

# Outline

- 1 Introduction to Character Tables
- 2 The Character Table for  $C_{2v}$
- 3 The Character Table for  $C_{3v}$

## Quote from Eugene Paul Wigner

See also: *Current Science*, vol. 69, no. 4, 25 August 1995, p. 375

From the preface to his book on group theory:

Wigner relates a conversation with von Laue on the use of group theory as the natural tool with which to tackle problems in quantum mechanics. "I like to recall his question as to which results... I considered most important. My answer was that the explanation of Laporte's rule (the concept of parity) and the quantum theory of the vector addition model appeared to me most significant. Since that time, I have come to agree with his answer that the recognition that almost all rules of spectroscopy follow from the symmetry of the problem is the most remarkable result."

# What Makes Up a Character Table

Character tables contain information about how functions transform in response to the operations of the group

## Five parts of a character table

- 1 At the upper left is the symbol for the point group
- 2 The top row shows the operations of the point group, organized into classes
- 3 The left column gives the Mulliken symbols for each of the irreducible representations
- 4 The rows at the center of the table give the characters of the irreducible representations
- 5 Listed at right are certain functions, showing the irreducible representation for which the function can serve as a basis

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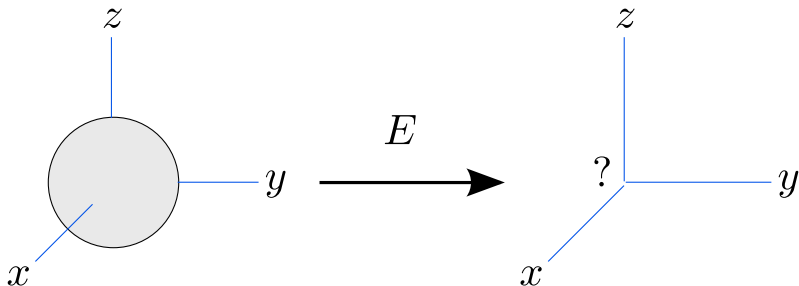
The  $C_{2v}$  Character Table

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



# Transformation Properties of an $s$ Orbital in $C_{2v}$

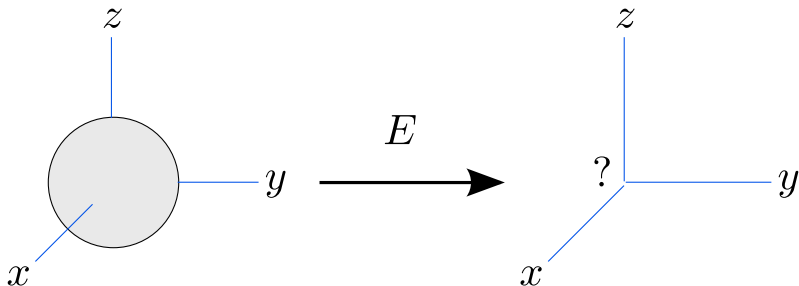
What happens when the  $E$  operation is applied?



- The  $E$  operation is a rotation by  $360^\circ$  about an arbitrary axis

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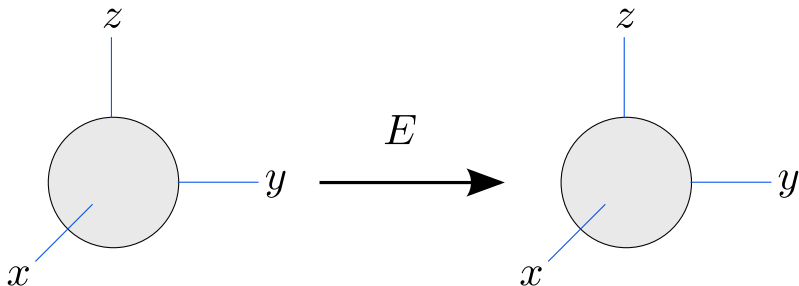
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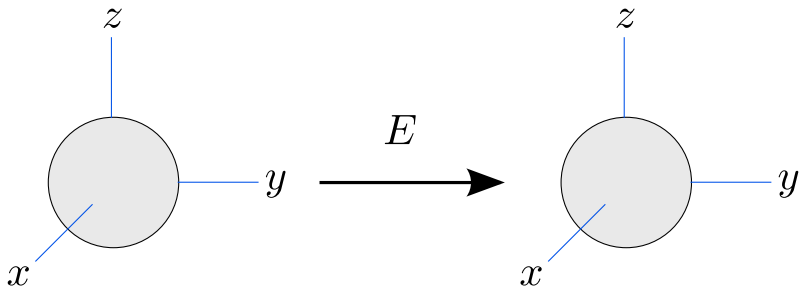
The  $E$  operation returns the original configuration of the  $s$  orbital



- The result of this corresponds to a character of 1

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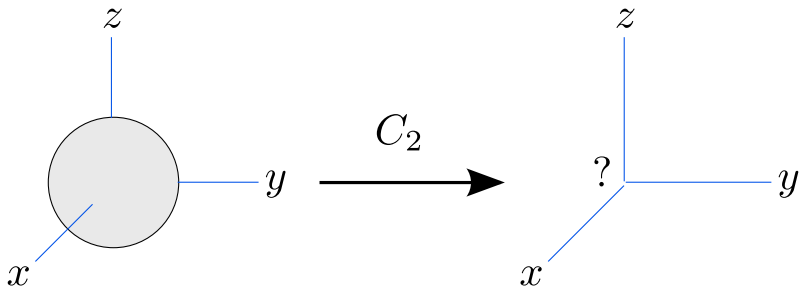
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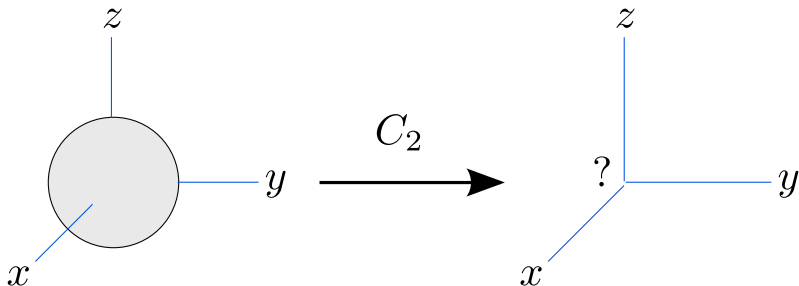
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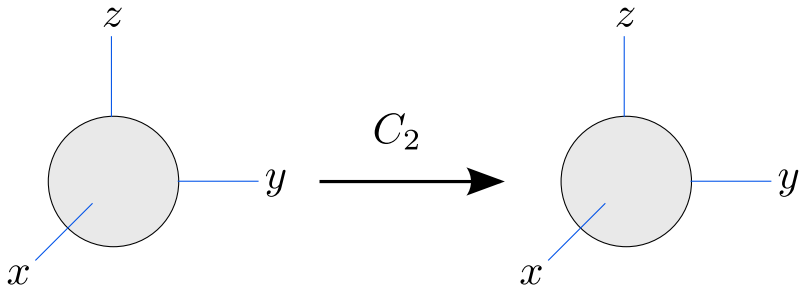
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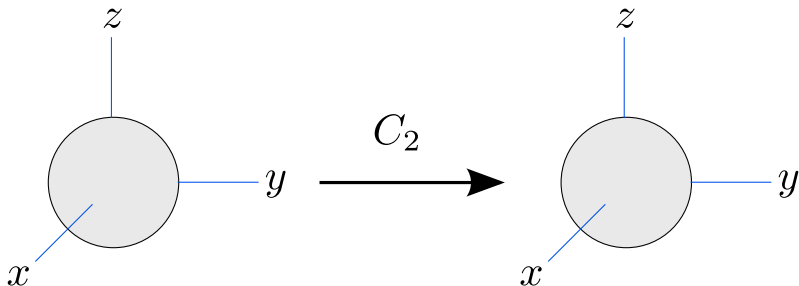
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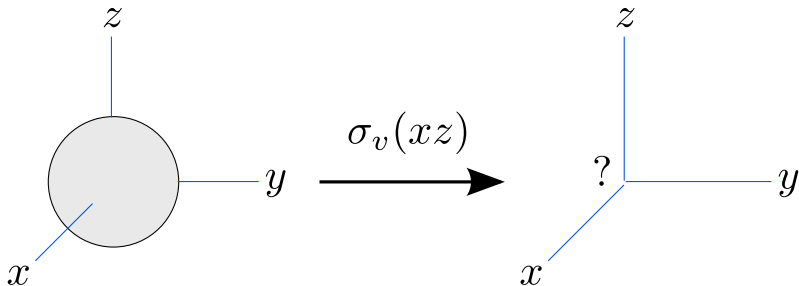


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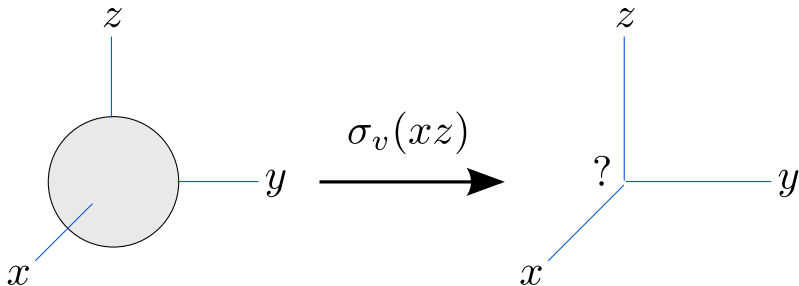
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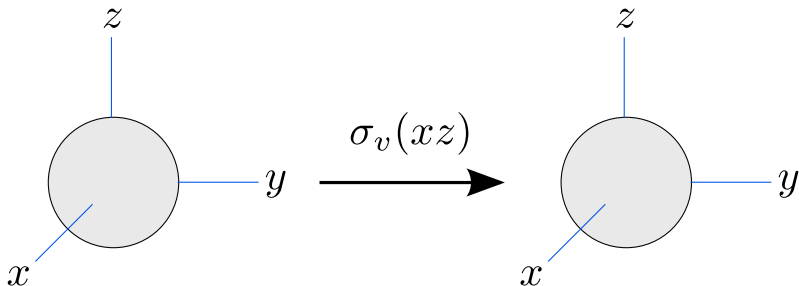
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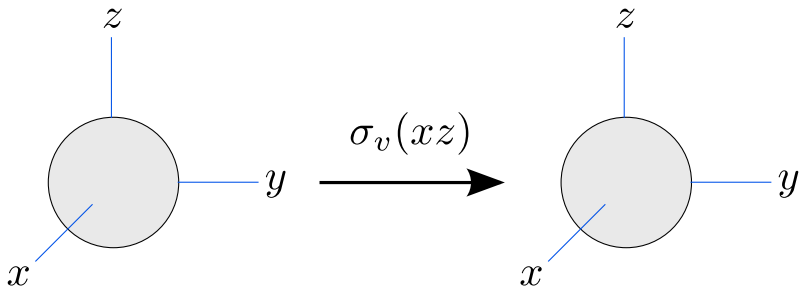
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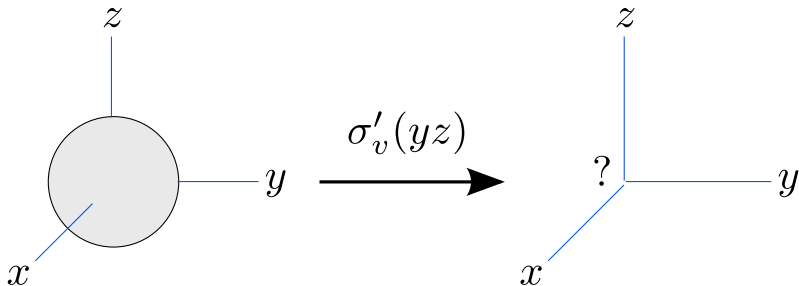
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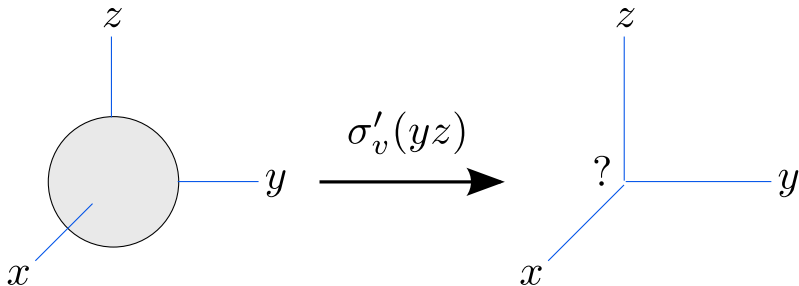
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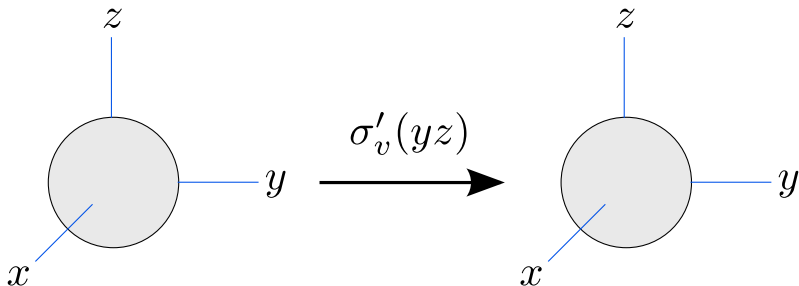
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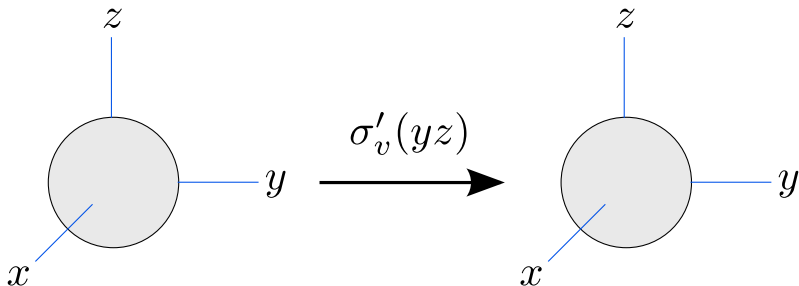
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# Transformation Properties of an $s$ Orbital

These observations pertain to any central-atom  $s$  orbital in any point group

- Consider an  $s$  orbital located on a central atom
- An example of a central atom is O in the case of water, or N in the case of ammonia
- Carrying out any operation on a central atom  $s$  orbital returns the  $s$  orbital in its original configuration
- The central-atom  $s$  orbital “belongs to” or “serves as a basis for” the totally symmetric ( $A_1$ ) irreducible representation
- All the characters of the totally symmetric irreducible representation are 1
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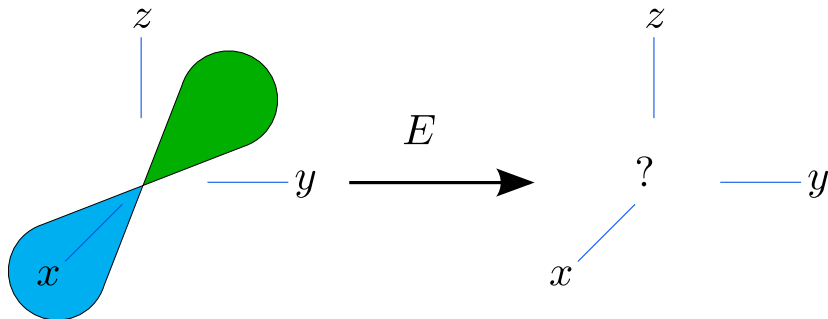
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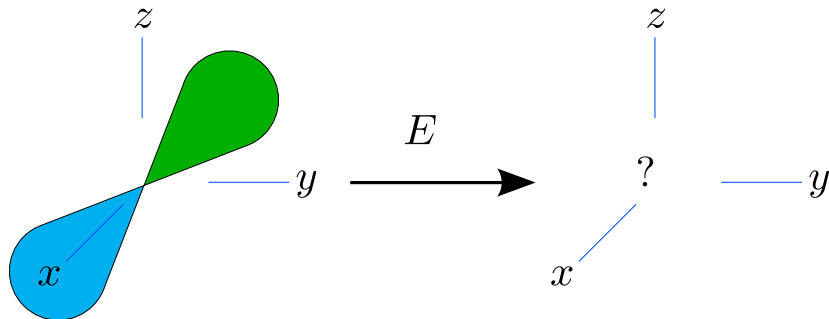
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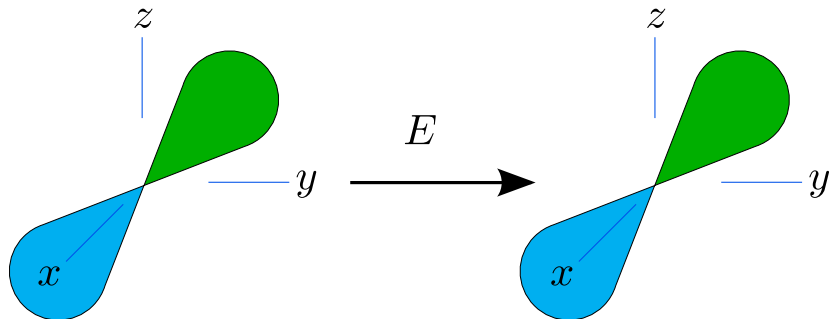


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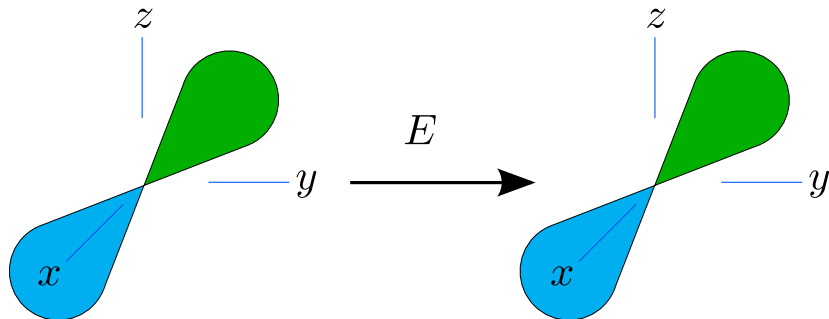
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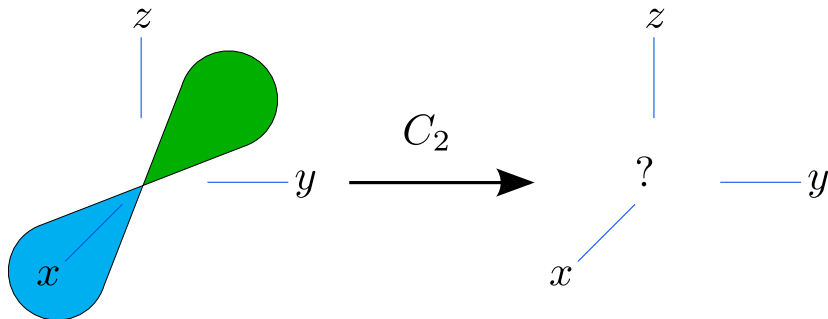
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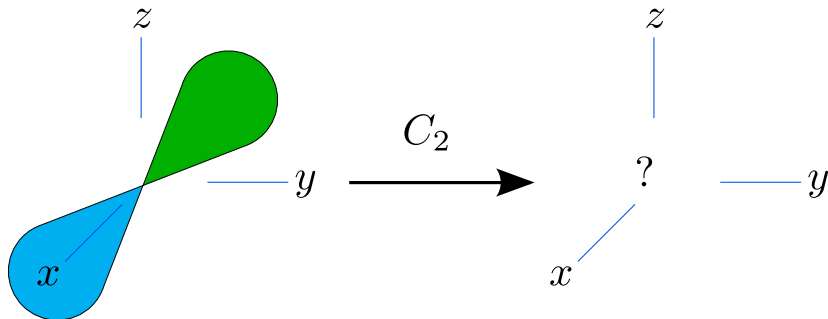
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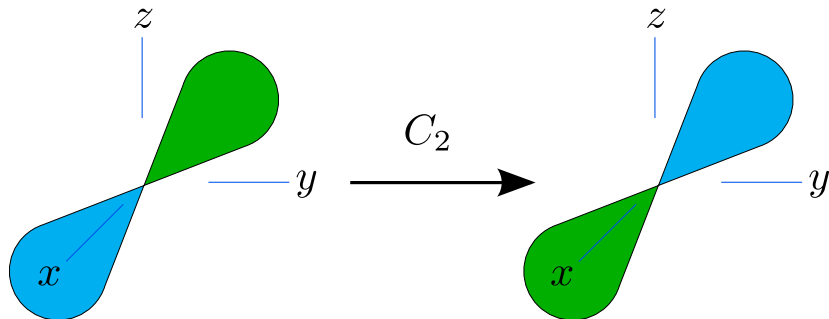
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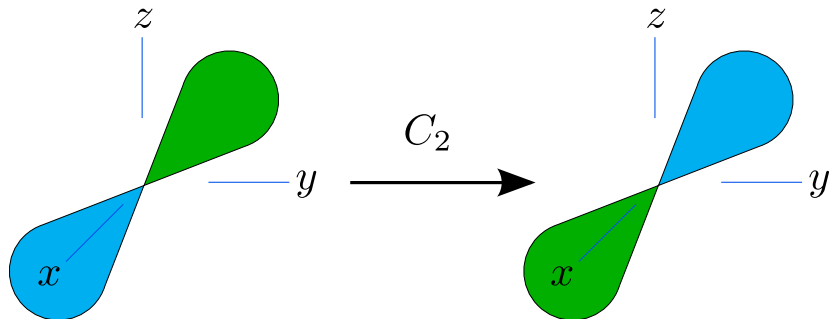
The  $C_2$  operation inverts the phase of the  $p_x$  orbital



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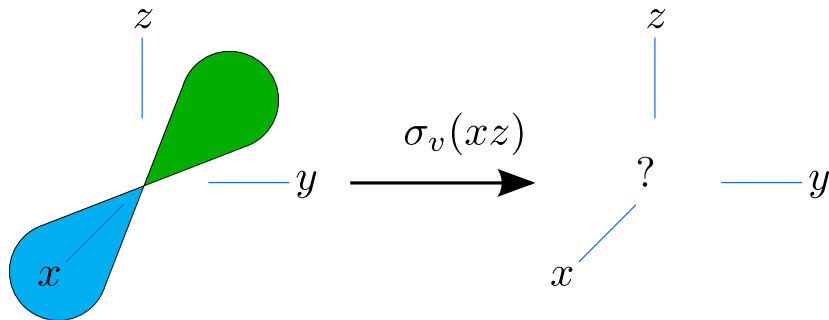
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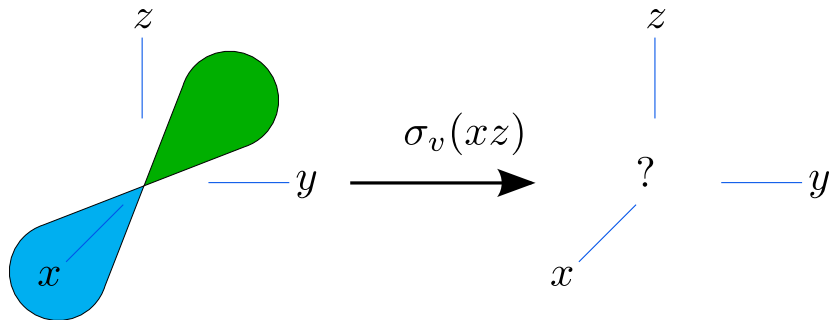
What happens when the  $\sigma_v(xz)$  operation is applied?



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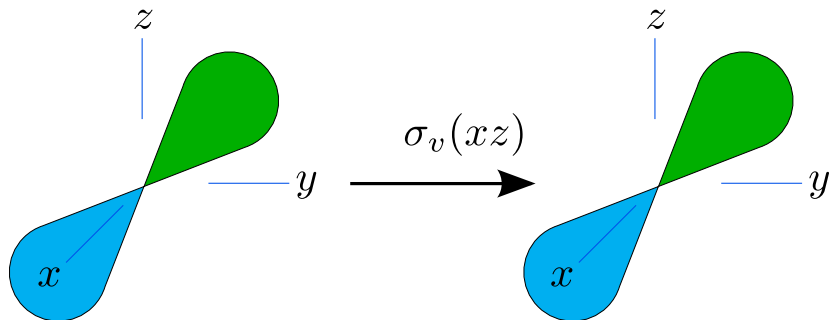


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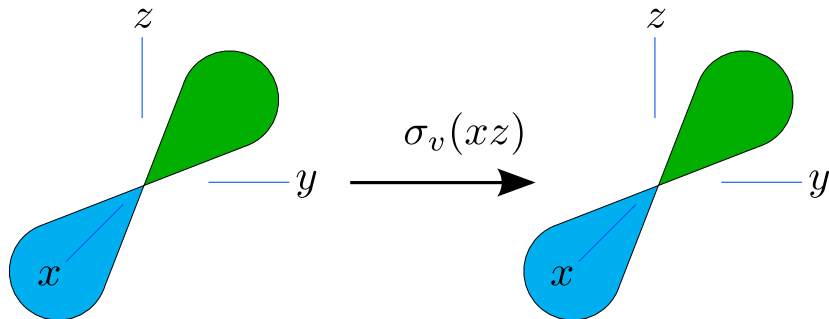
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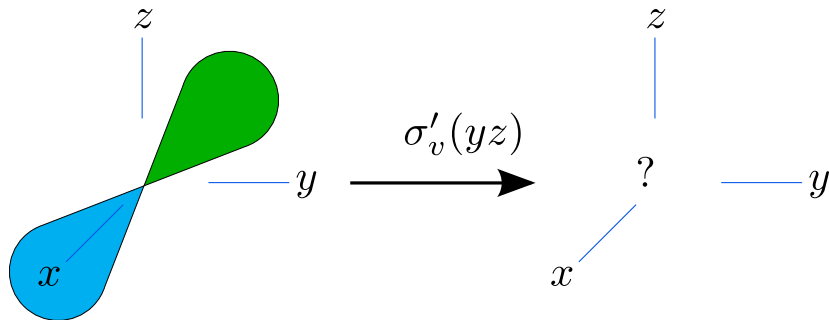
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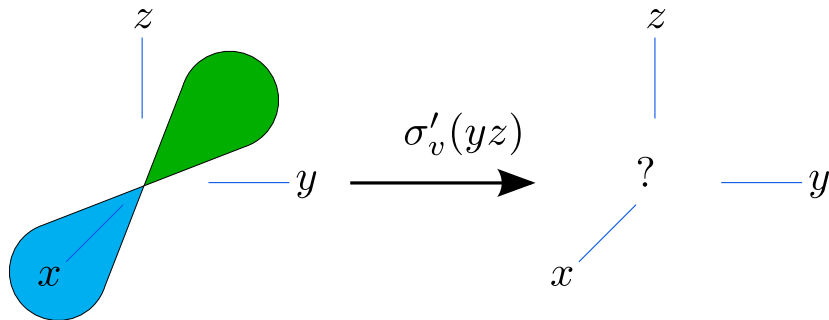
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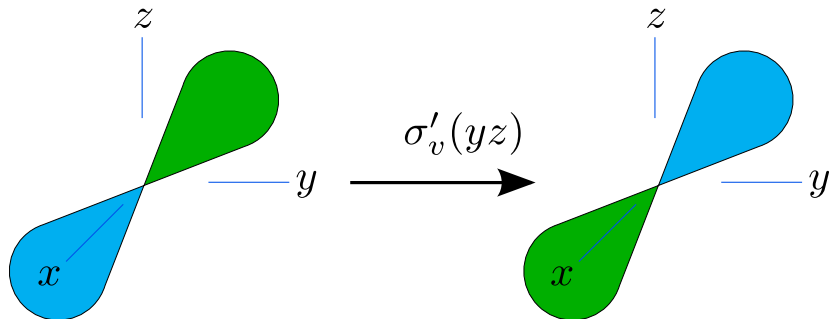
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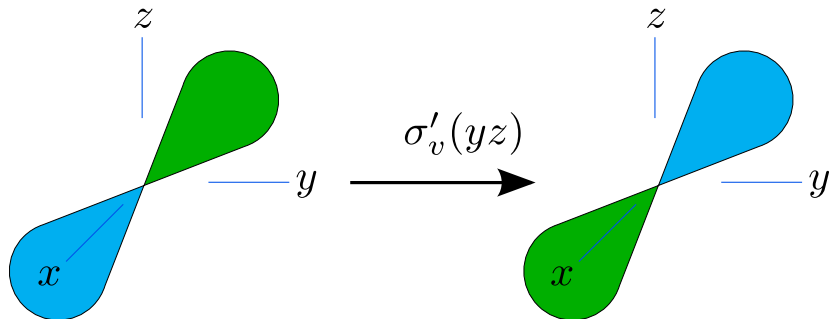
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# A $p_x$ Orbital has $B_1$ Symmetry in $C_{2v}$

- We carried out the operations of  $C_{2v}$  on a central-atom  $p_x$  orbital
- This generated the following row of characters:  $1, -1, 1, -1$
- This row of characters in the  $C_{2v}$  character table is labeled  $B_1$
- Any orbital having these transformation properties in  $C_{2v}$  is said to have  $B_1$  symmetry

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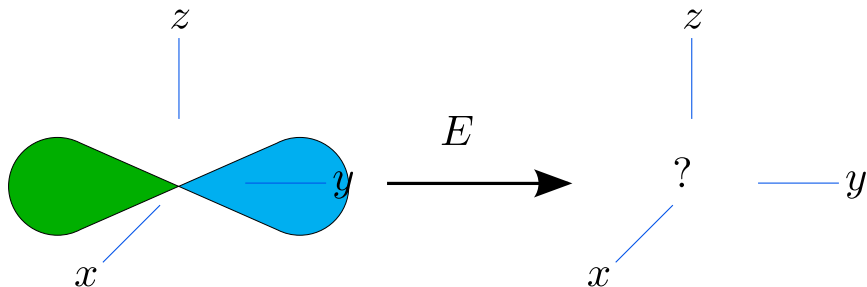
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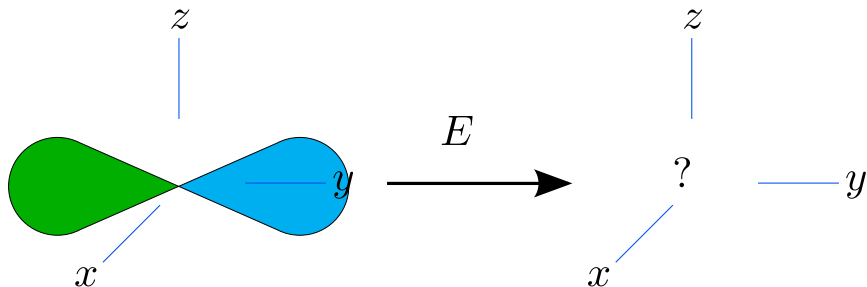
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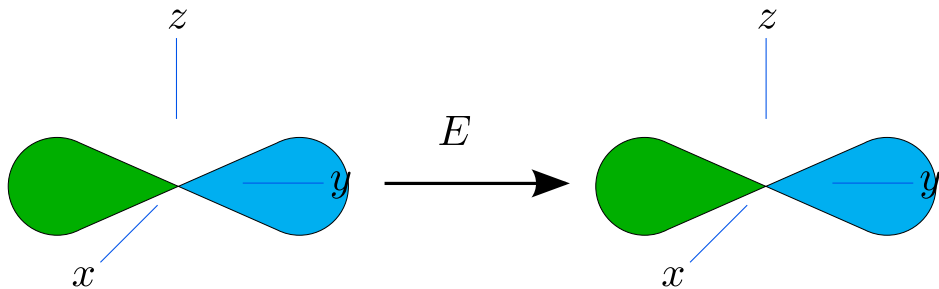
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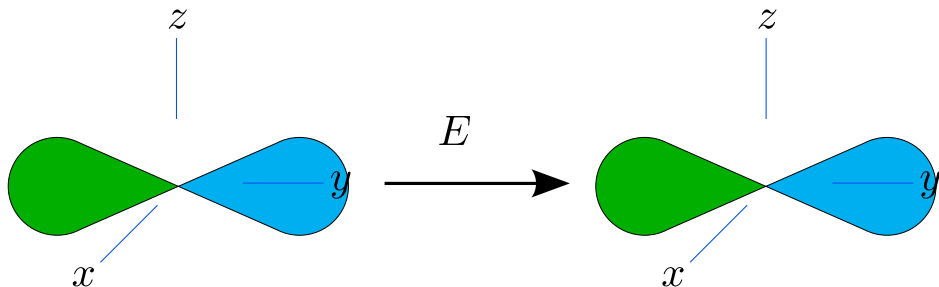
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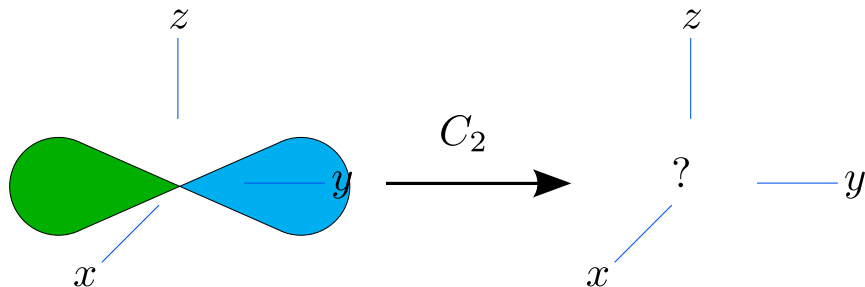
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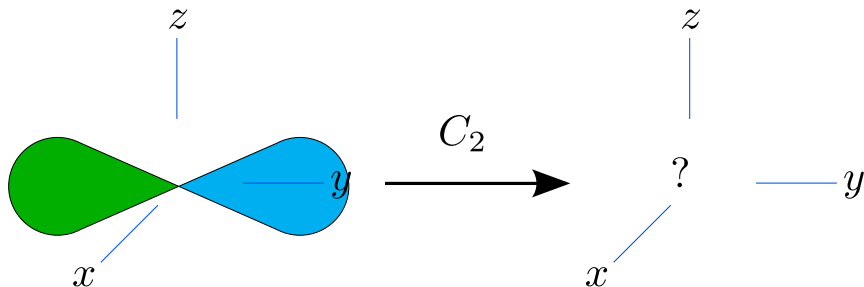
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# Transformation Properties of a $p_y$ Orbital in $C_{2v}$

What happens when the  $C_2$  operation is applied?

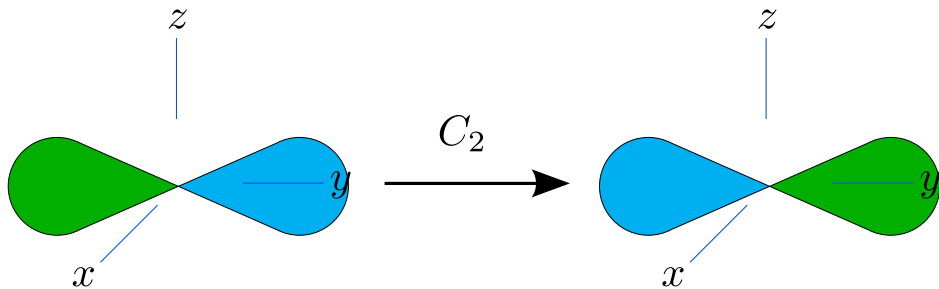


- The  $C_2$  operation is a rotation by  $180^\circ$  about the  $z$  axis



# Transformation Properties of a $p_y$ Orbital in $C_{2v}$

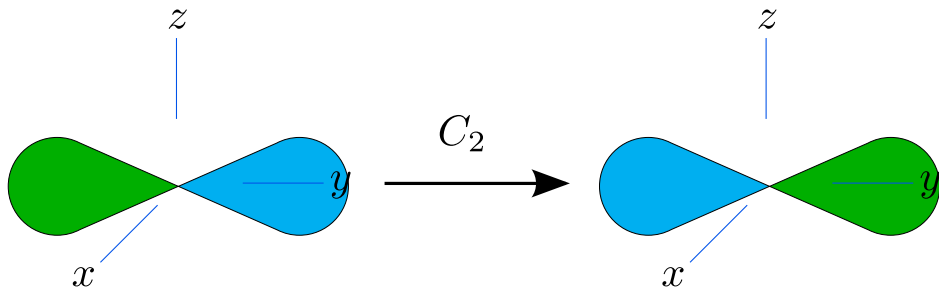
The  $C_2$  operation inverts the phase of the  $p_y$  orbital



- The result of this corresponds to a character of  $-1$

# Transformation Properties of a $p_y$ Orbital in $C_{2v}$

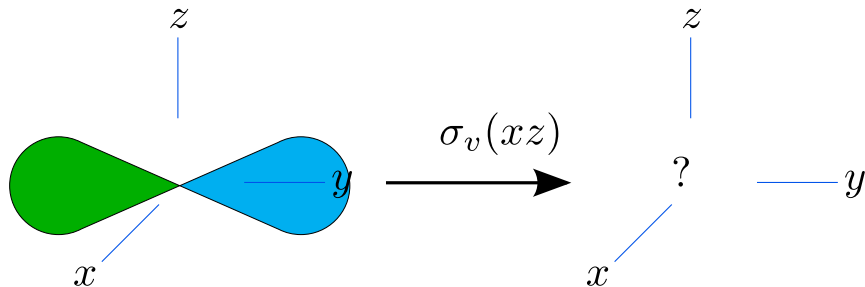
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Transformation Properties of a  $p_y$  Orbital in  $C_{2v}$ 

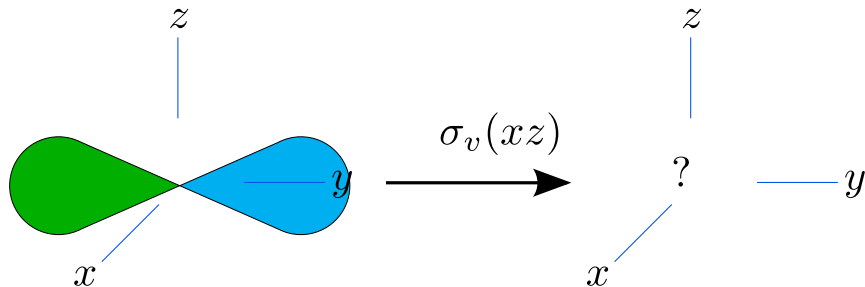
What happens when the  $\sigma_v(xz)$  operation is applied?



- The  $\sigma_v(xz)$  operation is a reflection through the  $xz$  plane

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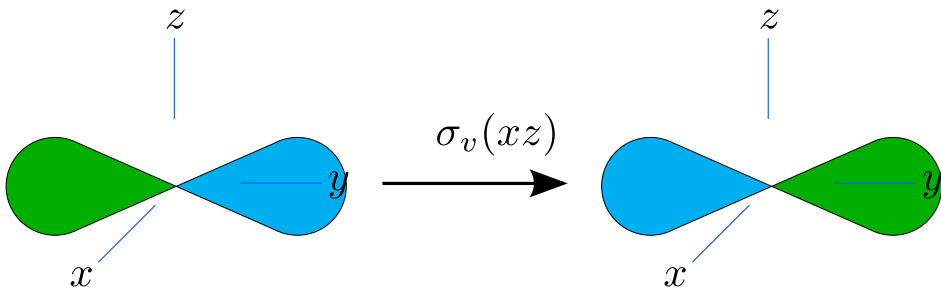
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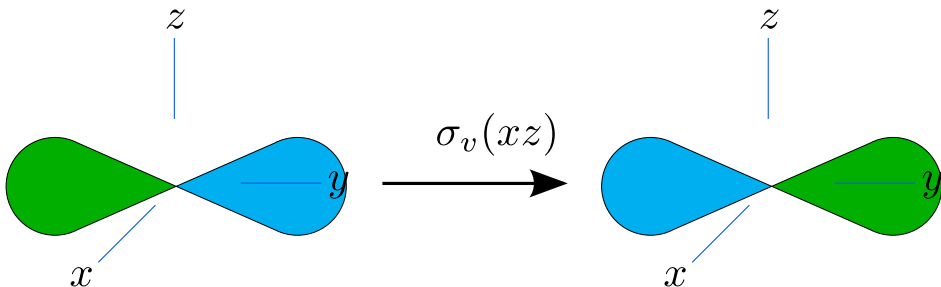
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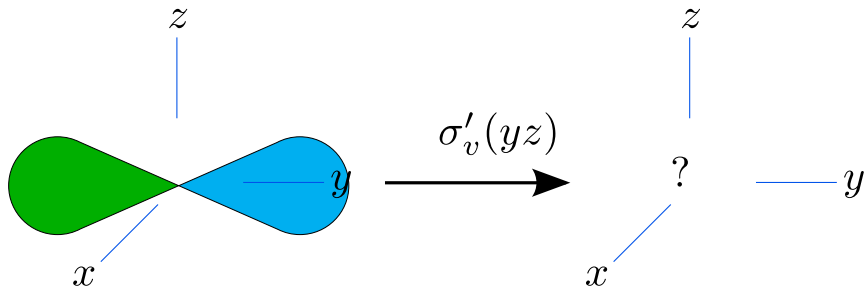
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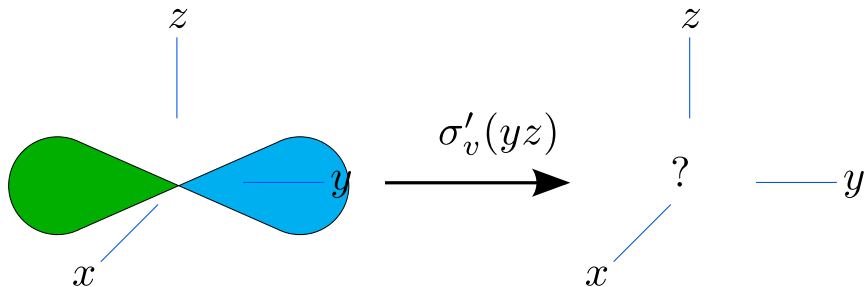
What happens when the  $\sigma'_v(yz)$  operation is applied?



- The  $\sigma'_v(yz)$  operation is a reflection through the  $yz$  plane

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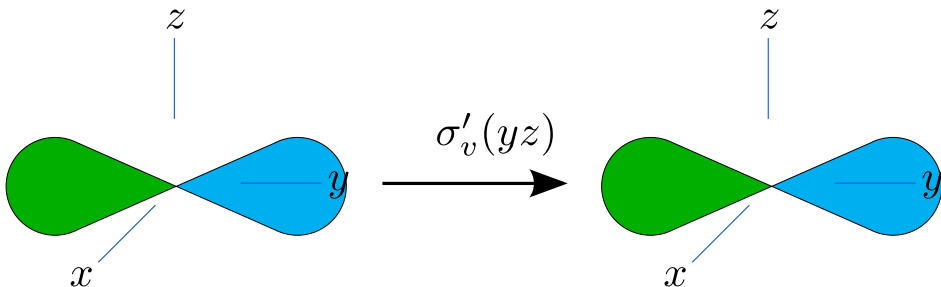


- The  $\sigma'_v(yz)$  operation is a reflection through the  $yz$  plane



# Transformation Properties of a $p_y$ Orbital in $C_{2v}$

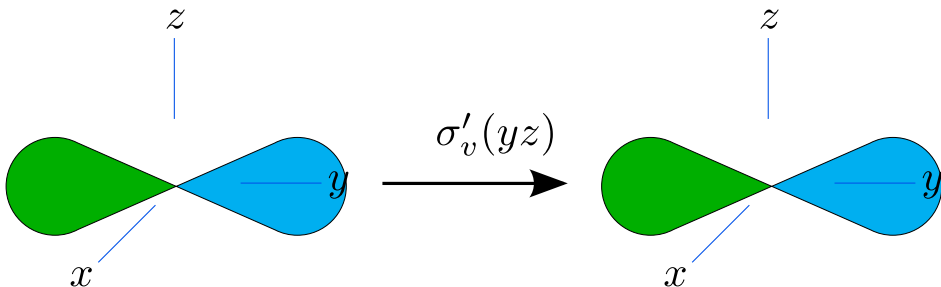
The  $\sigma'_v(yz)$  operation does nothing to the phase of the  $p_y$  orbital



- The result of this corresponds to a character of 1

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# A $p_y$ Orbital has $B_2$ Symmetry in $C_{2v}$

- We carried out the operations of  $C_{2v}$  on a central-atom  $p_y$  orbital
- This generated the following row of characters:  $1, -1, -1, 1$
- This row of characters in the  $C_{2v}$  character table is labeled  $B_2$
- Any orbital having these transformation properties in  $C_{2v}$  is said to have  $B_2$  symmetry

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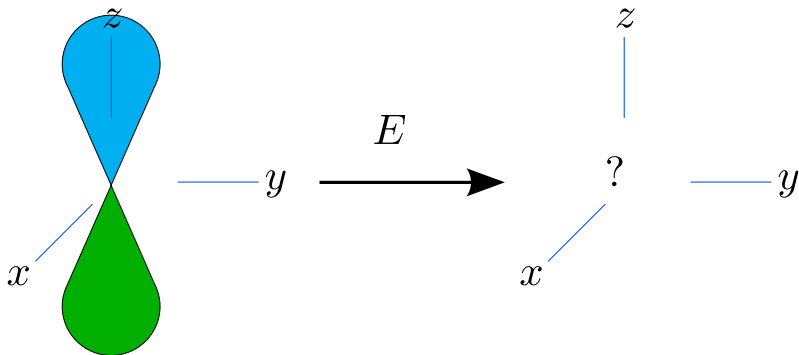
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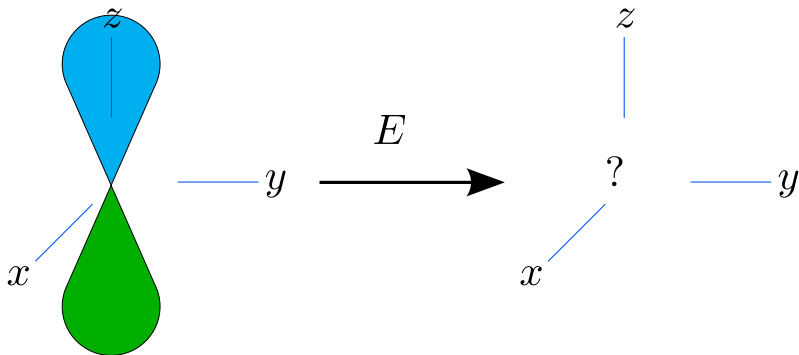
What happens when the  $E$  operation is applied?



- The  $E$  operation is a rotation by  $360^\circ$  about an arbitrary axis

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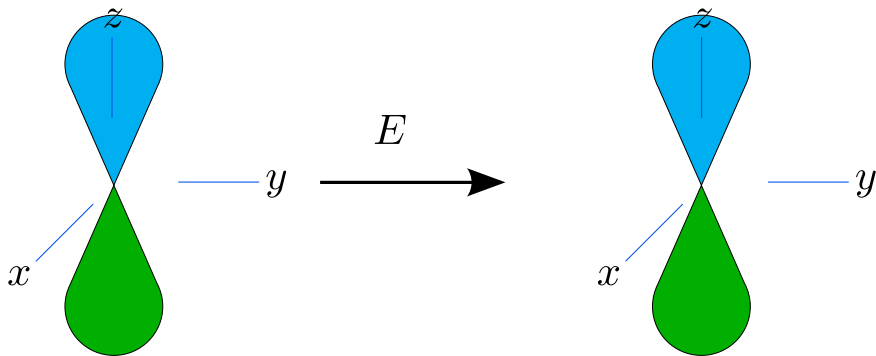


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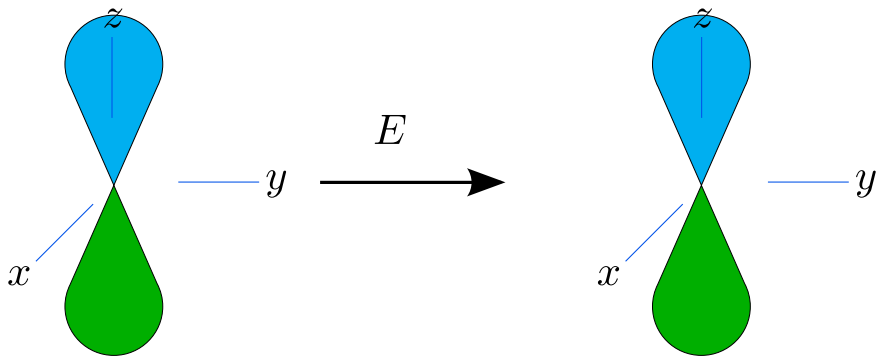
The  $E$  operation returns the original configuration of the  $p_z$  orbital



- The result of this corresponds to a character of 1

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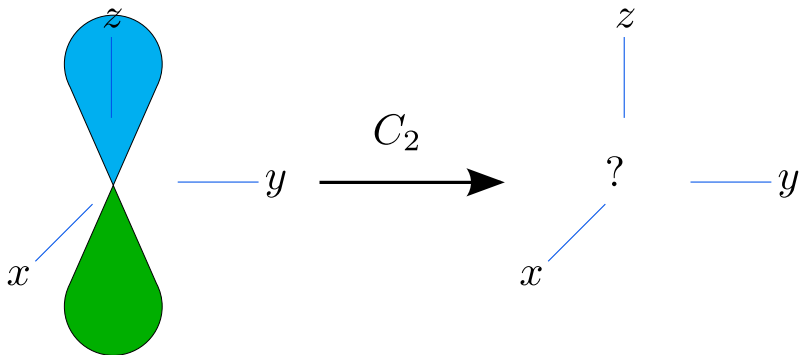
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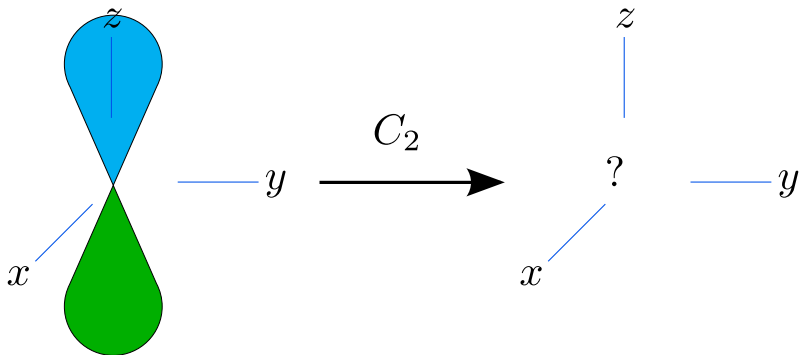
What happens when the  $C_2$  operation is applied?



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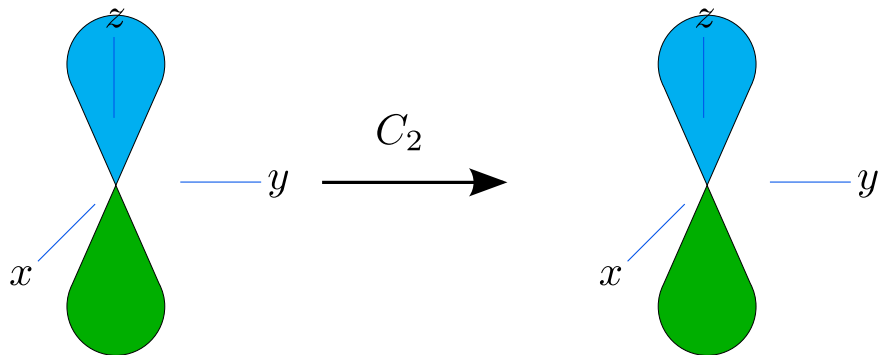
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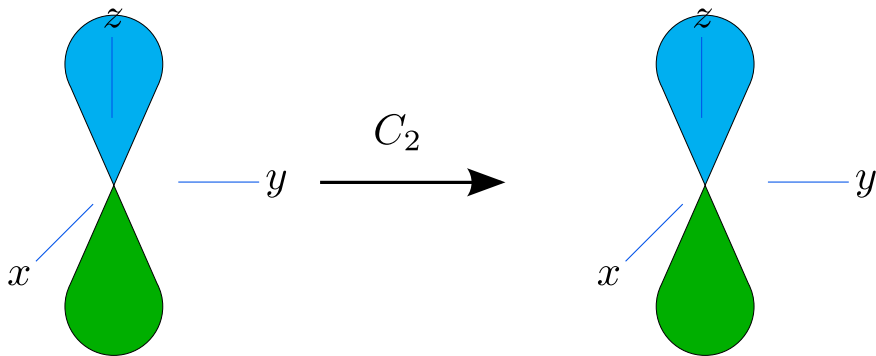
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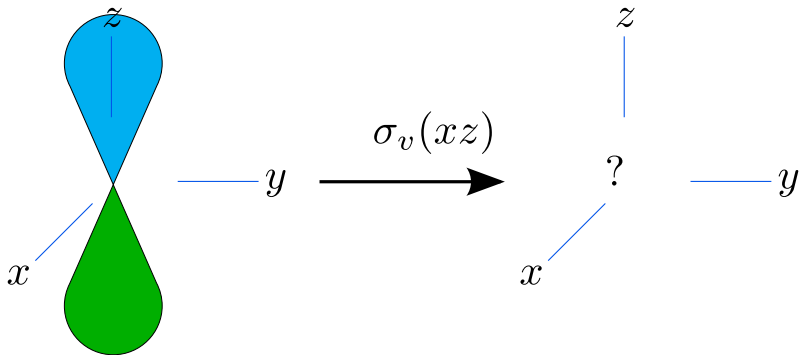
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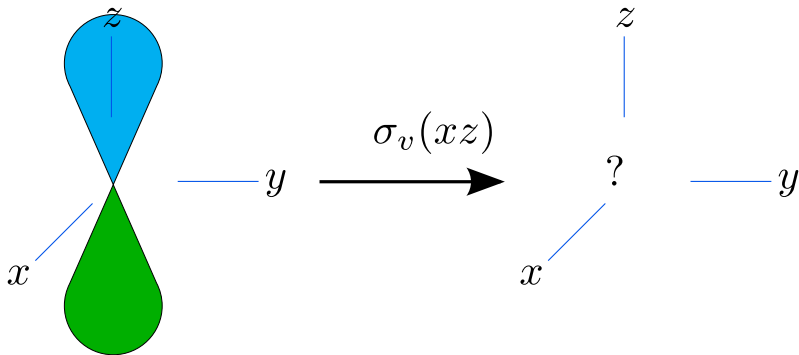
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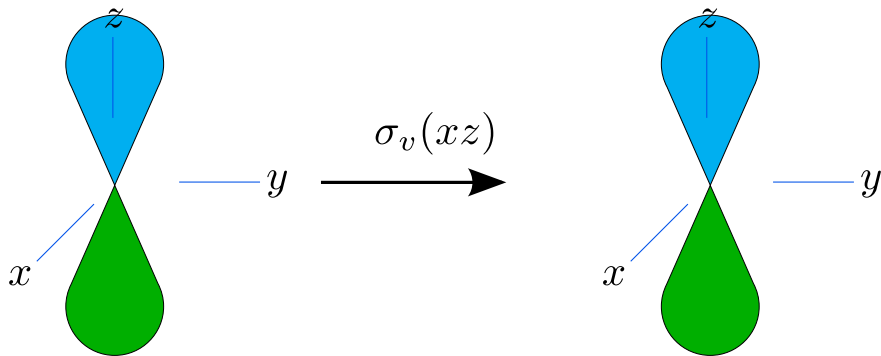


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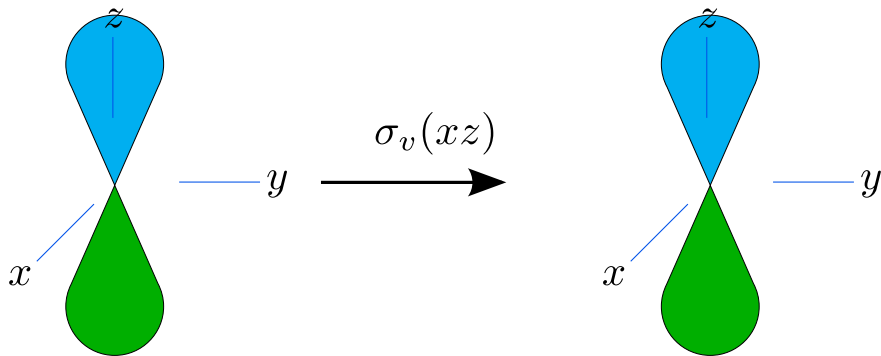
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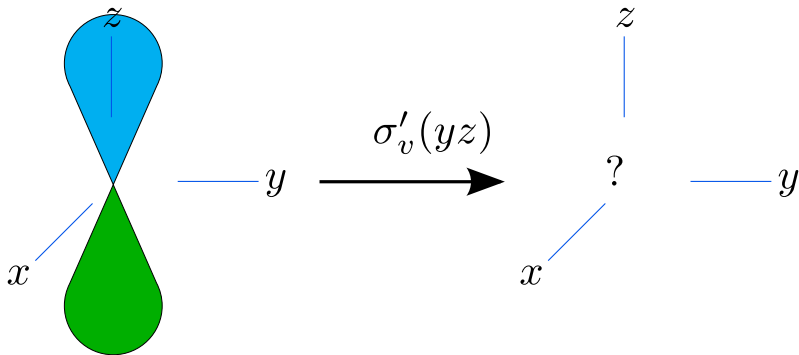
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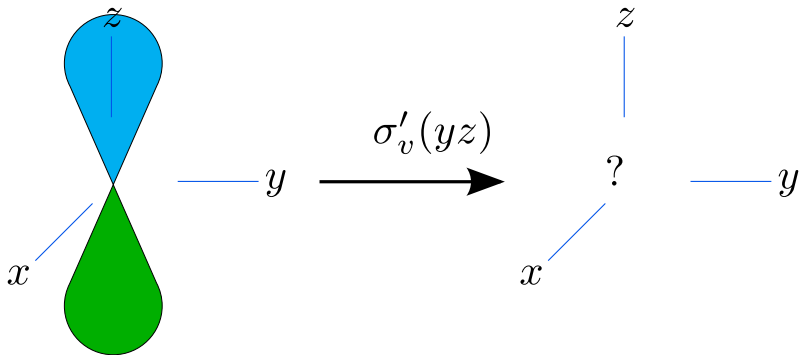
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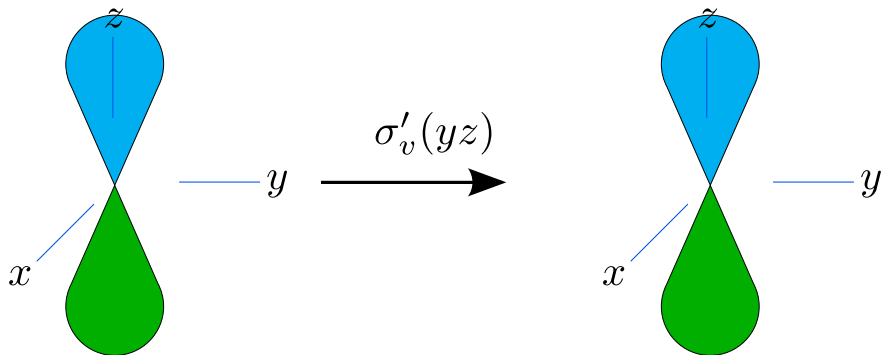
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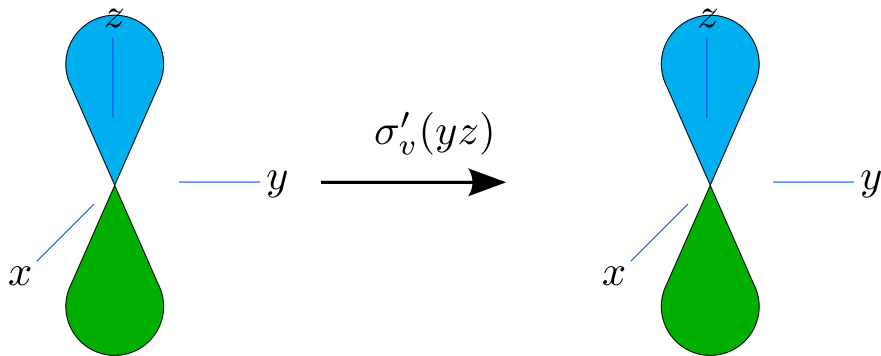
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# Symmetry Restrictions on Molecular Orbitals (MOs)

- Only orbitals of the same symmetry may mix
- “Orbitals of the same symmetry” belong to the same irreducible representation
- For the  $C_{2v}$  water molecule, the oxygen  $s$  and  $p_z$  atomic orbitals may contribute to any molecular orbital of  $A_1$  symmetry, but  $p_x$  and  $p_y$  may not
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# The $C_{2v}$ Character 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	$y, R_x$	$yz$

# The Molecular Orbitals of Water

- Notice that the water HOMO is a pure oxygen  $p_x$  orbital of  $B_1$  symmetry
- The hydrogen atoms with their  $1s$  valence orbitals lie in the nodal plane of the oxygen  $p_x$  orbital
- The two hydrogen  $1s$  orbitals give rise to linear combinations of  $A_1$  and  $B_2$  symmetry
- The O-H bonding molecular orbitals must likewise be of  $A_1$  and  $B_2$  symmetry
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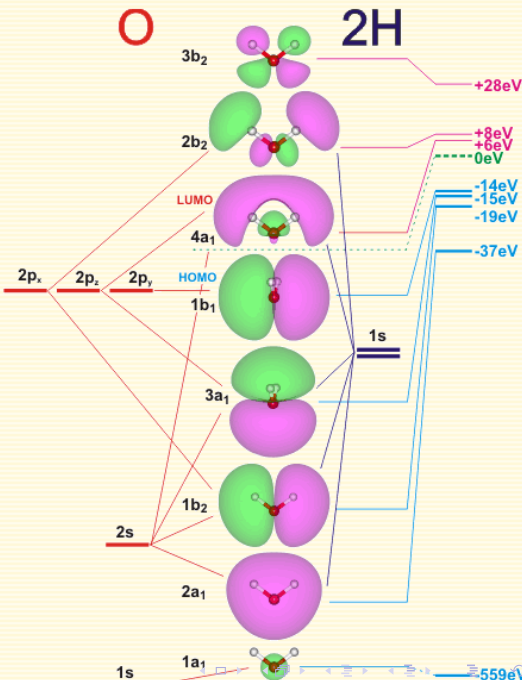
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# Molecular Orbitals for Water ( $\text{H}_2\text{O}$ )

The five occupied and the lowest three unoccupied molecular orbitals of the isolated molecule ( $1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2$ ) were calculated using the Restricted Hartree-Fock wave function (RHF) using the 6-31G\*\* basis set (experimental data is given in [1289]). They are set out with the lowest energy (that is, most negative energy) molecular orbitals at the bottom. They are all given in the xz plane (z-axis upwards) except  $1b_1$  and  $3a_1$ , which are in the yz plane (z-axis upwards).<sup>a</sup> The two lowest energy orbitals  $1a_1$  and  $2a_1$  are contributed from the 1s and 2s (mostly) orbitals of the oxygen atom, respectively, and are consequentially approximately spherical. The three highest energy occupied orbitals ( $1b_2$ ,  $3a_1$ ,  $1b_1$ ) are orthogonal around the oxygen atom and without obvious  $sp^3$  hybridization characteristics.

The relative energies of these orbitals have been found to be somewhat different from these theoretical values. The lowest energy transitions are broad at 7.61 and 9.36 eV for the  $3s/4a_1 \leftarrow 1b_1$  ( $\tilde{A}^1B_1$ ) and  $3s/4a_1 \leftarrow 3a_1$  ( $\tilde{B}^2A_1$ ) transitions respectively [1561] for the gas phase and at 8.09 and 9.74 eV in the liquid [1561, 1562].

The highest occupied molecular orbital (HOMO),  $1b_1$ , is predominantly  $p_z^2$  in character with no contribution from the hydrogen 1s



# The $C_{3v}$ Character Table

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

- Note that the  $E$  irreducible representation begins with a 2
- This means that orbitals of  $E$  symmetry in  $C_{3v}$  are doubly degenerate

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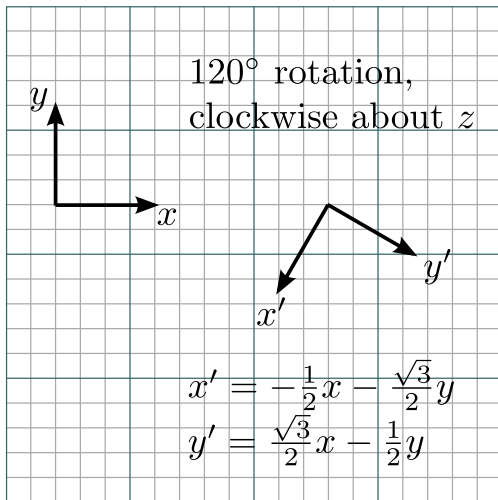
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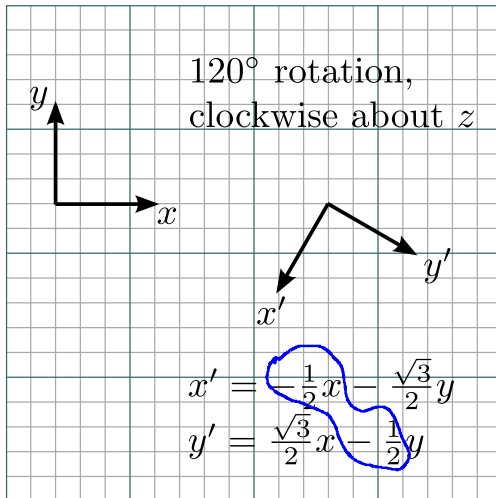
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# The $C_{3v}$ Character Table: Definition of “Character”

- a *character* is the trace of a matrix
- that means the sum of its diagonal elements
- physically, it means the amount of the original function remaining after the operation
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- physically, it means the amount of the original function remaining after the operation
- here,  $C_3$  on  $(x, y)$  gives a character of  $-\frac{1}{2} - \frac{1}{2} = -1$

## The $C_{3v}$ Character Table: Definition of “Character”

- a *character* is the trace of a matrix
- that means the sum of its diagonal elements
- physically, it means the amount of the original function remaining after the operation
- here,  $C_3$  on  $(x, y)$  gives a character of  $-\frac{1}{2} - \frac{1}{2} = -1$

# The $C_{3v}$ Character Table

reflection,  
through  $yz$  plane

$$x' = -1x + 0y$$
$$y' = 0x + 1y$$
$$\text{character} = -1 + 1 = 0$$

# The $C_{3v}$ Character Table

reflection,  
through another  $\sigma_v$  plane

$$x' = \frac{1}{2}x + \frac{\sqrt{3}}{2}y$$
$$y' = \frac{\sqrt{3}}{2}x - \frac{1}{2}y$$
$$\text{character} = \frac{1}{2} - \frac{1}{2} = 0$$



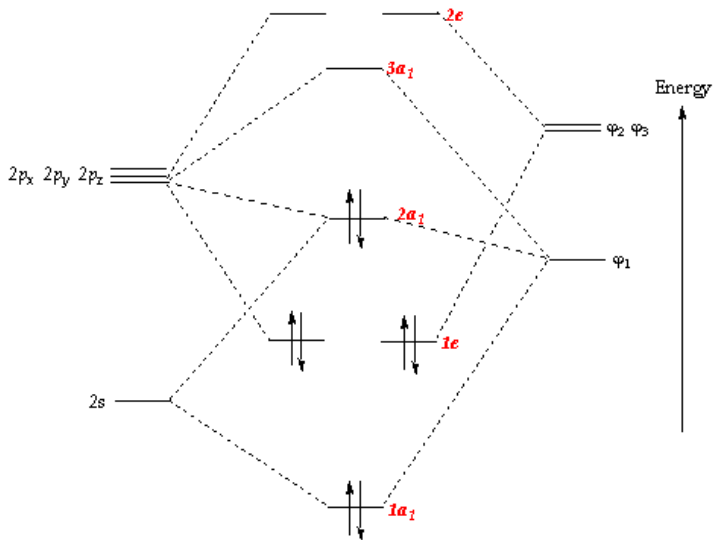
# The $C_{3v}$ Character Table

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

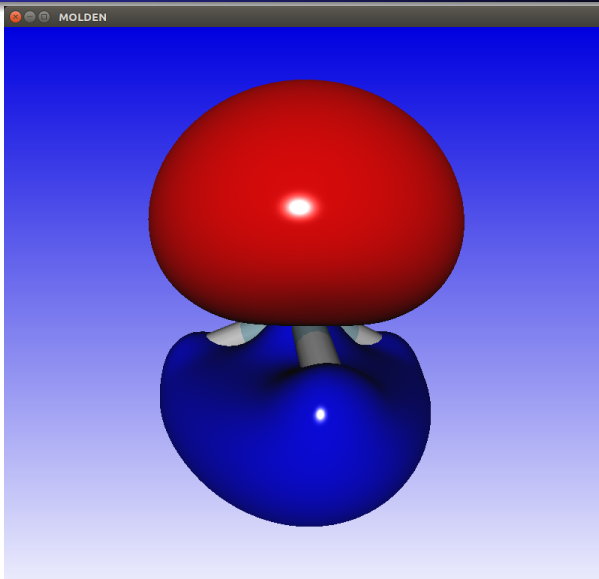
# The $O_h$ Character Table

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

# Molecular Orbital Diagram for Ammonia, $NH_3$



# Highest Occupied MO of Ammonia, $NH_3$



# $E$ Symmetry Bonding MO of Ammonia, $NH_3$

