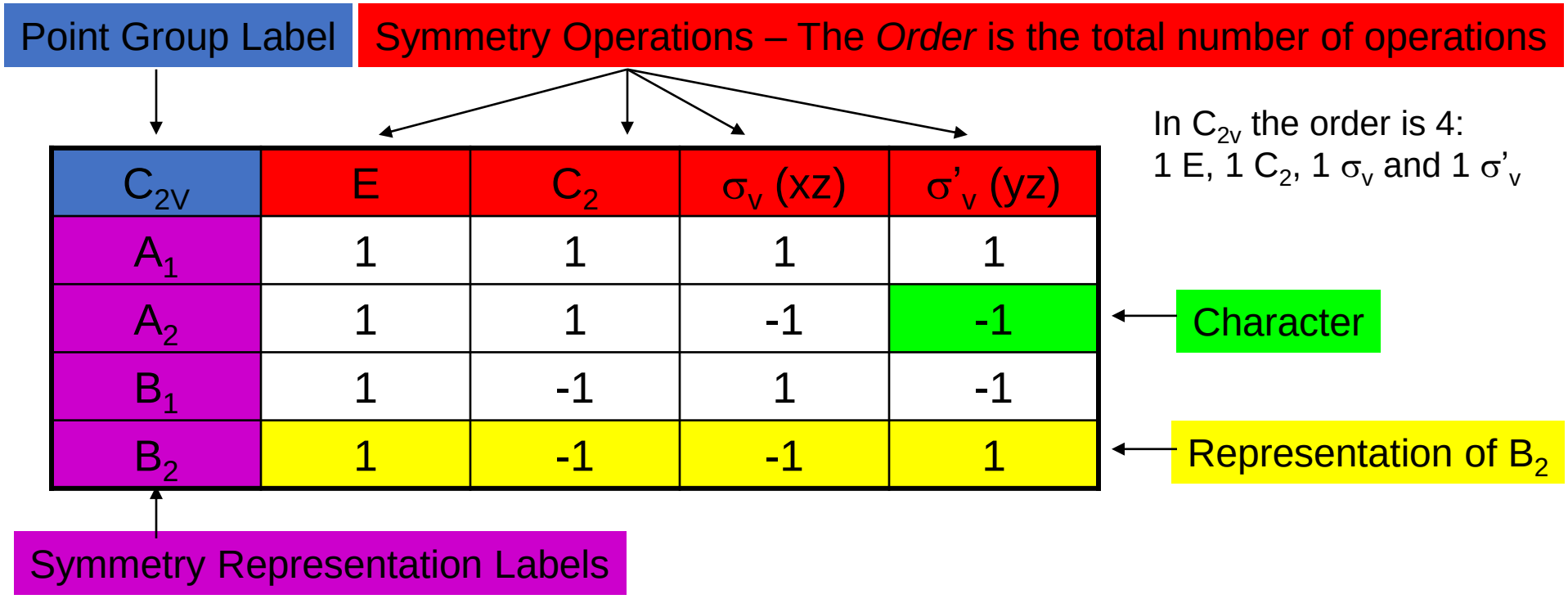
Character Tables for Point Groups

Each point group has a complete set of possible symmetry operations that are conveniently listed as a matrix known as a *Character Table*. As an example, we will look at the character table for the C_{2v} point group.



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

Representations are subsets of the complete point group – they indicate the effect of the symmetry operations on different kinds of mathematical functions. Representations are orthogonal to one another. The *Character* is an integer that indicates the effect of an operation in a given representation..

Symmetry of Orbitals and Functions

The effect of symmetry elements on mathematical functions is useful to us because orbitals are mathematical functions! Analysis of the symmetry of a molecule will provide us with insight into the orbitals used in bonding.

Symmetry of Functions

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

Notes about symmetry labels and characters:

- "A" means symmetric with regard to rotation about the principal axis.
- "B" means anti-symmetric with regard to rotation about the principal 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".

Symmetry of Orbitals and Functions

1. Choose basis function (three Cartesian coordinates or a specific bond)
2. Apply operations

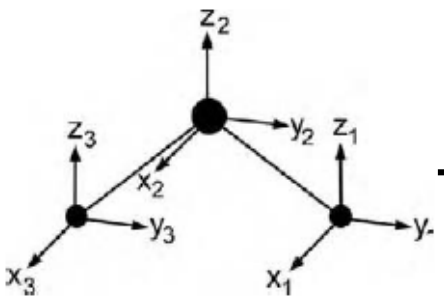
    -if the basis stays the same = +1

    -if the basis is reversed = -1

    -if it is a more complicated change = 0

Example: H_2O

1. Assign a point group
2. Choose basis function
3. Apply operations
   - -if the basis stays the same = +1
   - -if the basis is reversed = -1
   - -if it is a more complicated change = 0

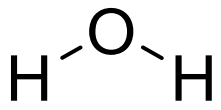


E

Atom 1: $x_1 = 1$, $y_1 = 1$, $z_1 = 1$

Atom 2: $x_2 = 1$, $y_2 = 1$, $z_2 = 1$

Atom 3: $x_3 = 1$, $y_3 = 1$, $z_3 = 1$



C_{2v} point group

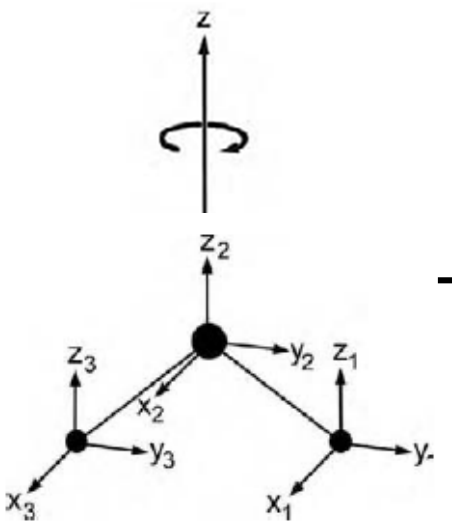
Basis: x_{1-3}, y_{1-3} and z_{1-3}

Atom:	1	2	3
E	3	3	3

$3 + 3 + 3 = 9$

Example: H_2O

1. Assign a point group
2. Choose basis function
3. Apply operations
   - -if the basis stays the same = +1
   - -if the basis is reversed = -1
   - -if it is a more complicated change = 0

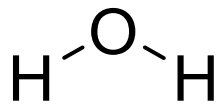


C_2 →

Atom 1: $x_1 = 0$, $y_1 = 0$, $z_1 = 0$

Atom 2: $x_2 = -1$, $y_2 = -1$, $z_2 = 1$

Atom 3: $x_3 = 0$, $y_3 = 0$, $z_3 = 0$



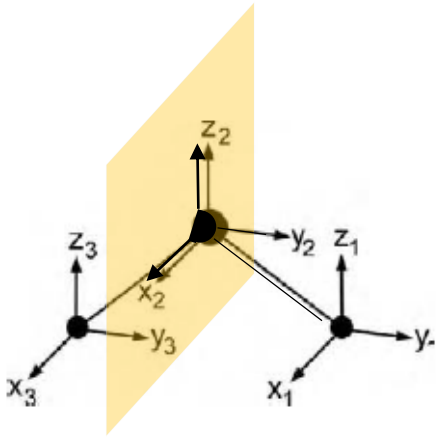
C_{2v} point group

Basis: x_{1-3}, y_{1-3} and z_{1-3}

Atom:	1	2	3	
E	3 +	3 +	3	= 9
C_2	0 +	-1 +	0	= -1

Example: H_2O

1. Assign a point group
2. Choose basis function
3. Apply operations
   - -if the basis stays the same = +1
   - -if the basis is reversed = -1
   - -if it is a more complicated change = 0

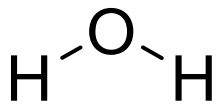


σ_{xz} →

Atom 1: $x_1 = 0$, $y_1 = 0$, $z_1 = 0$

Atom 2: $x_2 = 1$, $y_2 = -1$, $z_2 = 1$

Atom 3: $x_3 = 0$, $y_3 = 0$, $z_3 = 0$



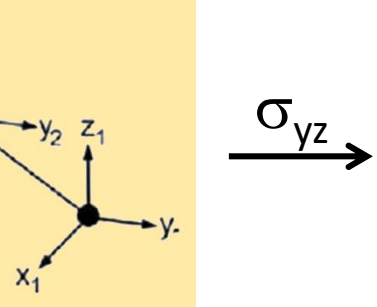
C_{2v} point group

Basis: x_{1-3}, y_{1-3} and z_{1-3}

Atom:	1	2	3	
E	3 +	3 +	3	= 9
C_2	0 +	-1 +	0	= -1
σ_{xz}	0 +	1 +	0	= 1

Example: H_2O

1. Assign a point group
2. Choose basis function
3. Apply operations
   - -if the basis stays the same = +1
   - -if the basis is reversed = -1
   - -if it is a more complicated change = 0



C_{2v} point group
Basis: x_{1-3}, y_{1-3} and z_{1-3}

σ_{yz} →

Atom 1: $x_1 = -1$, $y_1 = 1$, $z_1 = 1$

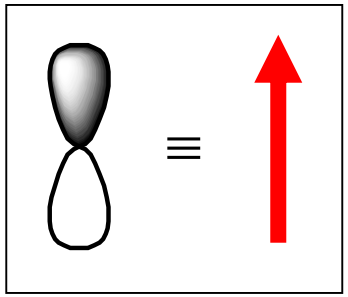
Atom 2: $x_2 = -1$, $y_2 = 1$, $z_2 = 1$

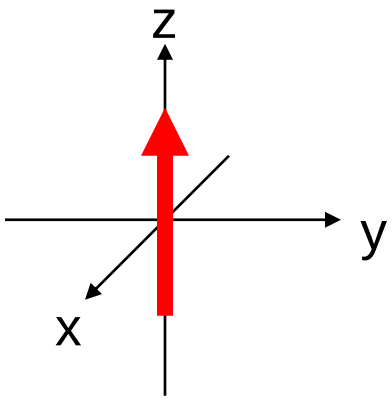
Atom 3: $x_3 = -1$, $y_3 = 1$, $z_3 = 1$

Atom:	1	2	3	
E	3	+ 3 +	3	= 9
C_2	0	+ -1 +	0	= -1
σ_{xz}	0	+ 1 +	0	= 1
σ_{yz}	1	+ 1 +	1	= 3

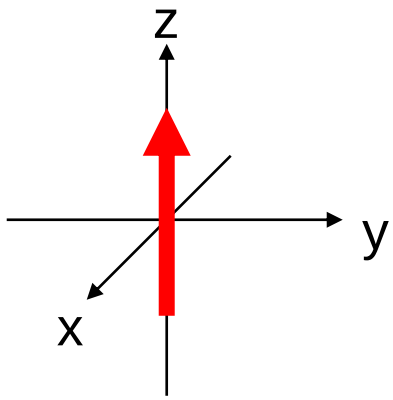
Symmetry of Orbitals and Functions

A $\mathbf{p_z}$ orbital has the same symmetry as an arrow pointing along the z-axis.





E
C_2
σ_v (xz)
σ'_v (yz)

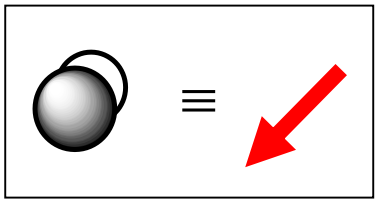


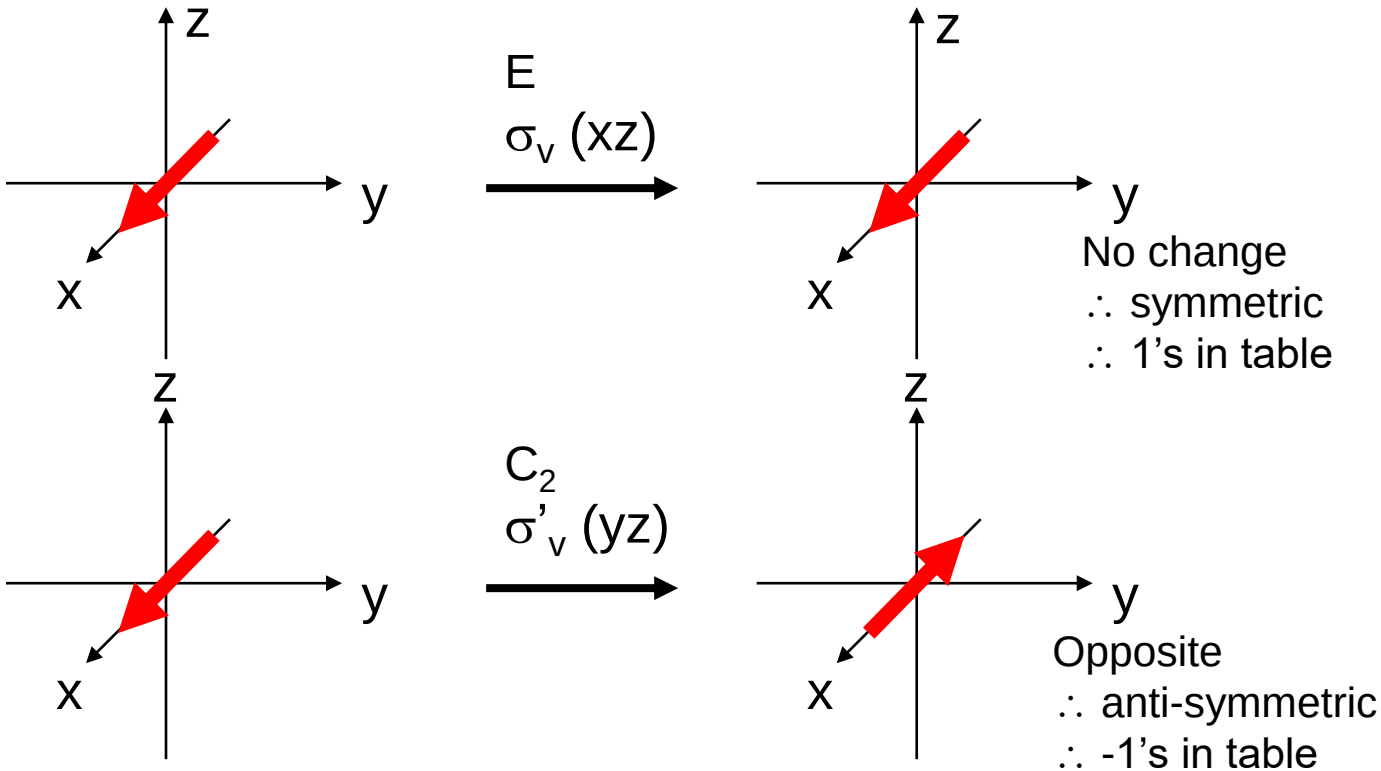
No change
$\therefore$ symmetric
$\therefore$ 1's in table

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

Symmetry of Orbitals and Functions

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

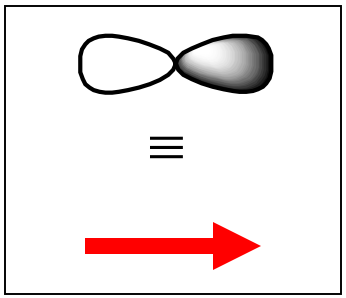




C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2,y^2,z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Symmetry of Orbitals and Functions

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



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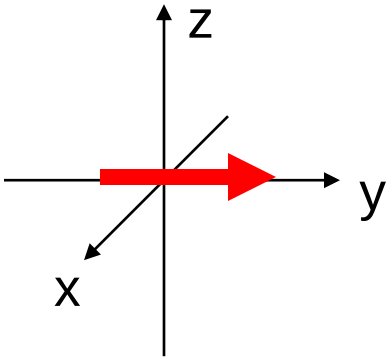
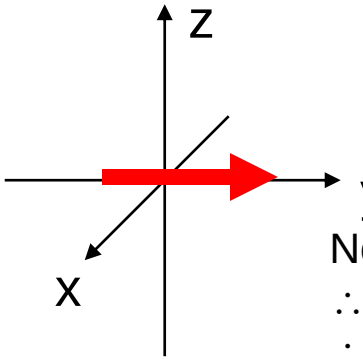
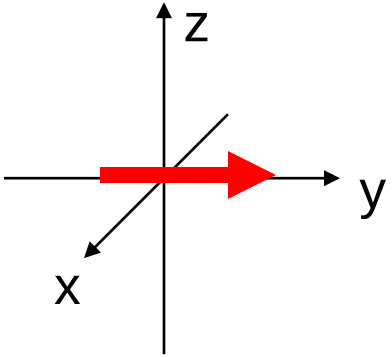


E

σ'_v (yz)

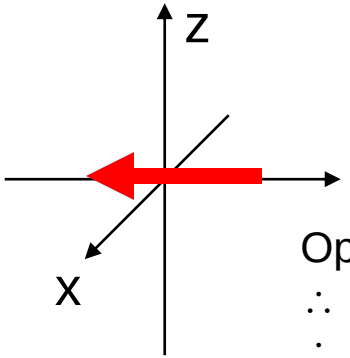


No change
∴ symmetric
∴ 1's in table



C_2

σ_v (xz)



Opposite
∴ anti-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

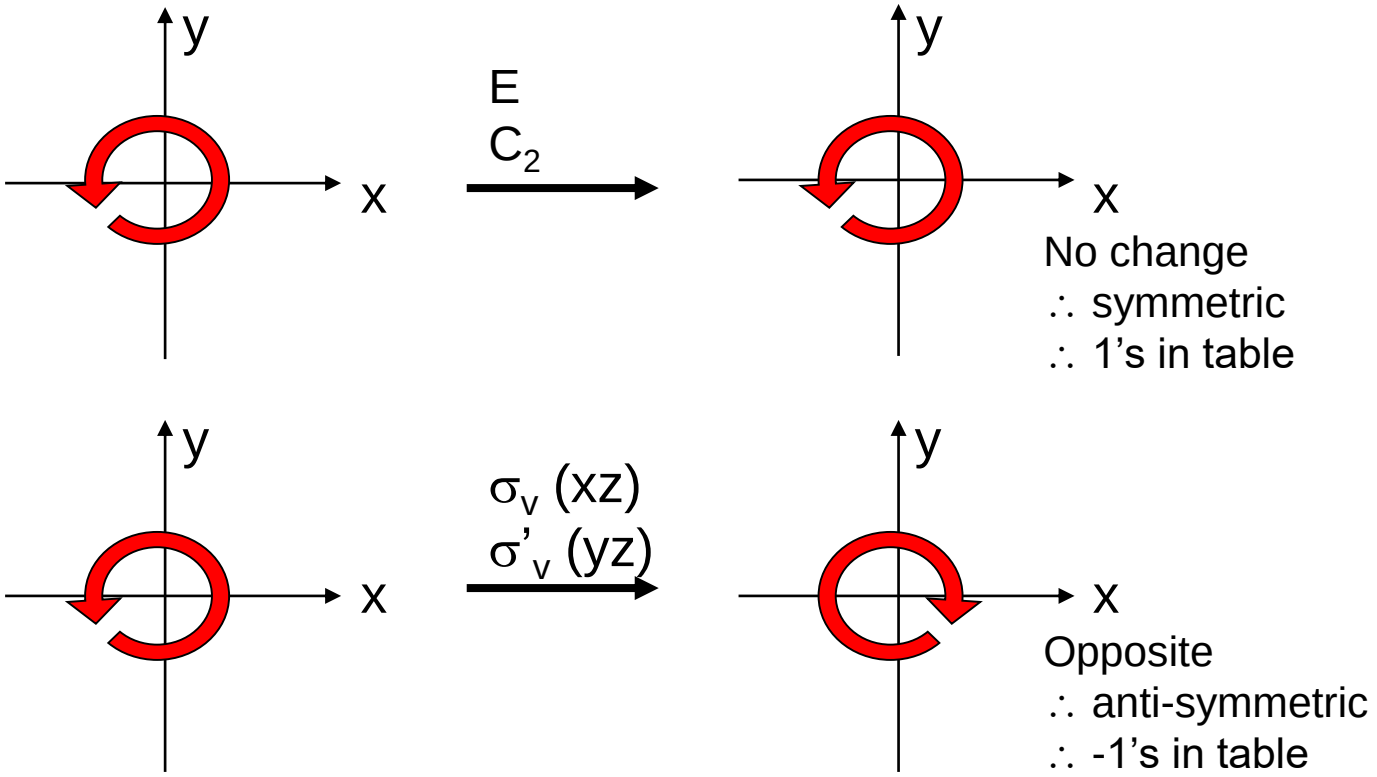
Symmetry of Orbitals and Functions

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.

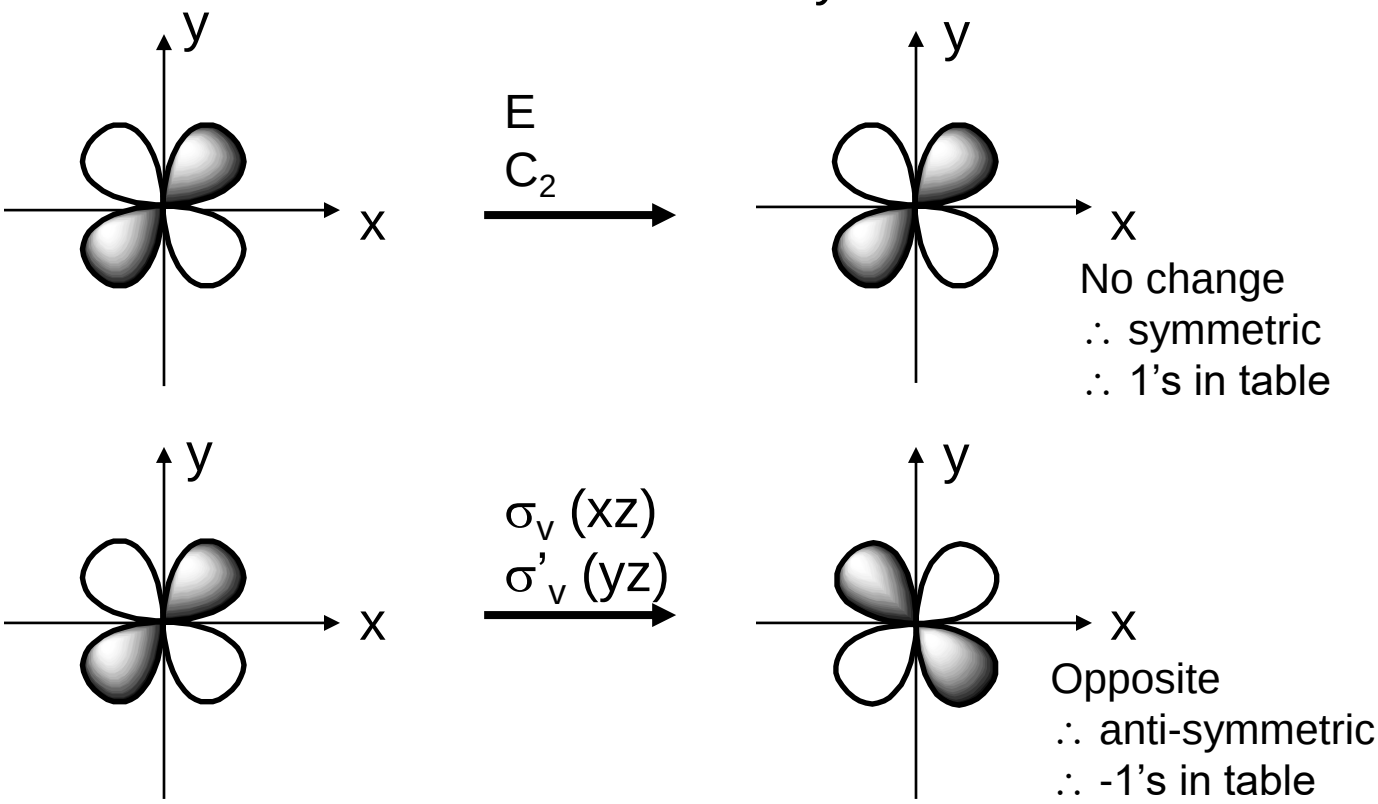


C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2,y^2,z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Symmetry of Orbitals and Functions

d orbital functions can also be treated in a similar way

The z axis is pointing out of the screen!

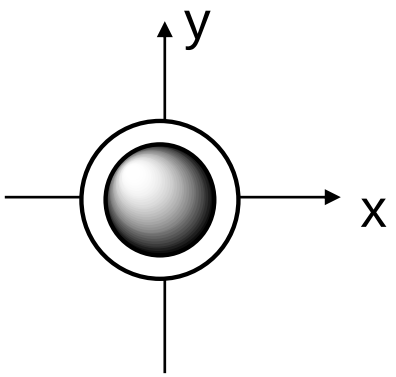


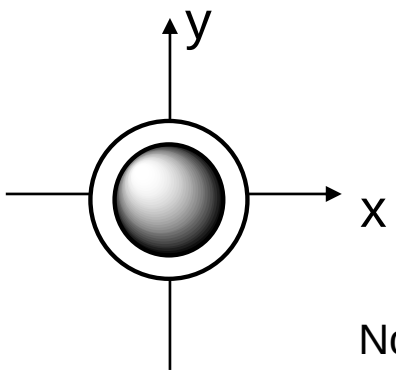
C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

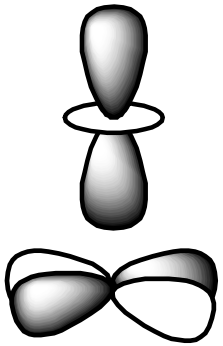
Symmetry of Orbitals and Functions

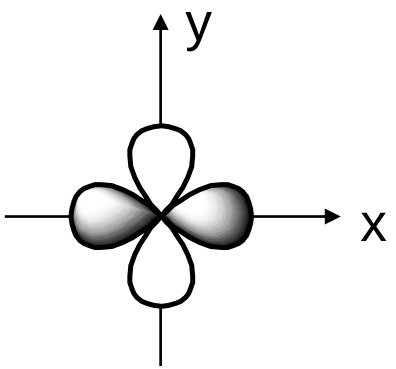
d orbital functions can also be treated in a similar way

The z axis is pointing out of the screen!
So these are representations of the view of the d_{z^2} orbital and $d_{x^2-y^2}$ orbital down the z-axis.

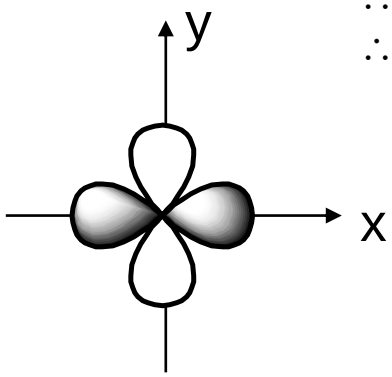








E
C_2
σ_v (xz)
σ'_v (yz)



No change
$\therefore$ symmetric
$\therefore$ 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

Symmetry of Orbitals and Functions

Note that the representation of orbital functions changes depending on the point group – thus it is important to be able to identify the point group correctly.

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_{3h}	E	2 C_3	3 C_2	σ_h	2 S_3	3 σ_v		
A'_1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A'_2	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x,y)	$(x^2 - y^2, xy)$
A''_1	1	1	1	-1	-1	-1		
A''_2	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)

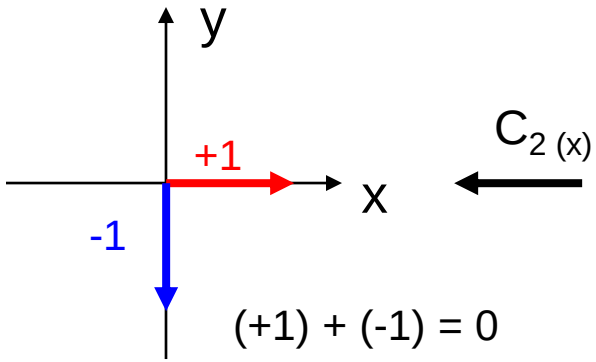
Symmetry of Orbitals and Functions

D_{3h}	E	2 C_3	3 C_2	σ_h	2 S_3	3 σ_v		
A'_1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A'_2	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x,y)	$(x^2 - y^2, xy)$
A''_1	1	1	1	-1	-1	-1		
A''_2	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)

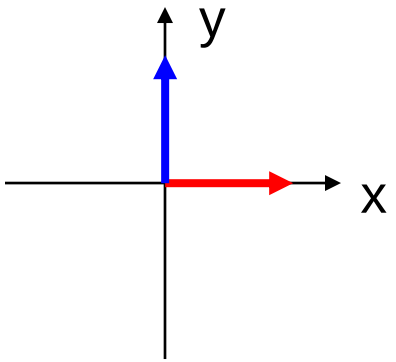
More notes about symmetry labels and characters:

- "E" indicates that the representation is doubly-degenerate – this means that the functions grouped in parentheses **must be treated as a pair** and can not be considered individually.
- The prime (') and (") double prime in the symmetry representation label indicates "symmetric" or "anti-symmetric" with respect to the σ_h.

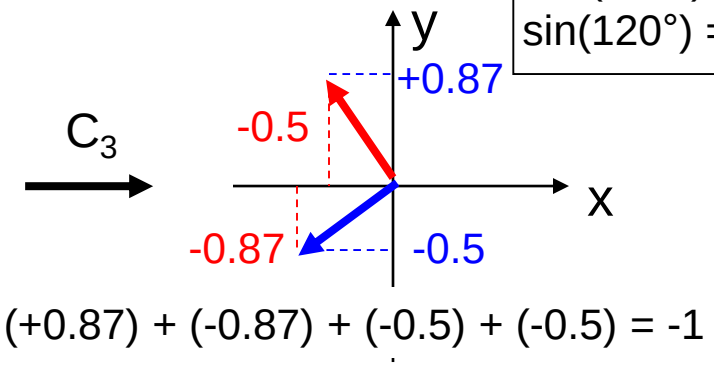
cos(120°) = -0.5
sin(120°) = 0.87



$C_{2\,(x)}$



C_3



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***.

Character Tables and Bonding

We can use character tables to determine the orbitals involved in bonding in a molecule. This process is done a few easy steps.

1. Determine the point group of the molecule.

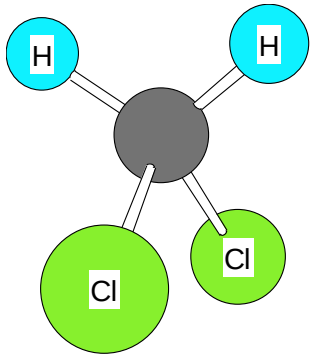
2. Determine the ***Reducible Representation*****, Γ,** for the type of bonding you wish to describe (e.g. σ, π, $\pi_{\perp}$, $\pi_{//}$). The Reducible Representation indicates how the bonds are affected by the symmetry elements present in the point group.

3. Identify the *Irreducible Representation* that provides the Reducible Representation; there is a simple equation to do this. The **Irreducible Representation (e.g. $2A_1 + B_1 + B_2$)** is the combination of symmetry representations in the point group that sum to give the Reducible Representation.

4. Identify which orbitals are involved from the Irreducible Representation and the character table.

Character Tables and Bonding

Example, the σ bonding in **dichloromethane**, CH_2Cl_2.



- The point group is C_{2v} so we must use the appropriate character table for the reducible representation of the sigma bonding, Γ_σ. To determine Γ_σ , all we have to do is see how each symmetry operation affects the 4 σ bonds in the molecule – if the bond moves, it is given a value of 0, if it stays in the same place, the bond is given a value of 1. **Put the sum of the 1's and 0's into the box corresponding to the symmetry operation.**

- The E operation leaves everything where it is, so all four bonds stay in the same place and the character is 4 (1+1+1+1).
- The C_2 operation moves all four bonds so the character is 0.
- Each σ_v operation leaves two bonds where they were and moves two bonds, so the character is 2 (1+1).
- Overall, the reducible representation is thus:

C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)
Γ_σ	4	0	2	2

Character Tables and Bonding

We now have to figure out what combination of symmetry representations will add up to give us this reducible representation. In this case, it can be done by inspection, but there is a simple equation that is useful for more complicated situations.

C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)
Γ_σ	4	0	2	2

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

Because the character under E is 4, there must be a total of 4 symmetry representations (sometimes called *basis functions*) that combine to make Γ_σ. Since the character under C_2 is 0, there must be two of A symmetry and two of B symmetry. The irreducible representation is ($2A_1 + B_1 + B_2$), which corresponds to: s, p_z, p_x, and p_y orbitals – the same as in VBT. You can often use your understanding of VBT to help you in finding the correct basis functions for the irreducible representation.

Character Tables and Bonding

C_{2V}	E	C_2	σ_v (xz)	σ'_v (yz)
Γ_σ	4	0	2	2

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 formula to figure out the **number of symmetry representations** of a given type is:

$$n_X = \frac{1}{\text{order}} \sum \left[(\#\text{ of operations in class}) \times (\text{character of RR}) \times (\text{character of X}) \right]$$

Thus, in our example:

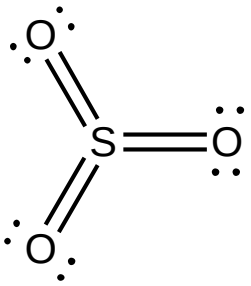
$$n_{A_1} = \frac{1}{4}\left[(1)(4)(1) + (1)(0)(1) + (1)(2)(1) + (1)(2)(1)\right] \qquad n_{B_1} = \frac{1}{4}\left[(1)(4)(1) + (1)(0)(-1) + (1)(2)(1) + (1)(2)(-1)\right]$$

$$n_{A_2} = \frac{1}{4}\left[(1)(4)(1) + (1)(0)(1) + (1)(2)(-1) + (1)(2)(-1)\right] \qquad n_{B_2} = \frac{1}{4}\left[(1)(4)(1) + (1)(0)(-1) + (1)(2)(-1) + (1)(2)(1)\right]$$

Which gives: 2 A_1's, 0 A_2's, 1 B_1 and 1 B_2.

Character Tables and Bonding

Example, the σ and π bonding in SO_3.



- The point group is D_{3h} so we must use the appropriate character table to find the reducible representation of the sigma bonding, Γ_σ first, then we can go the representation of the π bonding, Γ_π. To determine Γ_σ all we have to do is see how each symmetry operation affects the 3 σ bonds in the molecule.
- The E and the σ_h operations leave everything where it is, so all three bonds stay in the same place and the character is 3 (1+1+1).
- The C_3 and S_3 operations move all three bonds so their characters are 0.
- The C_2 operation moves two of the bonds and leaves one where it was so the character is 1.
- Each σ_v operation leaves one bond where it was and moves two bonds, so the character is 1.
- Overall, the reducible representation for the sigma bonding is:

D_{3h}	E	2 C_3	3 C_2	σ_h	2 S_3	3 σ_v
Γ_σ	3	0	1	3	0	1

D_{3h}	E	$2\,C_3$	$3\,C_2$	σ_h	$2\,S_3$	$3\,\sigma_v$
Γ_σ	3	0	1	3	0	1

D_{3h}	E	$2\,C_3$	$3\,C_2$	σ_h	$2\,S_3$	$3\,\sigma_v$		
A'_1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A'_2	1	1	-1	1	1	-1	R_z	
E’	2	-1	0	2	-1	0	(x,y)	$(x^2 - y^2, xy)$
A''_1	1	1	1	-1	-1	-1		
A''_2	1	1	-1	-1	-1	1	z	
E’’	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)

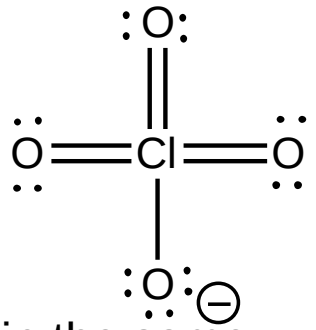
$$n_{A'_1} = \frac{1}{12}\left[(1)(3)(1) + (2)(0)(1) + (3)(1)(1) + (1)(3)(1) + (2)(0)(1) + (3)(1)(1)\right] \qquad n_{A'_1} = \frac{12}{12} = 1$$

$$n_{A'_2} = \frac{1}{12}\left[(1)(3)(1) + (2)(0)(1) + (3)(1)(-1) + (1)(3)(1) + (2)(0)(1) + (3)(1)(-1)\right] \qquad n_{A'_2} = \frac{0}{12} = 0$$

$$n_{E'} = \frac{1}{12}\left[(1)(3)(2) + (2)(0)(-1) + (3)(1)(0) + (1)(3)(2) + (2)(0)(-1) + (3)(1)(0)\right] \qquad n_{E'} = \frac{12}{12} = 1$$

We can stop here because the combination (A'_1 + E’) produces the Γ_σ that we determined. None of the other representations can contribute to the σ bonding (i.e. $n_{A''1}$, $n_{A''1}$ and $n_{E''}$ are all 0). The irreducible representation (A'_1 + E’) shows us that the orbitals involved in bonding are the s and the p_x and p_y pair; this corresponds to the sp^2 combination we find in VBT.

Character Tables and Bonding



- Example, the σ bonding in ClO_4^-.
- The point group is T_d so we must use the appropriate character table to find the reducible representation of the sigma bonding, Γ_σ first.
- The E operation leaves everything where it is, so all four bonds stay in the same place and the character is 4.
- Each C_3 operation moves three bonds leaves one where it was so the character is 1.
- The C_2 and S_4 operations move all four bonds so their characters are 0.
- Each σ_d operation leaves two bonds where they were and moves two bonds, so the character is 2.

T_d	E	8 C_3	3 C_2	6 S_4	6 σ_d
Γ_σ	4	1	0	0	2

T_d	E	8 C_3	3 C_2	6 S_4	6 σ_d
Γ_σ	4	1	0	0	2

T_d	E	8 C_3	3 C_2	6 S_4	6 σ_d		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

- The irreducible representation for the σ bonding is $(A_1 + T_2)$, which corresponds to the s orbital and the (p_x, p_y, p_z) set that we would use in VBT to construct a the sp^3 hybrid orbitals suitable for a tetrahedral arrangement of atoms. To get the representation for the π bonding
- we must do the same procedure that we did for SO_3, except that in the point group T_d, one can not separate the representations into parallel and perpendicular components. This is because the three-fold symmetry of the bond axis requires the orthogonal. vectors to be treated as an inseparable pair.