Character Tables

Decomposition of reducible representations into irreducible representations

General form of Character Tables:

(a)	(b)	
(f)	(c)	(d) (e)

(a) Gives the Schonflies symbol for the point group.

(b) Lists the symmetry operations (by class) for that group.

(c) Lists the characters, for all irreducible representations for each class of operation.

(d) Shows the irreducible representation for which the six vectors T_x, T_y, T_z, and R_x, R_y, R_z, provide the basis.

(e) Shows how functions that are binary combinations of x,y,z (xy or z^2) provide bases for certain irreducible representation.(Raman d orbitals)

(f) List conventional symbols for irreducible representations: **Mulliken** symbols

Mulliken symbols: Labelling

All one dimensional irreducible representations are labelled **A** or **B.**

All two dimensional irreducible representations are labelled **E.**

(Not to be confused with Identity element)

All three dimensional representations are labelled **T.**

For ***linear*** point groups one dimensional representations are given the symbol Σ with two and three dimensional representations being Π and Δ.

Mulliken symbols: Labelling

1)

A one dimensional irreducible representation is labelled **A** if it is symmetric with respect to rotation about the highest order axis C_n.

(Symmetric means that $\chi = +1$ for the operation.)
If it is anti-symmetric with respect to the operation $\chi = -1$ and it is labelled **B**.

2)

A subscript **1** is given if the irreducible representation is symmetric with respect to rotation about a C_2 axis perpendicular to C_n or (in the absence of such an axis) to reflection in a σ_v plane. An anti-symmetric representation is given the subscript **2**.

For linear point groups symmetry with respect to s is indicated by a superscript
+ (symmetric) or **–** (anti-symmetric)

Mulliken symbols: Labelling

3)

Subscripts **g** (gerade) and **u** (ungerade) are given to irreducible representations That are symmetric and anti-symmetric respectively, with respect to inversion at a centre of symmetry.

4)

Superscripts **‘** and **“** are given to irreducible representations that are symmetric and anti-symmetric respectively with respect o reflection in a σ_h plane.

Note: Points 1) and 2) apply to one-dimensional representations only.
Points 3) and 4) apply equally to one-, two-, and three- dimensional representations.

Character Table (C_{2v})

Point Group Label

Symmetry Operations – The *Order* is the total number of operations

In C_{2v} the order is 4:
1 E, 1 C_2, 1 σ_v and 1 σ'_v

C_{2v}	E	C_2	σ_v (xz)	σ'_v (yz)
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

Character

Representation of B_2

Symmetry Representation Labels

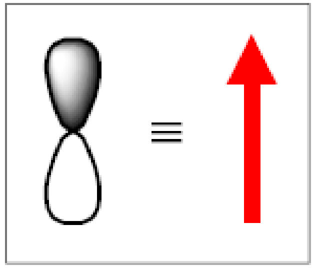
"A" means symmetric with regard to rotation about the principle axis.
"B" means anti-symmetric with regard to rotation about the principle axis.
Subscript numbers are used to differentiate symmetry labels, if necessary.
"1" indicates that the operation leaves the function unchanged: it is called "symmetric".
"-1" indicates that the operation reverses the function: it is called "anti-symmetric".

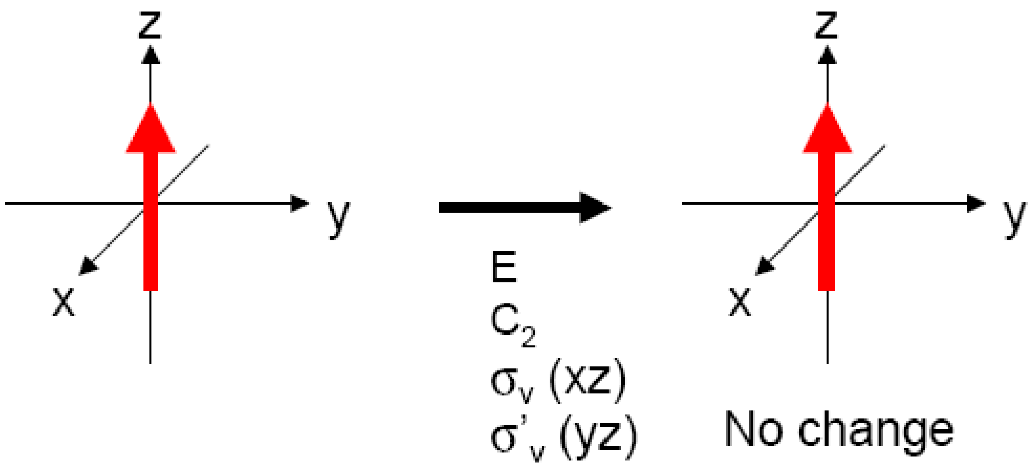
Character Table (C_{2v})

C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)	Symmetry of Functions	
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 functions to the right are called *basis functions*. They represent mathematical functions such as orbitals, rotations, etc.

A p_z orbital has the same symmetry as an arrow pointing along the z-axis.





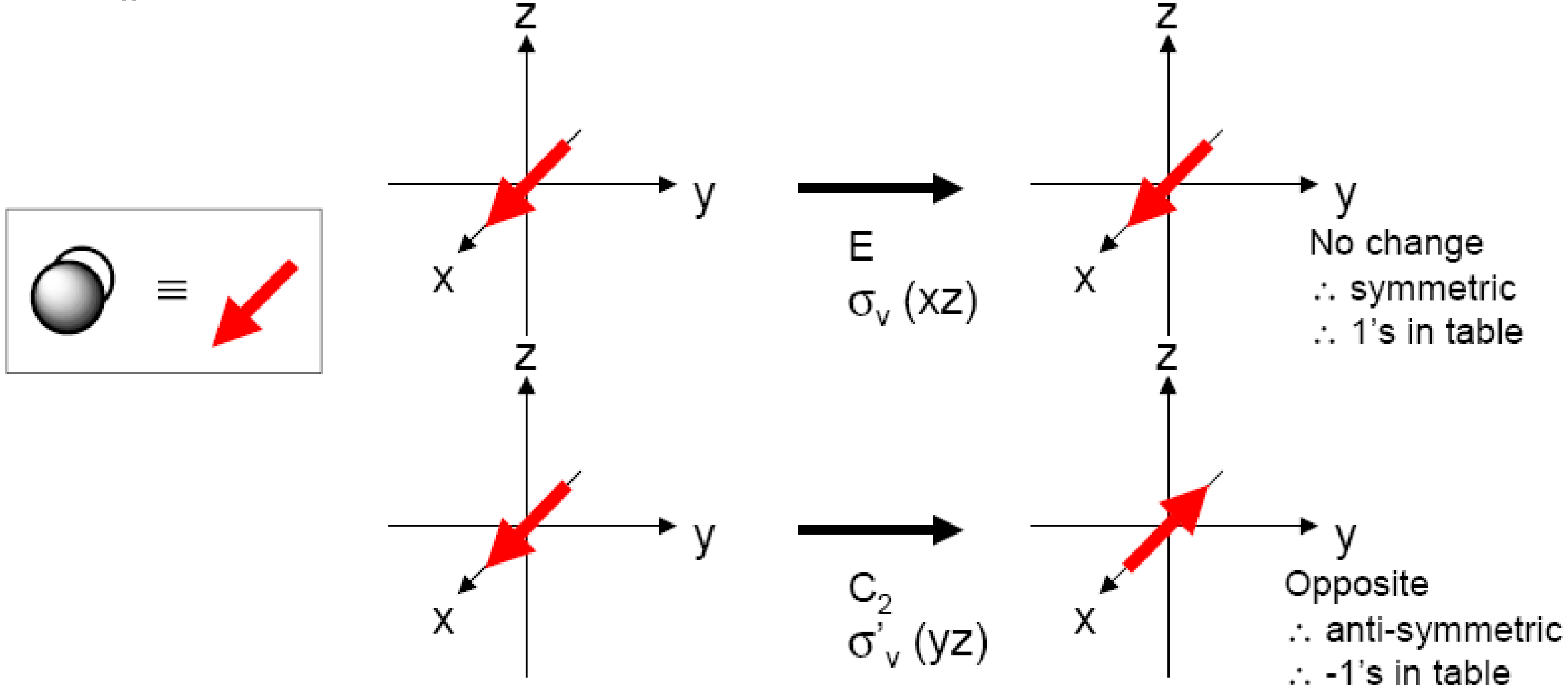
No change

∴ symmetric

∴ 1's in table

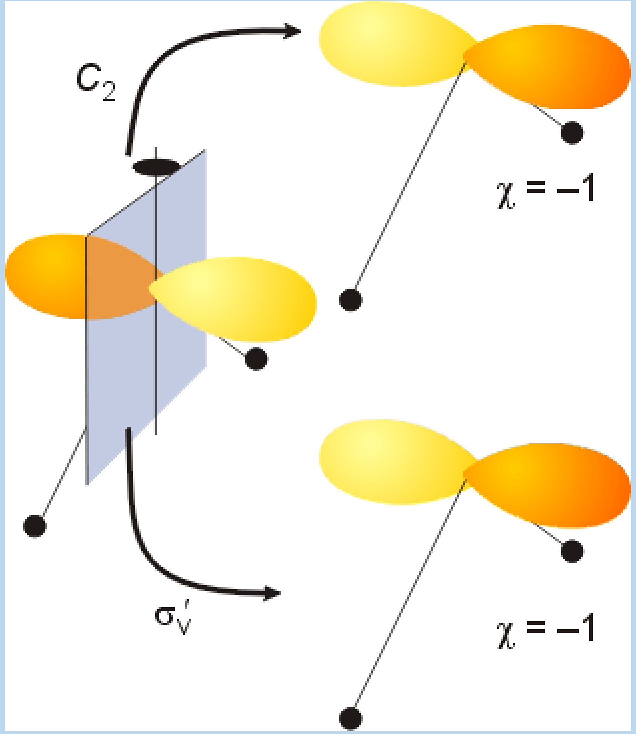
C_{2v}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2,y^2,z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

A p_x orbital has the same symmetry as an arrow pointing along the x-axis.



C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
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 p_x orbital



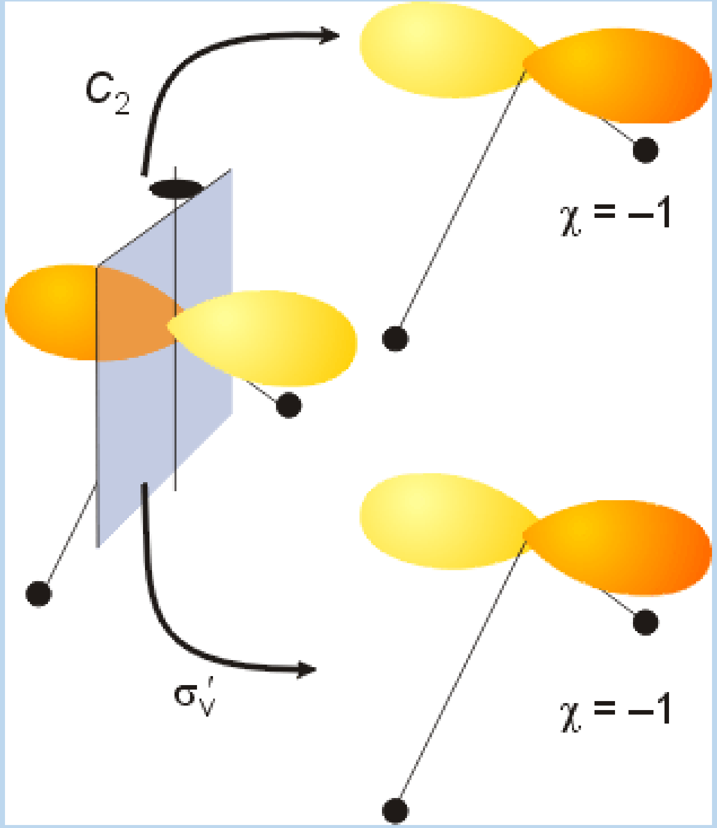
If a p_x orbital on the central atom of a molecule with C_{2v} symmetry is rotated about the C_2 axis, the orbital is reversed, so the character will be -1.

The p_x orbital

If a p_x orbital on the central atom of a molecule with C_{2v} symmetry is rotated about the C_2 axis, the orbital is reversed, so the character will be -1.

C_{2v}	E	C_2	σ_v (xz)	σ'_v (yz)		
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 p_x orbital



If a p_x orbital on the central atom of a molecule with C_{2v} symmetry is reflected in the yz plane, the orbital is also reversed, and the character will be -1.

The p_x orbital

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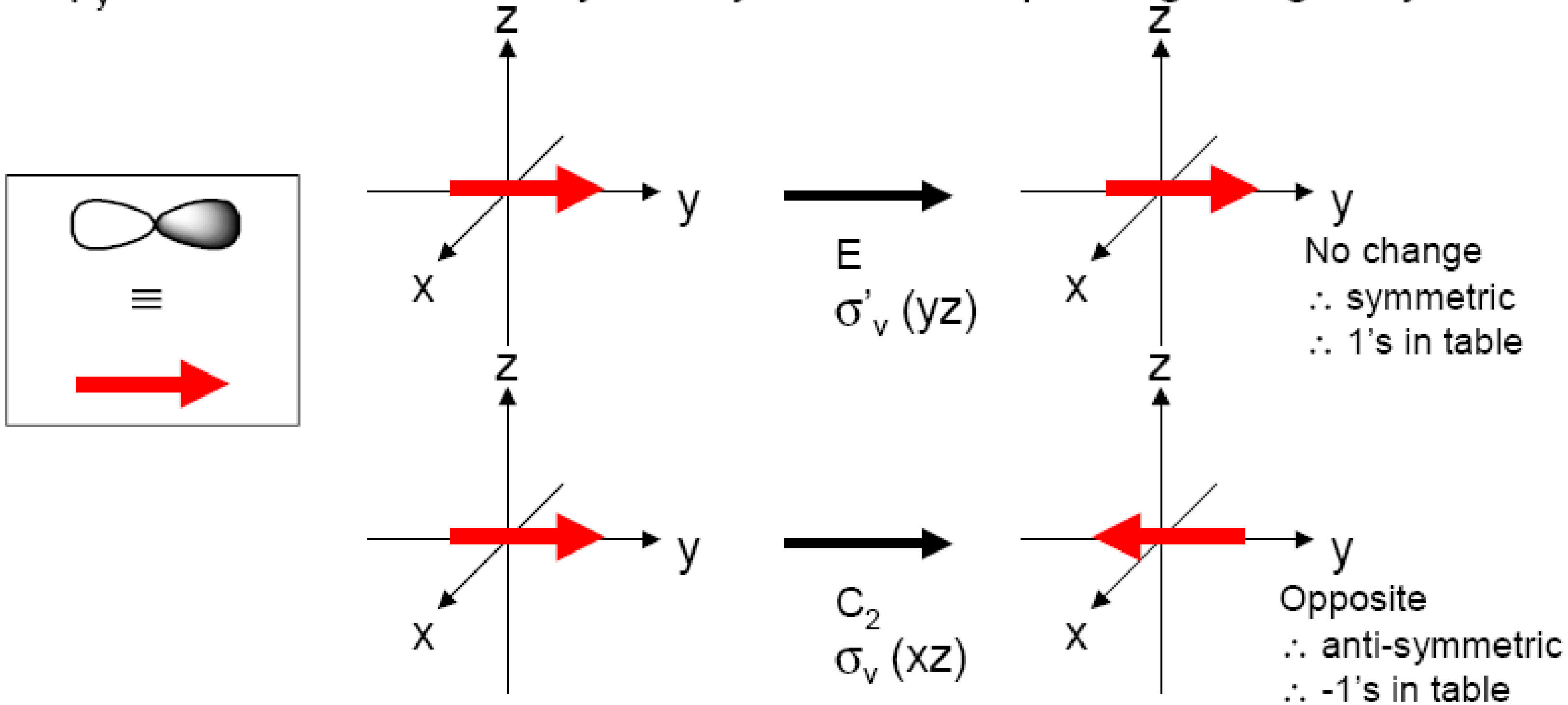
C_{2v}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

The p_x orbital

If a p_x orbital on the central atom of a molecule with C_{2v} symmetry is reflected in the xz plane, the orbital is unchanged, so the character is +1.

C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
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

A p_y orbital has the same symmetry as an arrow pointing along the y-axis.



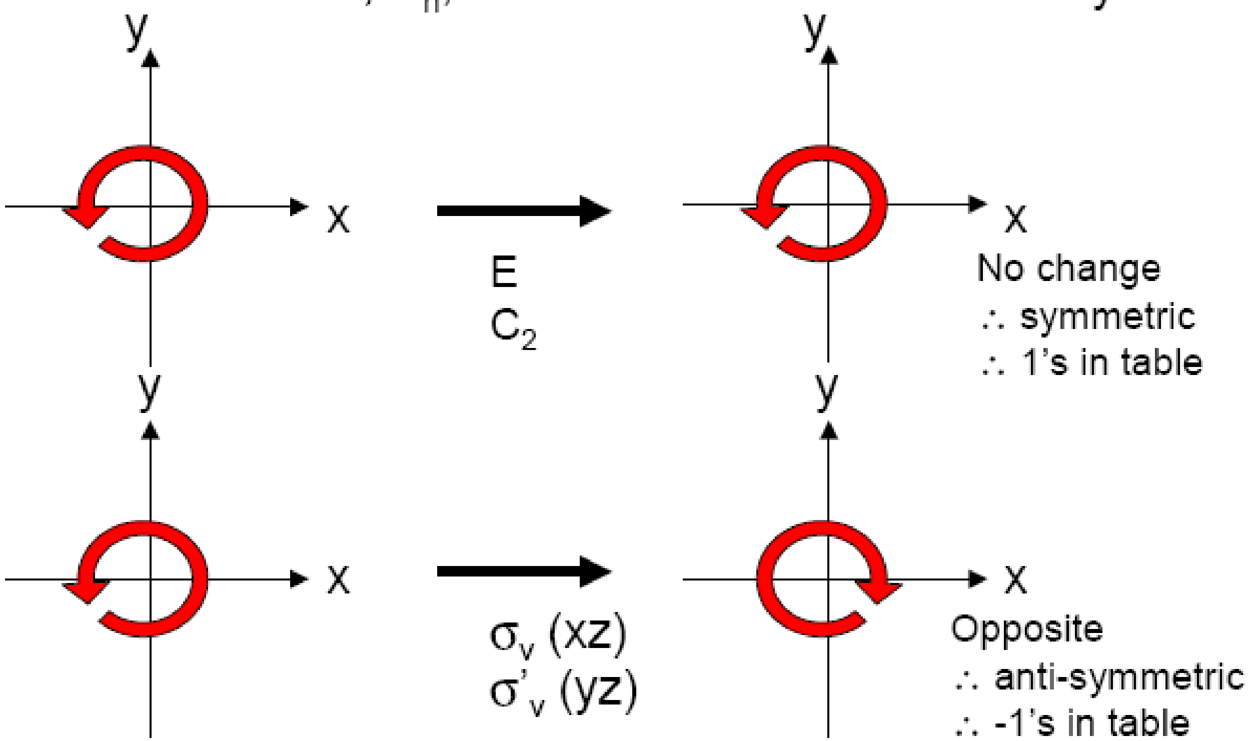
C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2,y^2,z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Rotation about the n axis, R_n, can be treated in a similar way.

The z axis is pointing out of the screen!

If the rotation is still in the same direction (e.g. counter clock-wise), then the result is considered symmetric.

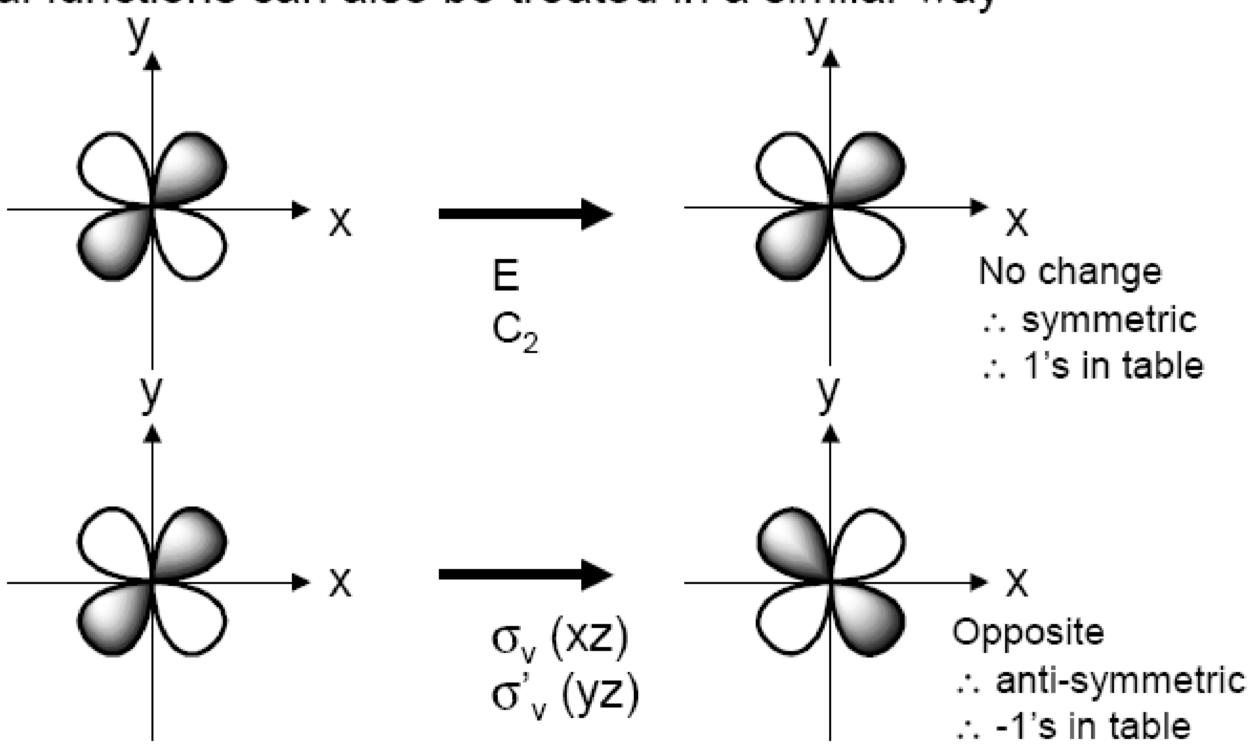
If the rotation is in the opposite direction (i.e. clock-wise), then the result is considered anti-symmetric.



C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
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

d orbital functions can also be treated in a similar way

The **z** axis is pointing out of the screen!



C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
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

Character Table Representations

1. Characters of +1 indicate that the basis function is unchanged by the symmetry operation.
2. Characters of -1 indicate that the basis function is reversed by the symmetry operation.
3. Characters of 0 indicate that the basis function undergoes a more complicated change.

Character Table Representations

1. An *A* representation indicates that the functions are symmetric with respect to rotation about the principal axis of rotation.
2. *B* representations are asymmetric with respect to rotation about the principal axis.
3. *E* representations are doubly degenerate.
4. *T* representations are triply degenerate.
5. Subscrips *u* and *g* indicate asymmetric (*ungerade*) or symmetric (*gerade*) with respect to a center of inversion.

Symmetry of orbitals and functions

O_h	E	8 C_3	6 C_2	6 C_4	3 C_2 (C_4^2)	*i*	6 S_4	8 S_6	3 σ_h	6 σ_d		
A_{1g}	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		
E_g	2	-1	0	0	2	2	0	-1	2	0		($2z^2 - x^2 - y^2$, $x^2 - y^2$)
T_{1g}	**3**	**0**	**-1**	**1**	**-1**	**3**	**1**	**0**	**-1**	**-1**	**(R_x, R_y, R_z)**	
T_{2g}	**3**	**0**	**1**	**-1**	**-1**	**3**	**-1**	**0**	**-1**	**1**		**(xz, yz, xy)**
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-2	0	1	-2	0		
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		

More notes about symmetry labels and characters:

-"T" indicates that the representation is triply-degenerate – this means that the functions grouped in parentheses must be treated as a threesome and can not be considered individually.

-The subscripts g (gerade) and u (ungerade) in the symmetry representation label indicates "symmetric" or "anti-symmetric" with respect to the inversion center, *i*.

Conversion of Reducible Representations into Irreducible Representations

Generating Reducible Representations

Summarising we get that Γ_{3n} for this molecule is:

C_{2v}	E	C_2	$\sigma_{(xz)}$	$\sigma_{(yz)}$
Γ_{3n}	+9	-1	+1	3

To reduce this we need the character table for the point groups

C_{2v}	E	C_2	$\sigma_{(xz)}$	$\sigma_{(yz)}$		
A_1	+1	+1	+1	+1	T_z	x^2, y^2, z^2
A_2	+1	+1	-1	-1	R_z	xy
B_1	+1	-1	+1	-1	T_x , R_x	xz
B_2	+1	-1	-1	+1	T_y , R_y	yz

Reducing Reducible Representations

We need to use the reduction formula:

$$a_p = \left(\frac{1}{g}\right)\sum_R n_R . \chi(R) . \chi_p(R)$$

Where a_p is the number of times the irreducible representation, p, occurs in any reducible representation.

g is the number of symmetry operations in the group

$\chi(R)$ is character of the **reducible** representation

$\chi_p(R)$ is character of the **irreducible** representation

n_R is the number of operations in the class

C_{2v}	1E	$1C_2$	$1\sigma_{(xz)}$	$1\sigma_{(yz)}$		
A_1	+1	+1	+1	+1	T_z	x^2, y^2, z^2
A_2	+1	+1	-1	-1	R_z	xy
B_1	+1	-1	+1	-1	T_x , R_x	xz
B_2	+1	-1	-1	+1	T_y , R_y	yz

For C_{2v} ; g = 4 and n_R = 1 for all operations

C_{2v}	E	C_2	$\sigma_{(xz)}$	$\sigma_{(yz)}$
Γ_{3n}	+9	-1	+1	3

$$a_p = \left(\frac{1}{g}\right)\sum_R n_R.\chi(R).\chi_p(R)$$

a_{A_1} = (1/4)[(1x9x1) + (1x-1x1) + (1x1x1) + (1x3x1)] = (12/4) =3

$$a_p = \left(\frac{1}{g}\right)\sum_R n_R.\chi(R).\chi_p(R)$$

C_{2v}	E	C_2	$\sigma_{(xz)}$	$\sigma_{(yz)}$
Γ_{3n}	+9	-1	+1	3

a_{A_1} = (1/4)[(1x9x1) + (1x-1x1) + (1x1x1) + (1x3x1)] = (12/4) =3

a_{A_2} = (1/4)[(1x9x1) + (1x-1x1) + (1x1x-1) + (1x3x-1)] = (4/4) =1

a_{B_1} = (1/4)[(1x9x1) + (1x-1x-1) + (1x1x1) + (1x3x-1)] = (8/4) =2

a_{B_2} = (1/4)[(1x9x1) + (1x-1x-1) + (1x1x-1) + (1x3x1)] = (12/4) =3

$$\Gamma_{3n} = 3A_1 + A_2 + 2B_1 + 3B_2$$