 \\ \sin\frac{2\pi}{3} & \cos\frac{2\pi}{3} & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -0.5 & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -0.5 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \rightarrow \quad \text{trace} = 0$$

THEREFORE: A *reducible* representation for a vector (x,y,z) in 3D space will have a character 0 for the symmetry element C_3.

HOMEWORK: Prove that a reducible representation for a vector (x,y,z) in 3D space will also have a character 0 for the symmetry operation C_3^2.

NOTE: The *reducible* representation for a vector (x,y,z) in 3D space is often shown at the bottom of a character table. For the C_{3v} character table it is:

C_{3v}	E	C_3	C_3^2	σ_v	σ_v'	σ_v''
$\Gamma_{x,y,z}$	3	0	0	1	1	1

3) The sum of the squares of all characters in any irreducible representation is equal to the order of the group.

… order of the group = number of symmetry operators …

C_{3v}	E	C_3	C_3^2	σ_v	σ_v'	σ_v''
A_1	1	1	1	1	1	1
A_2	1	1	1	-1	-1	-1
E	2	-1	-1	0	0	0

Check A_1: $1^2 + 1^2 + 1^2 + 1^2 + 1^2 + 1^2 = 6$
Check A_2: $1^2 + 1^2 + 1^2 + (-1)^2 + (-1)^2 + (-1)^2 = 6$
Check E: $2^2 + (-1)^2 + (-1)^2 + 0^2 + 0^2 + 0^2 = 6$

4) The point product of the characters of any two irreducible representations is 0.

… let's check that with the C_{3v} character table above:

$\Gamma_{A1} * \Gamma_{A2} = (1x1) + (1x1) + (1x1) + (1x-1) + (1x-1) + (1x-1) = 0$

$\Gamma_{A2} * \Gamma_{E} = (1x2) + (1x-1) + (1x-1) + (-1x0) + (-1x0) + (-1x0) = 0$

… This is equivalent to saying that all irreducible representations are ORTHOGONAL!

5) The sum of the squares of the dimensions of the irreducible representations is equal to the order of the group.

Def.: The dimension of a representation is the trace of the matrix of the identity operator (E).

Example: A vector (x,y,z) in 3D space is (obviously) 3-dimensional:

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \rightarrow \text{trace} = 3$$

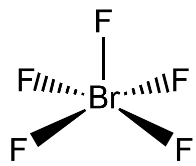
Since the characters in the character table are the traces of matrices:

In the point group C_{3v}, the *irreducible* representation A_1 is 1-dimensional
A_2 is 1-dimensional
E is 2-dimensional

The order of the group is 6: $1^2 + 1^2 + 2^2 = 6$

A fully worked out example:

The derivation of the C_{4v} character table



The symmetry operations in this point group are: E, C_4, $C^2_4 = C_2$, C^3_4, σ_v, σ'_v, σ_d, σ'_d.

There are five classes of symmetry operations derived using a multiplication table:

[E], [C_2], [C_4,C^3_4], [σ_v,σ'_v], and [σ_d,σ'_d], i.e. there will be five irreducible representations.

- There is always a totally symmetric representation denoted by a set of 1x1 matrices:

  i.e., We need ALL symmetry operations! **none are redundant**

C_{4v}	[E]	[C_4	$^3C_4$]	[$C_2 = {}^2C_4$]	[σ_v	σ'_v]	[σ_d	σ'_d]
Γ_1	[1]	[1	1]	[1]	[1	1]	[1	1]
Γ_2								
Γ_3								
Γ_4								
Γ_5								

- Theorem 5 says, that the sum of the squares of the dimensions of the group must be equal to the order of the group:

C_{4v}	E	C_4	$^3C_4$	C_2	σ_v	σ'_v	σ_d	σ'_d
Γ_1	1	1	1	1	1	1	1	1
Γ_2	1							
Γ_3	1							
Γ_4	1							
Γ_5	2							

… because $1^2 + 1^2 + 1^2 + 1^2 + 2^2 = 8$ = order of the group, i.e. one of the irreducible representations will be two-dimensional !

- based on the theorems we also know that …

- the characters of all operations in the same class are the same in each the irreducible representations

- the sum of the squares of each row must be = 8

- the point product of any two rows must be = 0 $\Leftarrow$ ORTHOGONAL!!

… ok let's play with that

C_{4v}	[E]	[C_4	C^3_4]	[C_2]	[σ_v	σ'_v]	[σ_d	σ'_d]
Γ_1	[1]	[1	1]	[1]	[1	1]	[1	1]
Γ_2	[1]	[1	1]	[1]	[-1	-1]	[-1	-1]
Γ_3	[1]	[-1	-1]	[1]	[-1	-1]	[1	1]
Γ_4	[1]	[-1	-1]	[1]	[1	1]	[-1	-1]
Γ_5	[2]	[	]	[ ]	[	]	[	]

… because of theorem # 2 we can actually simplify this a little:

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
Γ_1	1	1	1	1	1
Γ_2	1	1	1	-1	-1
Γ_3	1	-1	1	-1	1
Γ_4	1	-1	1	1	-1
Γ_5	2	a	b	c	d

- Using theorem # 4 we can now write down 4 equations that uniquely determine the remaining 4 unknown characters a, b, c, d:

$\Gamma_1 * \Gamma_5 = 1 * 2 + 2 * 1 * a + 1 * b * + 2 * 1 * c + 2 * 1 * d$

$= 2 + 2a + b + 2c + 2d = 0$

$\Gamma_2 * \Gamma_5 = 2 + 2a + b - 2c - 2d = 0$

$\Gamma_3 * \Gamma_5 = 2 - 2a + b + -2c + 2d = 0$

$\Gamma_4 * \Gamma_5 = 2 - 2a + b + 2c - 2d = 0$

From this we find: a = 0, b = -2, c = 0, d = 0

- Using our definitions of Mulliken symbols, we can complete the character table by naming the reducible representations:

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
B_1	1	-1	1	-1	1
B_2	1	-1	1	1	-1
E	2	0	-2	0	0

3.4.2. Using Character tables … you will be doing this a lot!

- Again the C_{4v} character table – this time the "extended version":

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$	Basis	Basis Function
A_1	1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	-1	-1	R_z	
B_1	1	-1	1	1	-1		x^2-y^2
B_2	1	-1	1	-1	1		xy
E	2	0	-2	0	0	(x,y) (R_x,R_y)	(xz, yz)

<u>**Basis and Basis functions:**</u>

- Consider the matrix representations of all the symmetry operations in C_{4v} :

$$C_4 = \begin{bmatrix} \cos\frac{2\pi}{4} & -\sin\frac{2\pi}{4} & 0 \\ \sin\frac{2\pi}{4} & \cos\frac{2\pi}{4} & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$C_4^3 = \begin{bmatrix} \cos\frac{3\pi}{2} & -\sin\frac{3\pi}{2} & 0 \\ \sin\frac{3\pi}{2} & \cos\frac{3\pi}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$C_2 = \begin{bmatrix} \cos\pi & -\sin\pi & 0 \\ \sin\pi & \cos\pi & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\sigma_{yz} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \sigma_{xz} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\sigma_d = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \sigma'_d = \begin{bmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Conclusions:

- z never "mixes" with x or y
- x and y are "mixed" by C_4 and σ_d

→ Can separate to set of *block diagonalized* matrices:

	E	**2 C_4**	**C_2**	**σ_{xz}**	**σ_{yz}**	**σ_d**	**σ'_d**
$\Gamma_{x,y}$	$\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix}$	$\begin{bmatrix}0 & -1\\1 & 0\end{bmatrix}$	$\begin{bmatrix}-1 & 0\\0 & -1\end{bmatrix}$	$\begin{bmatrix}1 & 0\\0 & -1\end{bmatrix}$	$\begin{bmatrix}-1 & 0\\0 & 1\end{bmatrix}$	$\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}$	$\begin{bmatrix}0 & -1\\-1 & 0\end{bmatrix}$
Γ_z	[1]	[1]	[1]	[1]	[1]	[1]	[1]

The characters of the matrices of **$\Gamma_{x,y}$** and **Γ_z** are:

Γ_z: all = 1

	E	**2 C_4**	**C_2**	**σ_{xz}**	**σ_{yz}**	**σ_d**	**σ'_d**
$\Gamma_{x,y}$	2	0	-2	0	0	0	0

Comparing this result with the complete character table above, we can say:

→ **x and y form a basis for the irreducible representation E in C_{4v}**

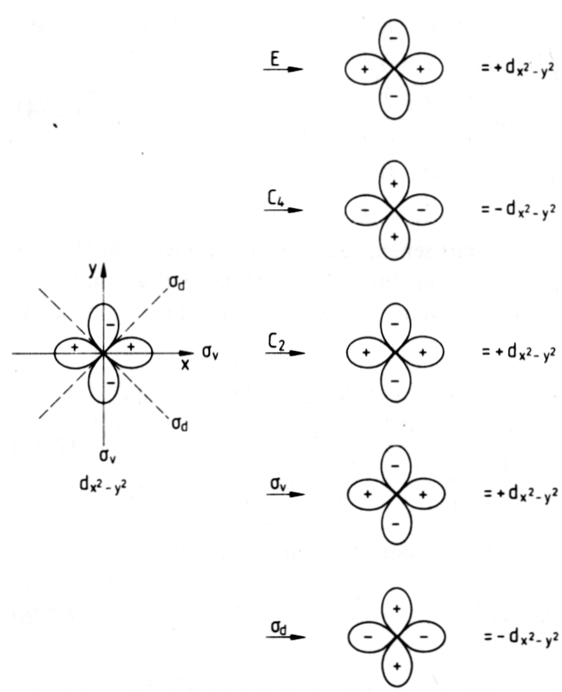
→ **z forms a basis for the irreducible representation A_1 in C_{4v}**

What can we do
with basis functions ?

Consider a d_{x2-y2} orbital:

- Any symmetry operation on C_{4v} transforms d_{x2-y2} onto itself or it's negative.

- The orbital transforms in a one-dimensional representation, i.e. with no mixing of coordinates.



The correct irreducible representation for a d_{x2-y2} under C_{4v} is thus:

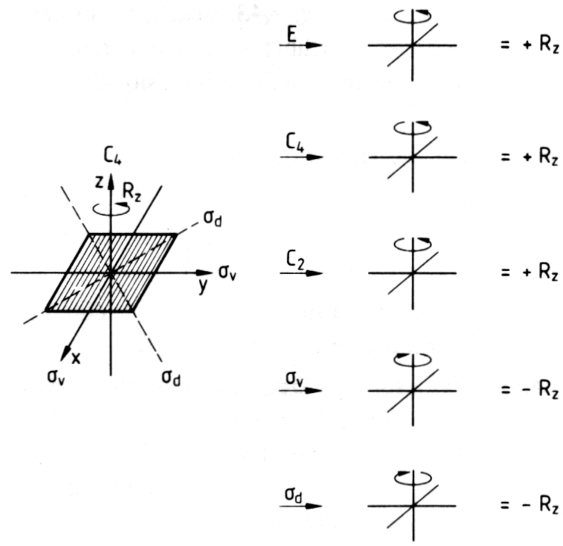
C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$	Basis	Basis Function
B_1	1	-1	1	1	-1		x^2-y^2

We say: "x^2-y^2 transforms like B_1 under C_{4v}"

Next consider a rotation about the z-axis shown here as a curved arrow:

Key: Look along the axis of rotation and determine the sense of rotation before and after the symmetry operation performed on the curved arrow.

→ Only the two σ operations have an effect leading to the following irreducible representation:



C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$	Basis	Basis Function
A_2	1	1	1	-1	-1	R_z	

"R_z transforms like A_2 under C_{4v}"

- Similarly one finds that rotations R_x and R_y mix and together form a basis for the E representation under C_{4v}.

In general the basis functions denoted by x, y, z, xz, xy, yz, x^2-y^2, and z^2 directly relate to the symmetries of the orbitals and their transformations in the point group of the molecule under consideration.

… further complications:

- Many point groups (in particular the ones with primary axis of rotation with an odd #) have imaginary characters represented either by ± i or ε and ε^*.

- for any point group with principal axis C_n: $\varepsilon = \exp(i2\pi / n)$

- Using Euler's relationship:

$$e^{i\theta} = \cos\theta + i\sin\theta$$
$$e^{i2\pi / n} = \cos(2\pi / n) + i\sin(2\pi / n)$$

- Imaginary characters always appear in pairs of conjugated complex numbers – their occurrence is a mathematical necessity.

e.g.: Point group C_3 (cf. $B(OH)_3$ from homework example):

C_3	E	C_3	C_3^2	$\epsilon = e^{2\pi i/3}$		
A	1	1	1	z, R_z	x^2+y^2, z^2	$z^3, x(x^2-3y^2), y(3x^2-y^2)$
E	$\left\{\begin{matrix}1\\1\end{matrix}\right.$	$\begin{matrix}\epsilon\\\epsilon^*\end{matrix}$	$\left.\begin{matrix}\epsilon^*\\\epsilon\end{matrix}\right\}$	$(x, y), (R_x, R_y)$	$(x^2-y^2, xy), (yz, xz)$	$(xz^2, yz^2), [xyz, z(x^2-y^2)]$
$\Gamma_{x,y,z}$	3	0	0			

Since the principle axis is C_3, ε = exp(2πi/3)

- In order to use this character table on a real physical problem, we need real numbers; they are obtained by adding the pair-wise complex conjugated numbers to give real numbers, e.g. for C_3:

$$\text{using} \quad e^{2\pi i/3} = \cos\frac{2\pi}{3} + i\sin\frac{2\pi}{3} = -\frac{1}{2} + i\frac{1}{2}\sqrt{3}$$

$$E = \begin{bmatrix} 1 & \varepsilon & \varepsilon^* \\ 1 & \varepsilon^* & \varepsilon \end{bmatrix} = \begin{bmatrix} 1 & \left(-\frac{1}{2} + i\frac{1}{2}\sqrt{3}\right) & \left(-\frac{1}{2} - i\frac{1}{2}\sqrt{3}\right) \\ 1 & \left(-\frac{1}{2} - i\frac{1}{2}\sqrt{3}\right) & \left(-\frac{1}{2} + i\frac{1}{2}\sqrt{3}\right) \end{bmatrix}$$

→ {1 + 1} {ε + ε*} {ε* + ε} = {2} {-1} {-1}

A usable form of the C_3 table is thus:

C_3	E	C_3	C^2_3
A	1	1	1
E	2	-1	-1

Meaning: x and y form a basis for the E representation

- Using the general rotation matrices developed earlier:

$$C_3 = \begin{bmatrix} \cos 2\pi/3 & -\sin 2\pi/3 \\ \sin 2\pi/3 & \cos 2\pi/3 \end{bmatrix} = \begin{bmatrix} -\frac{1}{2} & \sqrt{\frac{3}{2}} \\ -\sqrt{\frac{3}{2}} & -\frac{1}{2} \end{bmatrix}$$

$$C^2{}_3 = \begin{bmatrix} \cos 4\pi/3 & -\sin 4\pi/3 \\ \sin 4\pi/3 & \cos 4\pi/3 \end{bmatrix} = \begin{bmatrix} -\frac{1}{2} & \sqrt{\frac{3}{2}} \\ -\sqrt{\frac{3}{2}} & -\frac{1}{2} \end{bmatrix}$$

The traces of these matrices are both = -1
These are the characters shown in the usable table.

3.4.3. Deconstructing reducible representations **will become v. important**

CONCEPT: An infinite number of reducible representations is possible. Each reducible representation can be deconstructed (reduced) to a sum of a finite set of irreducible representations.

e.g.: Consider an arbitrary reducible representation Γ_{red} in C_{2v} symmetry:

C_{2v}	E	C_2	σ_v	σ'_v
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1
Γ_{red}	3	1	3	1

By inspection, we see that it is the sum of two A_1 and one B_1 irreducible representations:

2 A_1	=	2	2	2	2
B_1	=	1	-1	1	-1
Γ_{red} = 2 A_1 + B_1	=	3	1	3	1

Clearly, in more complicated case, the inspection method can be extremely difficult.

There exists a very simple formula that deconvolutes any reducible representation into its irreducible components:

$$a_i = \frac{1}{h}\sum_R \chi^R \times \chi_i^R$$

a_i = number of times that the irreducible representation Γ_i occurs in the reducible representation Γ_{red} under investigation.

h = order of the point group (= number of symmetry operations)

R = operation in the point group

χ^R = character of the operation R in Γ_{red}

χ_i^R = character of the operation R in Γ_i

… let's apply this formula to the previous example in C_{2v}:

	E	**C_2**	**σ_v**	**σ'_v**
Γ_{red}	3	1	3	1

$$a_{A_1} = \frac{1}{4}\sum_R \chi^R \times \chi_{A_1}^R = \frac{1}{4}\left(\overbrace{3}\times 1 + \overbrace{1}\times 1 + \overbrace{3}\times 1 + \overbrace{1}\times 1\right) = 2$$ i.e., need 2 x A_1

$$a_{A_2} = \frac{1}{4}\left(3\times 1 + 1\times 1 + 3\times(-1) + 1\times(-1)\right) = 0$$

$$a_{B_1} = \frac{1}{4}\left(3\times 1 + 1\times(-1) + 3\times 1 + 1\times(-1)\right) = 1$$

$$a_{B_2} = \frac{1}{4}\left(3\times 1 + 1\times(-1) + 3\times(-1) + 1\times)\right) = 0$$

→ $\Gamma_{red} = 2\,A_1 + B_1$

3.4.4. The Direct Product (… for completeness sake, important in spectroscopy)

Def.: The direct product of two (ir)reducible representations is obtained by multiplying the respective characters of the representations. The result is again an (ir)reducible representation of the same group.

e.g.:

D_3	E	2 C_3	3 C_2
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
A_1 x E	2	-1	0
A_2 x E	2	-1	0
E x E	4	1	0
A_2 x A_2	1	1	1

Literature list for further reading on symmetry (if you like…):

"Chemical Applications of Group Theory"
F. Albert Cotton, Wiley Interscience, 1990, New York.
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