

# 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.

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

| $C_{2v}$ | E | $C_2$ | $\sigma_v(xz)$ | $\sigma'_v(yz)$ |
|----------|---|-------|----------------|-----------------|
| $A_1$    | 1 | 1     | 1              | 1               |
| $A_2$    | 1 | 1     | -1             | -1              |
| $B_1$    | 1 | -1    | 1              | -1              |
| $B_2$    | 1 | -1    | -1             | 1               |

In  $C_{2v}$  the order is 4:  
1 E, 1  $C_2$ , 1  $\sigma_v$  and 1  $\sigma'_v$

← Character

← Representation of  $B_2$

↑ Symmetry Representation Labels

*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 | $C_2$ | $\sigma_v (xz)$ | $\sigma'_v (yz)$ |          |                 |
|----------|---|-------|-----------------|------------------|----------|-----------------|
| $A_1$    | 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”.

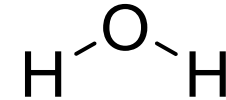
# Symmetry of Orbitals and Functions

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

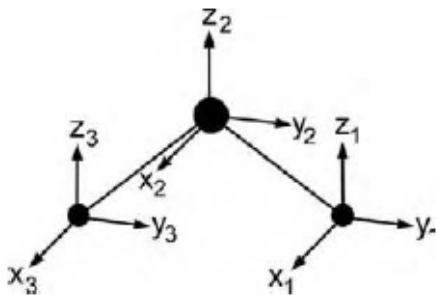
# Example: H<sub>2</sub>O

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<sub>2v</sub> point group  
Basis: x<sub>1-3</sub>, y<sub>1-3</sub> and z<sub>1-3</sub>



Atom 1: x<sub>1</sub> = 1  
y<sub>1</sub> = 1  
z<sub>1</sub> = 1

Atom 2: x<sub>2</sub> = 1  
y<sub>2</sub> = 1  
z<sub>2</sub> = 1

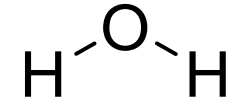
Atom 3: x<sub>3</sub> = 1  
y<sub>3</sub> = 1  
z<sub>3</sub> = 1

|       |   |   |   |     |
|-------|---|---|---|-----|
| Atom: | 1 | 2 | 3 |     |
| E     | 3 | + | 3 | +   |
|       | 3 | + | 3 | = 9 |

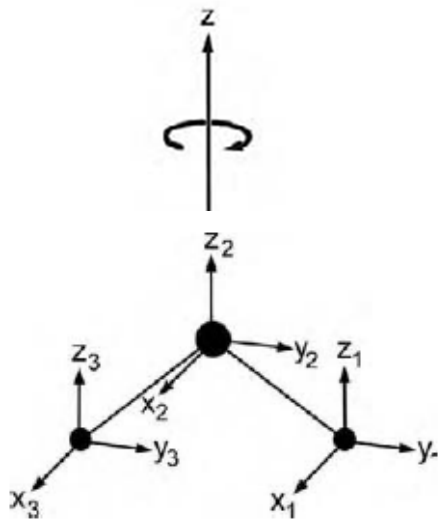
# Example: H<sub>2</sub>O

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<sub>2v</sub> point group  
Basis: x<sub>1-3</sub>, y<sub>1-3</sub> and z<sub>1-3</sub>



$C_2$

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

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

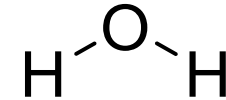
Atom 3:  $x_3 = 0$   
 $y_3 = 0$   
 $z_3 = 0$

| Atom:          | 1 | 2    | 3   |      |
|----------------|---|------|-----|------|
| E              | 3 | + 3  | + 3 | = 9  |
| C <sub>2</sub> | 0 | + -1 | + 0 | = -1 |

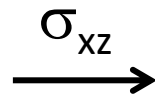
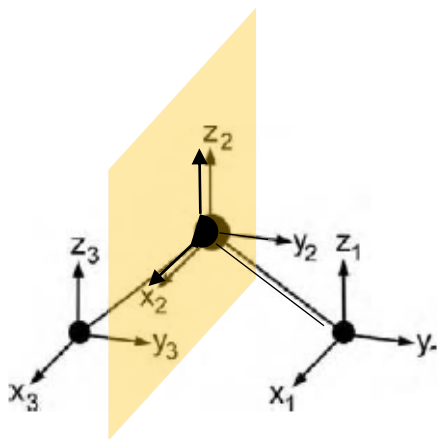
# Example: H<sub>2</sub>O

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<sub>2v</sub> point group  
Basis: x<sub>1-3</sub>, y<sub>1-3</sub> and z<sub>1-3</sub>



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

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

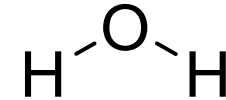
Atom 3:  $x_3 = 0$   
 $y_3 = 0$   
 $z_3 = 0$

| Atom:           | 1 | 2    | 3   |      |
|-----------------|---|------|-----|------|
| E               | 3 | + 3  | + 3 | = 9  |
| C <sub>2</sub>  | 0 | + -1 | + 0 | = -1 |
| σ <sub>xz</sub> | 0 | + 1  | + 0 | = 1  |

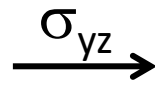
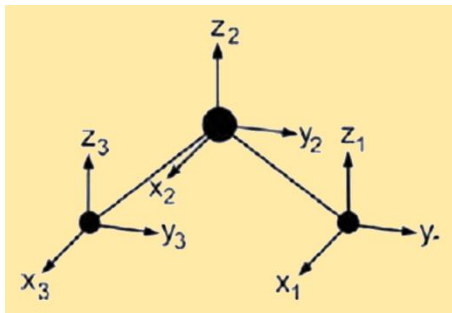
# Example: H<sub>2</sub>O

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<sub>2v</sub> point group  
Basis: x<sub>1-3</sub>, y<sub>1-3</sub> and z<sub>1-3</sub>



Atom 1: x<sub>1</sub> = 1  
y<sub>1</sub> = 1  
z<sub>1</sub> = 1

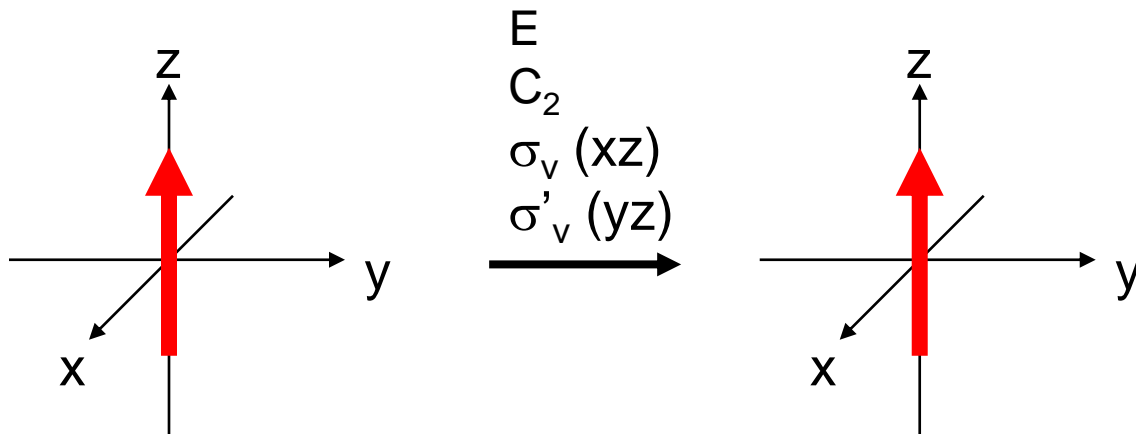
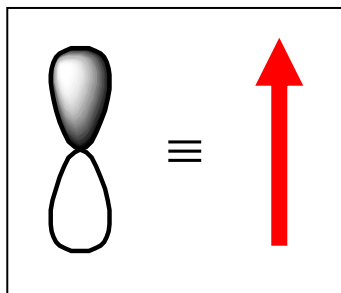
Atom 2: x<sub>2</sub> = 1  
y<sub>2</sub> = 1  
z<sub>2</sub> = 1

Atom 3: x<sub>3</sub> = 1  
y<sub>3</sub> = 1  
z<sub>3</sub> = 1

| Atom:           | 1 | 2    | 3   |      |
|-----------------|---|------|-----|------|
| E               | 3 | + 3  | + 3 | = 9  |
| C <sub>2</sub>  | 0 | + -1 | + 0 | = -1 |
| σ <sub>xz</sub> | 0 | + 1  | + 0 | = 1  |
| σ <sub>yz</sub> | 1 | + 1  | + 1 | = 3  |

# Symmetry of Orbitals and Functions

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



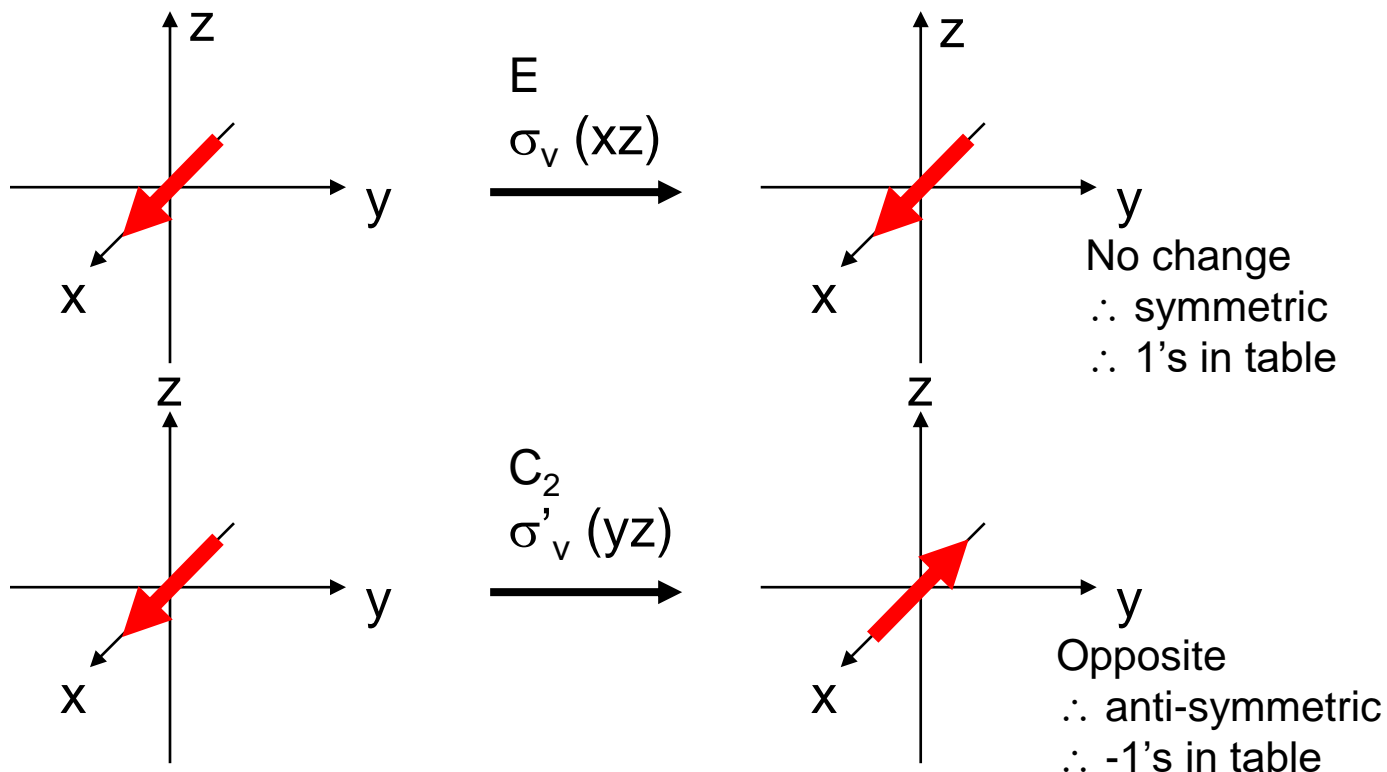
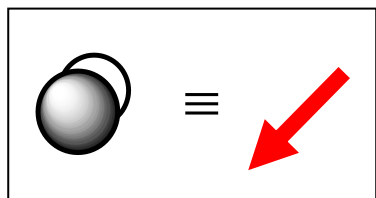
No change  
 $\therefore$  symmetric  
 $\therefore$  1's in table

| $C_{2V}$ | E | $C_2$ | $\sigma_v(xz)$ | $\sigma'_v(yz)$ |          |                 |
|----------|---|-------|----------------|-----------------|----------|-----------------|
| $A_1$    | 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

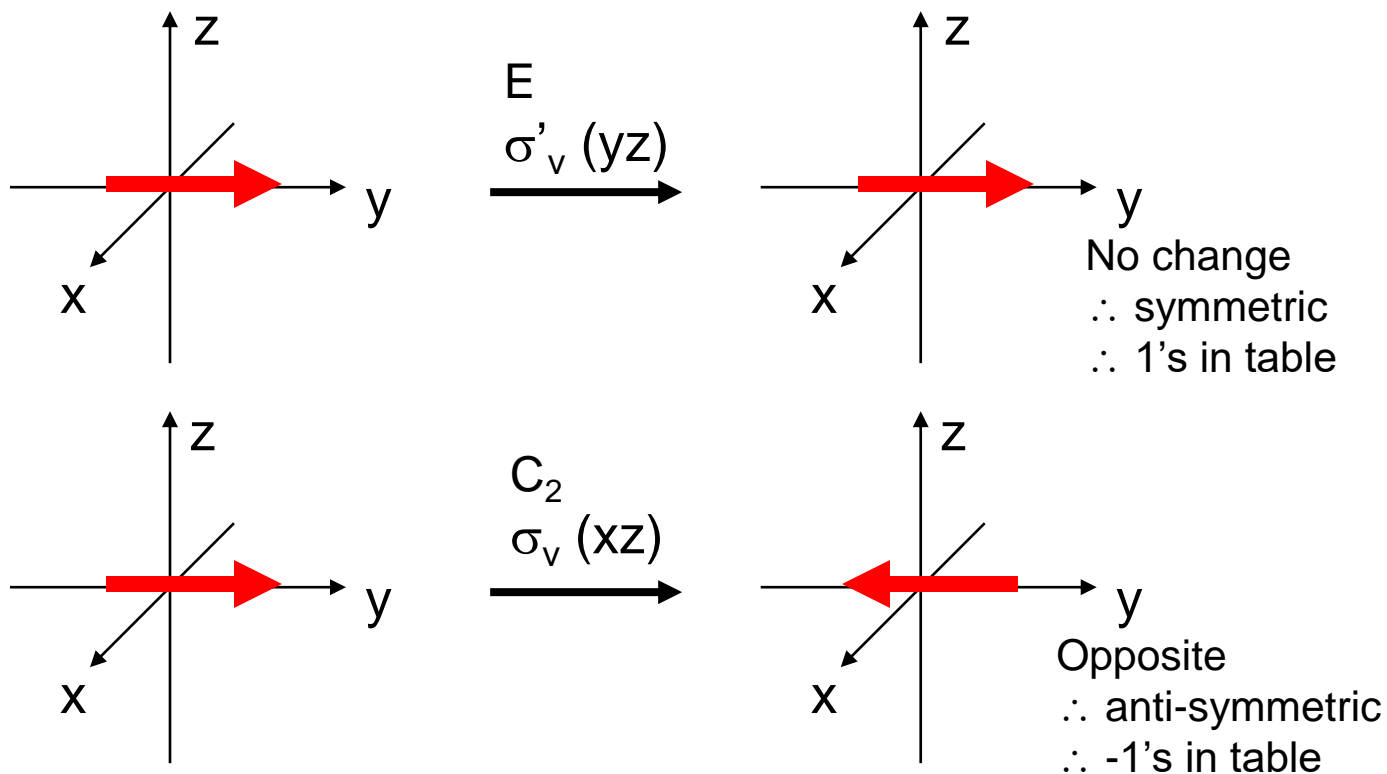
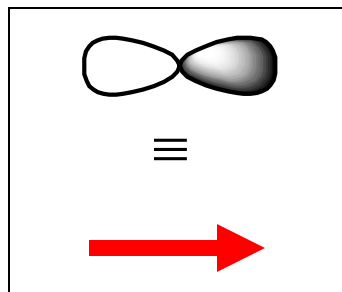
A  $p_x$  orbital has the same symmetry as an arrow pointing along the x-axis.



| $C_{2v}$ | $E$ | $C_2$ | $\sigma_v(xz)$ | $\sigma'_v(yz)$ |          |                 |
|----------|-----|-------|----------------|-----------------|----------|-----------------|
| $A_1$    | 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.



| $C_{2v}$ | $E$ | $C_2$ | $\sigma_v (xz)$ | $\sigma'_v (yz)$ |          |                 |
|----------|-----|-------|-----------------|------------------|----------|-----------------|
| $A_1$    | 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                | $y, R_x$ | $yz$            |

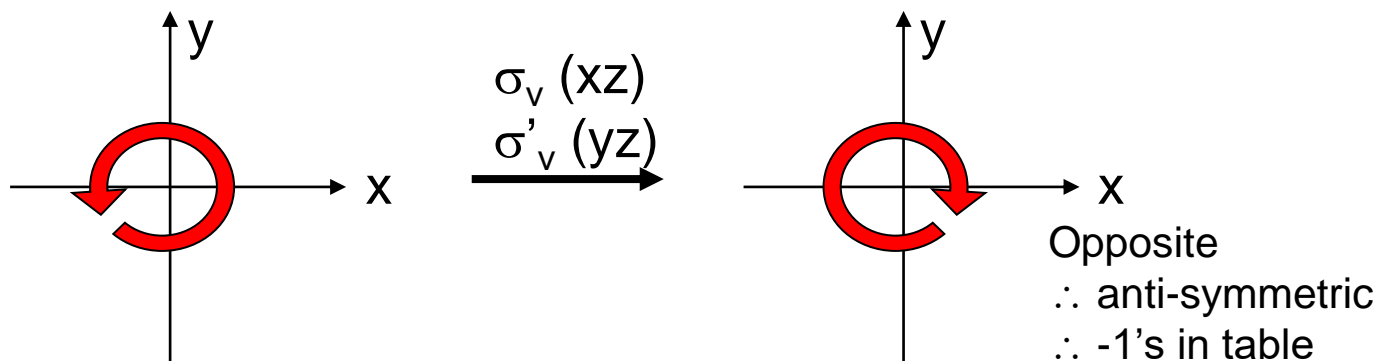
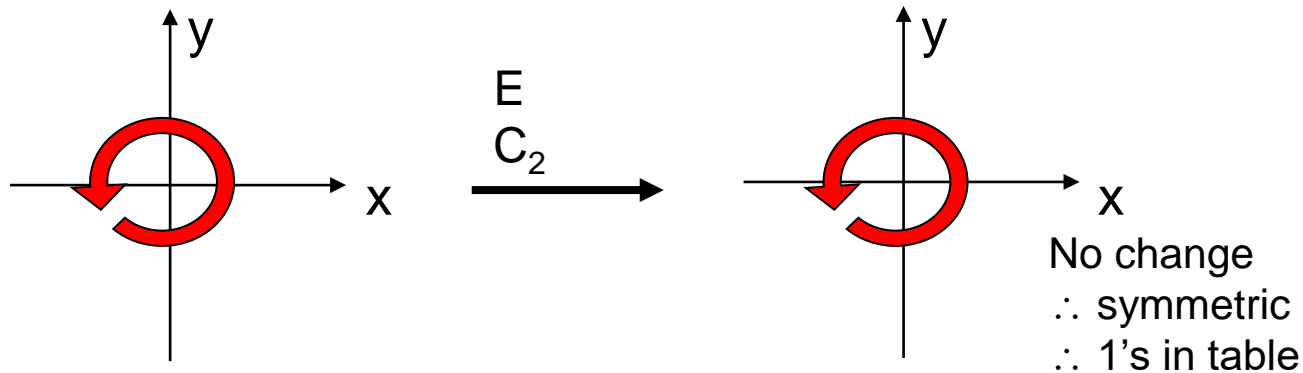
# Symmetry of Orbitals and Functions

Rotation about the  $z$  axis,  $R_z$ , 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.

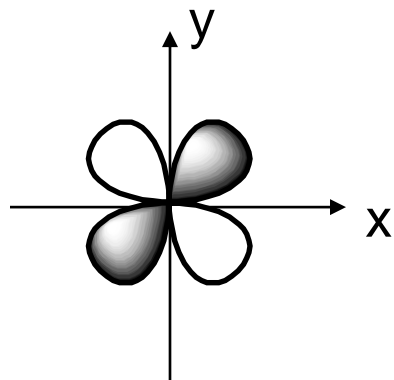


| $C_{2v}$ | $E$ | $C_2$ | $\sigma_v(xz)$ | $\sigma'_v(yz)$ |          |                 |
|----------|-----|-------|----------------|-----------------|----------|-----------------|
| $A_1$    | 1   | 1     | 1              | 1               | $z$      | $x^2, y^2, z^2$ |
| $A_2$    | 1   | 1     | -1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

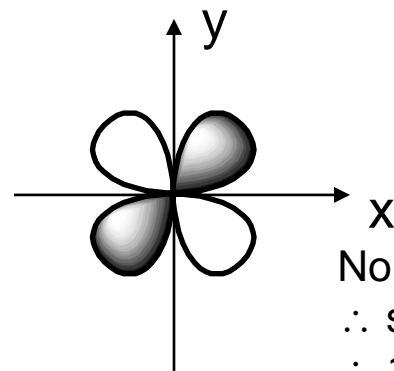
# Symmetry of Orbitals and Functions

d orbital functions can also be treated in a similar way

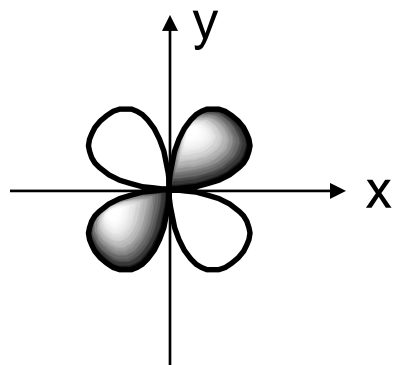
The z axis is pointing out of the screen!



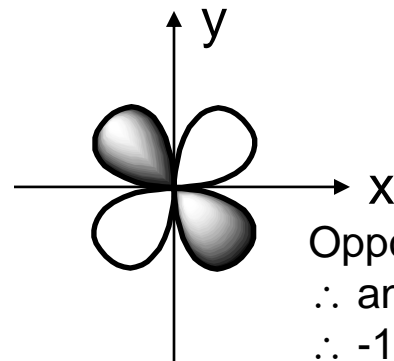
$E$   
 $C_2$



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



$\sigma_v(xz)$   
 $\sigma'_v(yz)$



Opposite  
 $\therefore$  anti-symmetric  
 $\therefore$  -1's in table

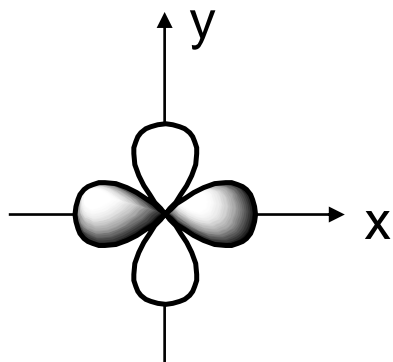
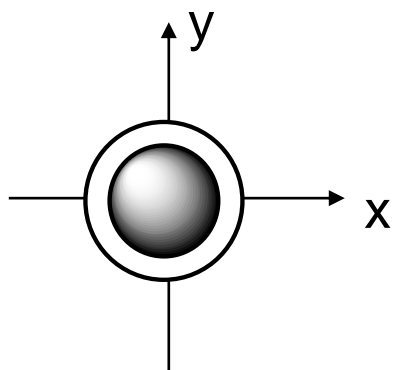
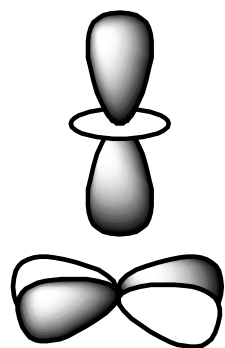
| $C_{2V}$ | $E$ | $C_2$ | $\sigma_v(xz)$ | $\sigma'_v(yz)$ |          |                 |
|----------|-----|-------|----------------|-----------------|----------|-----------------|
| $A_1$    | 1   | 1     | 1              | 1               | $z$      | $x^2, y^2, z^2$ |
| $A_2$    | 1   | 1     | -1             | -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

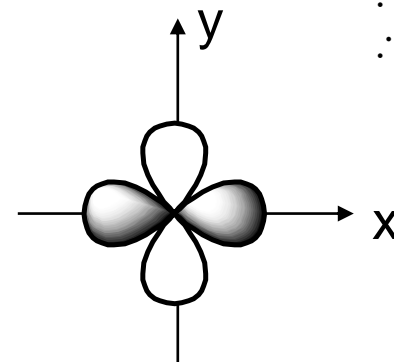
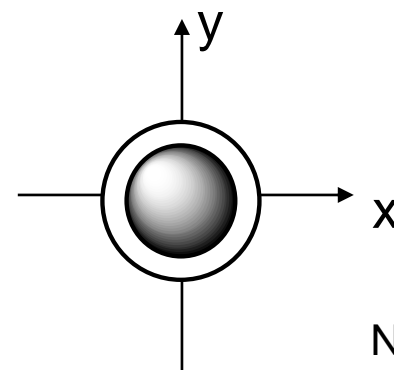
d orbital functions can also be treated in a similar way

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<sub>2</sub>  
σ<sub>v</sub> (xz)  
σ'<sub>v</sub> (yz)



No change  
∴ symmetric  
∴ 1's in table

| C <sub>2v</sub> | E | C <sub>2</sub> | σ <sub>v</sub> (xz) | σ' <sub>v</sub> (yz) |                   |  |
|-----------------|---|----------------|---------------------|----------------------|-------------------|--|
| A <sub>1</sub>  | 1 | 1              | 1                   | 1                    | z                 | x <sup>2</sup> , y <sup>2</sup> , z <sup>2</sup> |
| A <sub>2</sub>  | 1 | 1              | -1                  | -1                   | R <sub>z</sub>    | xy   |
| B <sub>1</sub>  | 1 | -1             | 1                   | -1                   | x, R <sub>y</sub> | xz   |
| B <sub>2</sub>  | 1 | -1             | -1                  | 1                    | y, R <sub>x</sub> | 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 | $C_2$ | $\sigma_v (xz)$ | $\sigma'_v (yz)$ |          |                 |
|----------|---|-------|-----------------|------------------|----------|-----------------|
| $A_1$    | 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              |

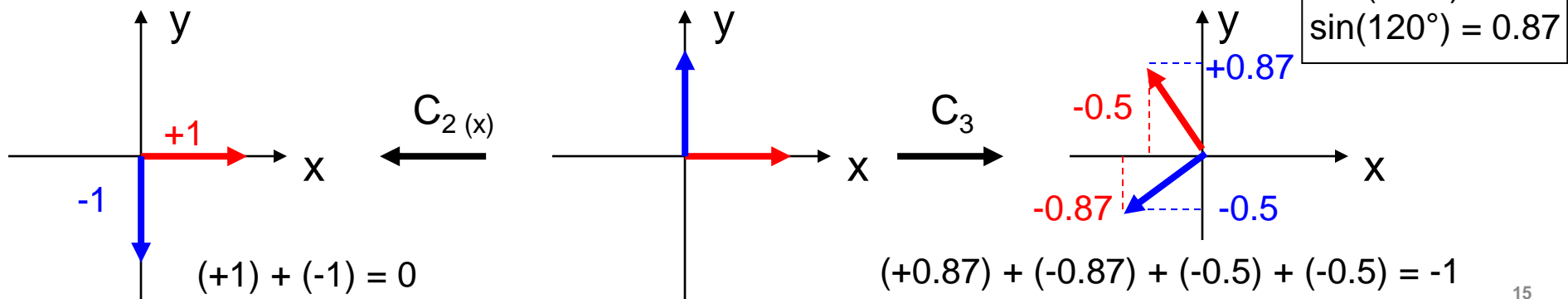
| $D_{3h}$ | E | $2 C_3$ | $3 C_2$ | $\sigma_h$ | $2 S_3$ | $3 \sigma_v$ |                |                   |
|----------|---|---------|---------|------------|---------|--------------|----------------|-------------------|
| $A'_1$   | 1 | 1       | 1       | 1          | 1       | 1            |                | $x^2 + y^2, z^2$  |
| $A'_2$   | 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)          |

# Symmetry of Orbitals and Functions

| $D_{3h}$ | E | $2 C_3$ | $3 C_2$ | $\sigma_h$ | $2 S_3$ | $3 \sigma_v$ |              |                   |
|----------|---|---------|---------|------------|---------|--------------|--------------|-------------------|
| $A'_1$   | 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            | $(R_x, R_y)$ | $(xz, yz)$        |

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  $\sigma_h$ .



# Symmetry of Orbitals and Functions

| $O_h$    | E | 8 $C_3$ | 6 $C_2$ | 6 $C_4$ | 3 $C_2$<br>( $C_4^2$ ) | $i$ | 6 $S_4$ | 8 $S_6$ | 3 $\sigma_h$ | 6 $\sigma_d$ |                   |                                 |
|----------|---|---------|---------|---------|------------------------|-----|---------|---------|--------------|--------------|-------------------|---------------------------------|
| $A_{1g}$ | 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

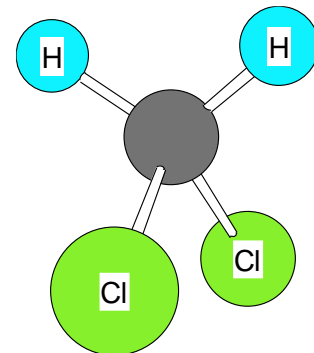
We can use character tables to determine the orbitals involved in bonding in a molecule. This process is done a few easy steps.

1. Determine the point group of the molecule.
2. Determine the *Reducible Representation*,  $\Gamma$ , for the type of bonding you wish to describe (e.g.  $\sigma$ ,  $\pi$ ,  $\pi_{\perp}$ ,  $\pi_{\parallel}$ ). 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  $\sigma$  bonding in **dichloromethane**,  $\text{CH}_2\text{Cl}_2$ .

- The point group is  $C_{2v}$  so we must use the appropriate character table for the reducible representation of the sigma bonding,  $\Gamma_\sigma$ . To determine  $\Gamma_\sigma$  all we have to do is see how each symmetry operation affects the 4  $\sigma$  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.**



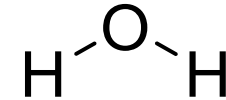
- The E operation leaves everything where it is, so all four bonds stay in the same place and the character is 4 (1+1+1+1).
- The  $C_2$  operation moves all four bonds so the character is 0.
- Each  $\sigma_v$  operation leaves two bonds where they were and moves two bonds, so the character is 2 (1+1).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

| $C_{2v}$        | E | $C_2$ | $\sigma_v$ (xz) | $\sigma'_v$ (yz) |
|-----------------|---|-------|-----------------|------------------|
| $\Gamma_\sigma$ | 4 | 0     | 2               | 2                |

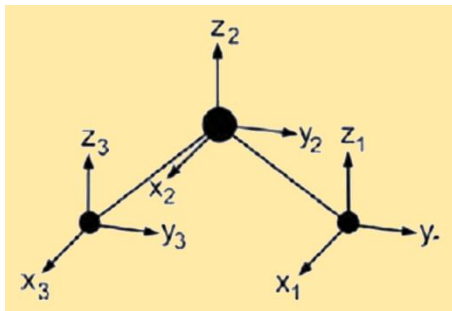
# Example: H<sub>2</sub>O

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<sub>2v</sub> point group  
Basis: x<sub>1-3</sub>, y<sub>1-3</sub> and z<sub>1-3</sub>



Atom 1: x<sub>1</sub> = 1  
y<sub>1</sub> = 1  
z<sub>1</sub> = 1

Atom 2: x<sub>2</sub> = 1  
y<sub>2</sub> = 1  
z<sub>2</sub> = 1

Atom 3: x<sub>3</sub> = 1  
y<sub>3</sub> = 1  
z<sub>3</sub> = 1

| Atom:           | 1 | 2    | 3   |      |
|-----------------|---|------|-----|------|
| E               | 3 | + 3  | + 3 | = 9  |
| C <sub>2</sub>  | 0 | + -1 | + 0 | = -1 |
| σ <sub>xz</sub> | 0 | + 1  | + 0 | = 1  |
| σ <sub>yz</sub> | 1 | + 1  | + 1 | = 3  |

# 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 | $C_2$ | $\sigma_v (xz)$ | $\sigma'_v (yz)$ |
| $\Gamma_\sigma$ | 4 | 0     | 2               | 2                |

| $C_{2V}$ | E | $C_2$ | $\sigma_v (xz)$ | $\sigma'_v (yz)$ |          |                 |
|----------|---|-------|-----------------|------------------|----------|-----------------|
| $A_1$    | 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  $\Gamma_\sigma$ . 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 | $C_2$ | $\sigma_v (xz)$ | $\sigma'_v (yz)$ |
| $\Gamma_\sigma$ | 4 | 0     | 2               | 2                |

|          |   |       |                 |                  |          |                 |
|----------|---|-------|-----------------|------------------|----------|-----------------|
| $C_{2V}$ | E | $C_2$ | $\sigma_v (xz)$ | $\sigma'_v (yz)$ |          |                 |
| $A_1$    | 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:

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

Thus, in our example:

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

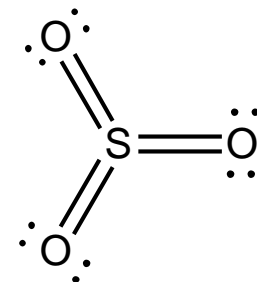
$$n_{A_2} = \frac{1}{4} [(1)(4)(1) + (1)(0)(1) + (1)(2)(-1) + (1)(2)(-1)] \quad n_{B_2} = \frac{1}{4} [(1)(4)(1) + (1)(0)(-1) + (1)(2)(-1) + (1)(2)(1)]$$

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

# Character Tables and Bonding

Example, the  $\sigma$  and  $\pi$  bonding in  $\text{SO}_3$ .

- The point group is  $D_{3h}$  so we must use the appropriate character table to find the reducible representation of the sigma bonding,  $\Gamma_\sigma$  first, then we can go the representation of the  $\pi$  bonding,  $\Gamma_\pi$ . To determine  $\Gamma_\sigma$  all we have to do is see how each symmetry operation affects the 3  $\sigma$  bonds in the molecule.



- The E and the  $\sigma_h$  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  $\sigma_v$  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 $C_2$ | $\sigma_h$ | 2 $S_3$ | 3 $\sigma_v$ |
|-----------------|---|---------|---------|------------|---------|--------------|
| $\Gamma_\sigma$ | 3 | 0       | 1       | 3          | 0       | 1            |

|                 |   |         |         |            |         |              |  |
|-----------------|---|---------|---------|------------|---------|--------------|--|
| $D_{3h}$        | E | 2 $C_3$ | 3 $C_2$ | $\sigma_h$ | 2 $S_3$ | 3 $\sigma_v$ |  |
| $\Gamma_\sigma$ | 3 | 0       | 1       | 3          | 0       | 1            |  |

| $D_{3h}$ | E | 2 $C_3$ | 3 $C_2$ | $\sigma_h$ | 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)          |

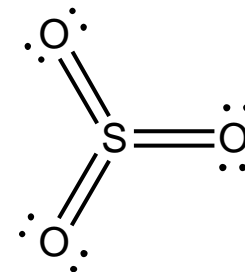
$$n_{A'_1} = \frac{1}{12} [(1)(3)(1) + (2)(0)(1) + (3)(1)(1) + (1)(3)(1) + (2)(0)(1) + (3)(1)(1)] \quad n_{A'_1} = \frac{12}{12} = 1$$

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

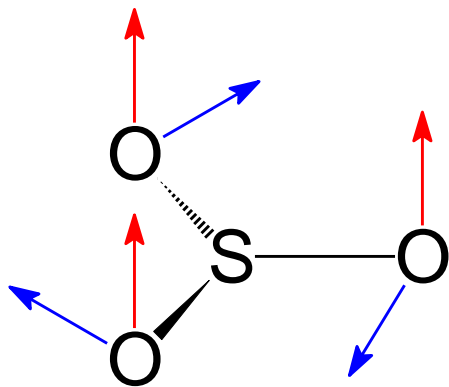
$$n_{E'} = \frac{1}{12} [(1)(3)(2) + (2)(0)(-1) + (3)(1)(0) + (1)(3)(2) + (2)(0)(-1) + (3)(1)(0)] \quad n_{E'} = \frac{12}{12} = 1$$

We can stop here because the combination ( $A'_1 + E'$ ) produces the  $\Gamma_\sigma$  that we determined. None of the other representations can contribute to the  $\sigma$  bonding (i.e.  $n_{A''_1}$ ,  $n_{A''_2}$  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



- Now we have to determine  $\Gamma$  for the  $\pi$  bonding in  $\text{SO}_3$ .
- To determine  $\Gamma_\pi$  we have to see how each symmetry operation affects the  $\pi$  systems in the molecule. The treatment is similar to what we did for sigma bonding but there are a few significant differences:
  1. *Pi bonds change sign across the inter-nuclear axis.* We must consider the effect of the symmetry operation on the signs of the lobes in a  $\pi$  bond.
  2. *There is the possibility of two different  $\pi$  type bonds for any given  $\sigma$  bond (oriented  $90^\circ$  from each other).* We must examine each of these.
- This means that we have to find reducible representations for both the  $\pi$  system perpendicular to the molecular plane ( $\pi_\perp$ , vectors shown in red) and the pi system in the molecular plane ( $\pi_\parallel$ , vectors shown in blue).

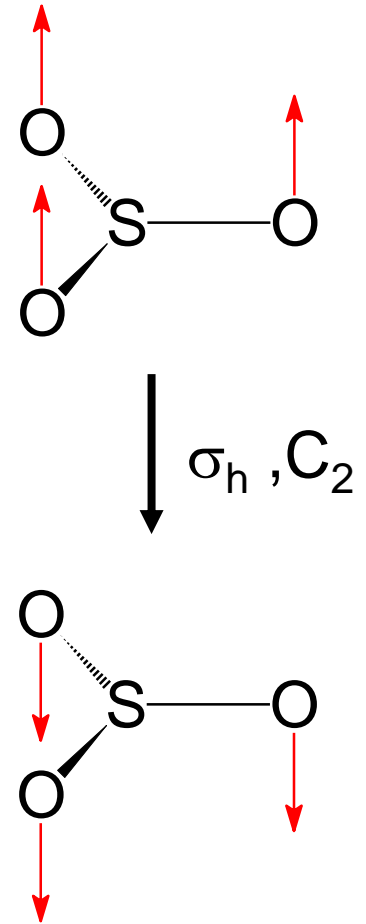


Note: These are just vectors that are associated with **each sigma bond** (not with any particular atom) – they could also be placed in the middle of each SO bond. The vectors should be placed to conform with the symmetry of the point group (e.g., the blue vectors conform to the  $C_3$  axis).



# Example, the $\sigma$ and $\pi$ bonding in $\text{SO}_3$

- First determine the reducible representation for the pi bonding perpendicular to the molecular plane,  $\Gamma_{\pi\perp}$ .
- The E operation leaves everything where it is so all three vectors stay in the same place and the character is 3.
- The  $C_3$  and  $S_3$  operations move all three vectors so their characters are 0.
- The  $C_2$  operation moves two of the vectors and reverses the sign of the other one so the character is -1.
- The  $\sigma_h$  operation reverses the sign of all three vectors so the character is -3.
- Each  $\sigma_v$  operation leaves one vector where it was and moves the two others so the character is 1.
- Overall, the reducible representation for the perpendicular  $\pi$  bonding is:



| $D_{3h}$            | E | $2 C_3$ | $3 C_2$ | $\sigma_h$ | $2 S_3$ | $3 \sigma_v$ |
|---------------------|---|---------|---------|------------|---------|--------------|
| $\Gamma_{\pi\perp}$ | 3 | 0       | -1      | -3         | 0       | 1            |

|                     |   |         |         |            |         |              |
|---------------------|---|---------|---------|------------|---------|--------------|
| $D_{3h}$            | E | 2 $C_3$ | 3 $C_2$ | $\sigma_h$ | 2 $S_3$ | 3 $\sigma_v$ |
| $\Gamma_{\pi\perp}$ | 3 | 0       | -1      | -3         | 0       | 1            |

Going through all the possibly symmetry representations, we find that the combination ( $A''_2 + E''$ ) produces the  $\Gamma_{\pi\perp}$  that we determined. The irreducible representation shows us that the possible orbitals involved in perpendicular  $\pi$  bonding are the  $p_z$  and the  $d_{xz}$  and  $d_{yz}$  pair. This is in agreement with the  $\pi$  bonding we would predict using VBT.

| $D_{3h}$ | E | 2 $C_3$ | 3 $C_2$ | $\sigma_h$ | 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            | $(R_x, R_y)$ | $(xz, yz)$        |

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

$$n_{A'_1} = \frac{0}{12} = 0$$

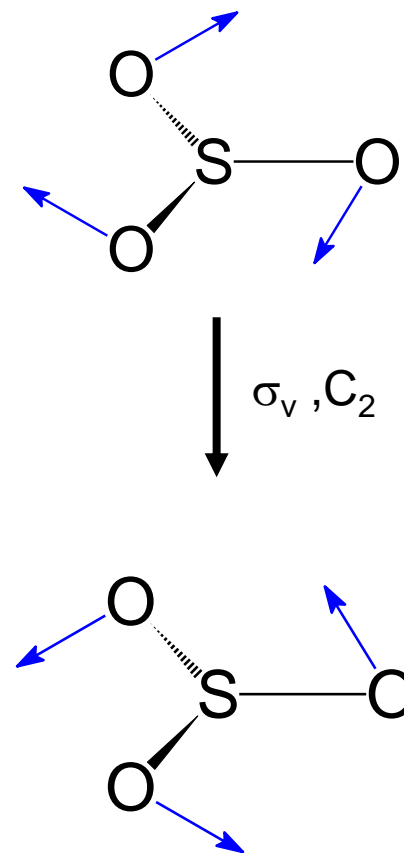
$$n_{A''_2} = \frac{1}{12} [(1)(3)(1) + (2)(0)(1) + (3)(-1)(-1) + (1)(-3)(-1) + (2)(0)(-1) + (3)(1)(1)]$$

$$n_{A''_2} = \frac{12}{12} = 1$$

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

$$n_{E''} = \frac{12}{12} = 1$$

- First determine the reducible representation for the  $\pi$  bonding in the molecular plane,  $\Gamma_{\pi//}$ .
- The E operation leaves everything where it is so all three vectors stay in the same place and the character is 3.
- The  $C_3$  and  $S_3$  operations move all three vectors so their characters are 0.
- The  $C_2$  operation moves two of the vectors and reverses the sign of the other one so the character is -1.
- The  $\sigma_h$  operation leaves all three vectors unchanged, so the character is 3.
- Each  $\sigma_v$  operation reverses the sign one vector where it was and moves the two others, so the character is -1.
- Overall, the reducible representation for the parallel  $\pi$  bonding is:



| $D_{3h}$         | E | 2 $C_3$ | 3 $C_2$ | $\sigma_h$ | 2 $S_3$ | 3 $\sigma_v$ |
|------------------|---|---------|---------|------------|---------|--------------|
| $\Gamma_{\pi//}$ | 3 | 0       | -1      | 3          | 0       | -1           |

|                  |   |         |         |            |         |              |  |
|------------------|---|---------|---------|------------|---------|--------------|--|
| $D_{3h}$         | E | 2 $C_3$ | 3 $C_2$ | $\sigma_h$ | 2 $S_3$ | 3 $\sigma_v$ |  |
| $\Gamma_{\pi//}$ | 3 | 0       | -1      | 3          | 0       | -1           |  |

| $D_{3h}$ | E | 2 $C_3$ | 3 $C_2$ | $\sigma_h$ | 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            | $(R_x, R_y)$ | $(xz, yz)$        |

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

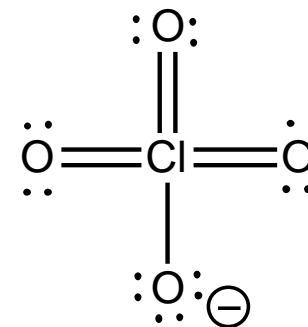
$$n_{A'_2} = \frac{1}{12} [(1)(3)(1) + (2)(0)(1) + (3)(-1)(-1) + (1)(3)(1) + (2)(0)(1) + (3)(-1)(-1)] \quad n_{A'_2} = \frac{12}{12} = 1$$

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

Going through all the possibly symmetry representations, we find that the combination ( $A'_2 + E'$ ) produces the  $\Gamma_{\pi//}$  that we determined. The possible orbitals involved in parallel  $\pi$  bonding are only the  $d_{x^2-y^2}$  and  $d_{xy}$  pair. The  $A'_2$  representation has no orbital equivalent. Note: **Such analyses do NOT mean that there is  $\pi$  bonding using these orbitals – it only means that it is possible based on the symmetry of the molecule.**

# Character Tables and Bonding

- Example, the  $\sigma$  and  $\pi$  bonding in  $\text{ClO}_4^-$ .
- The point group is  $T_d$  so we must use the appropriate character table to find the reducible representation of the sigma bonding,  $\Gamma_\sigma$  first, then we can go the representation of the  $\pi$  bonding,  $\Gamma_\pi$ .
- 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  $\sigma_d$  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 $\sigma_d$ |
|-----------------|---|---------|---------|---------|--------------|
| $\Gamma_\sigma$ | 4 | 1       | 0       | 0       | 2            |

|                 |   |         |         |         |              |
|-----------------|---|---------|---------|---------|--------------|
| $T_d$           | E | 8 $C_3$ | 3 $C_2$ | 6 $S_4$ | 6 $\sigma_d$ |
| $\Gamma_\sigma$ | 4 | 1       | 0       | 0       | 2            |

| $T_d$ | E | 8 $C_3$ | 3 $C_2$ | 6 $S_4$ | 6 $\sigma_d$ |                   |                                 |
|-------|---|---------|---------|---------|--------------|-------------------|---------------------------------|
| $A_1$ | 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  $\sigma$  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  $\pi$  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.

# Example, the $\sigma$ and $\pi$ bonding in $\text{ClO}_4^-$

- The analysis of how the 8 vectors are affected by the symmetry operations gives:

|              |   |         |         |         |              |
|--------------|---|---------|---------|---------|--------------|
| $T_d$        | E | 8 $C_3$ | 3 $C_2$ | 6 $S_4$ | 6 $\sigma_d$ |
| $\Gamma_\pi$ | 8 | -1      | 0       | 0       | 0            |

| $T_d$ | E | 8 $C_3$ | 3 $C_2$ | 6 $S_4$ | 6 $\sigma_d$ |                   |                                 |
|-------|---|---------|---------|---------|--------------|-------------------|---------------------------------|
| $A_1$ | 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  $\pi$  bonding is  $(E + T_1 + T_2)$ , which corresponds to the  $d_{x^2-y^2}$  and  $d_{xy}$  pair for E and either the  $(p_x, p_y, p_z)$  set or the  $(d_{xy}, d_{xz}, d_{yz})$  set for  $T_2$ , since  $T_1$  does not correspond to any of the orbitals that might be involved in bonding. Because the  $(p_x, p_y, p_z)$  set has already been used in the  $\sigma$  bonding, only the  $(d_{xy}, d_{xz}, d_{yz})$  set may be used for  $\pi$  bonding.