Concept of a basis

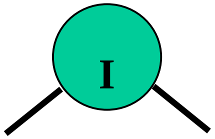
A basis refers to a type of function that is transformed by the symmetry operations of a point group. Examples include the spherical harmonics, vectors, internal coordinates (e..g bonds, angles, torsions), translations, rotations and any other function needed to describe the electronic or nuclear properties of a molecule.

The spherical harmonics include the orbitals, s, p, d etc. and can have more than one dimension. Thus, we need to examine how those functions are changed by the operations.

Based on this treatment we can assign the basis to one of the irreducible representations of the point group.

Orbital basis

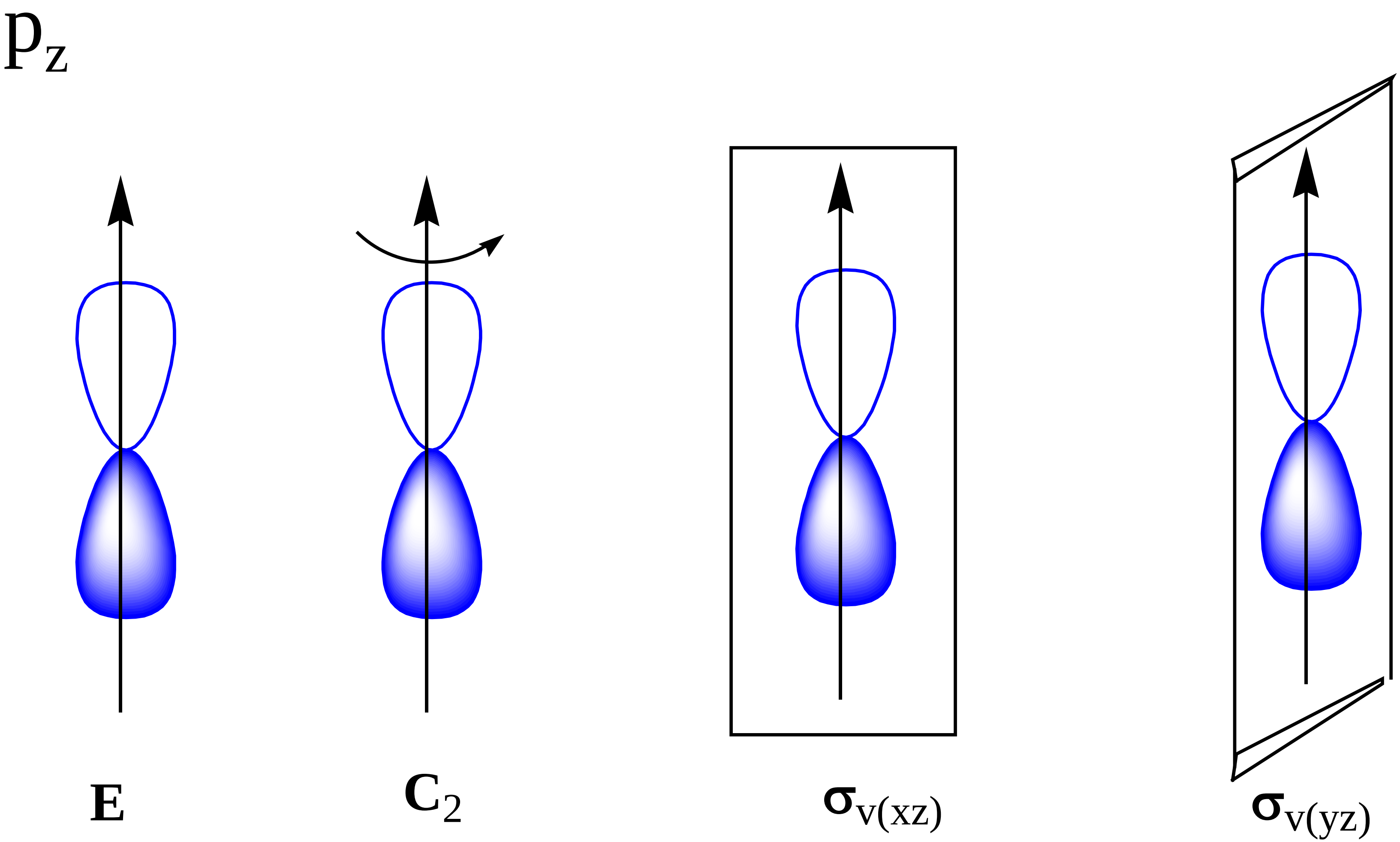
Oxygen s-orbitals in water,



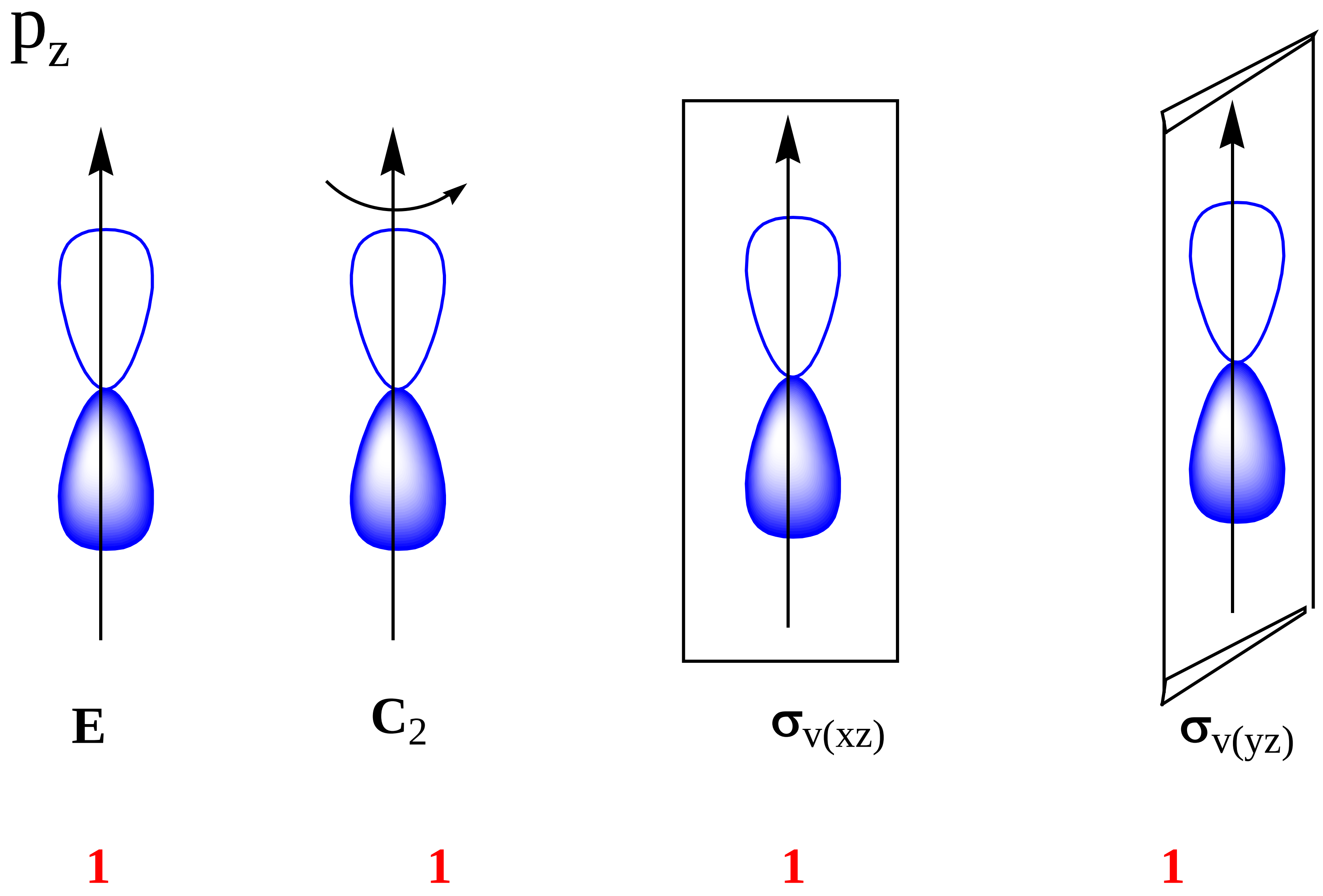
C_{2v}	E	C_2	σ_v	σ_v'
$\Gamma_{O(s)}$	+1	+1	+1	+1

$$\Gamma_{O(s)} = a_1$$

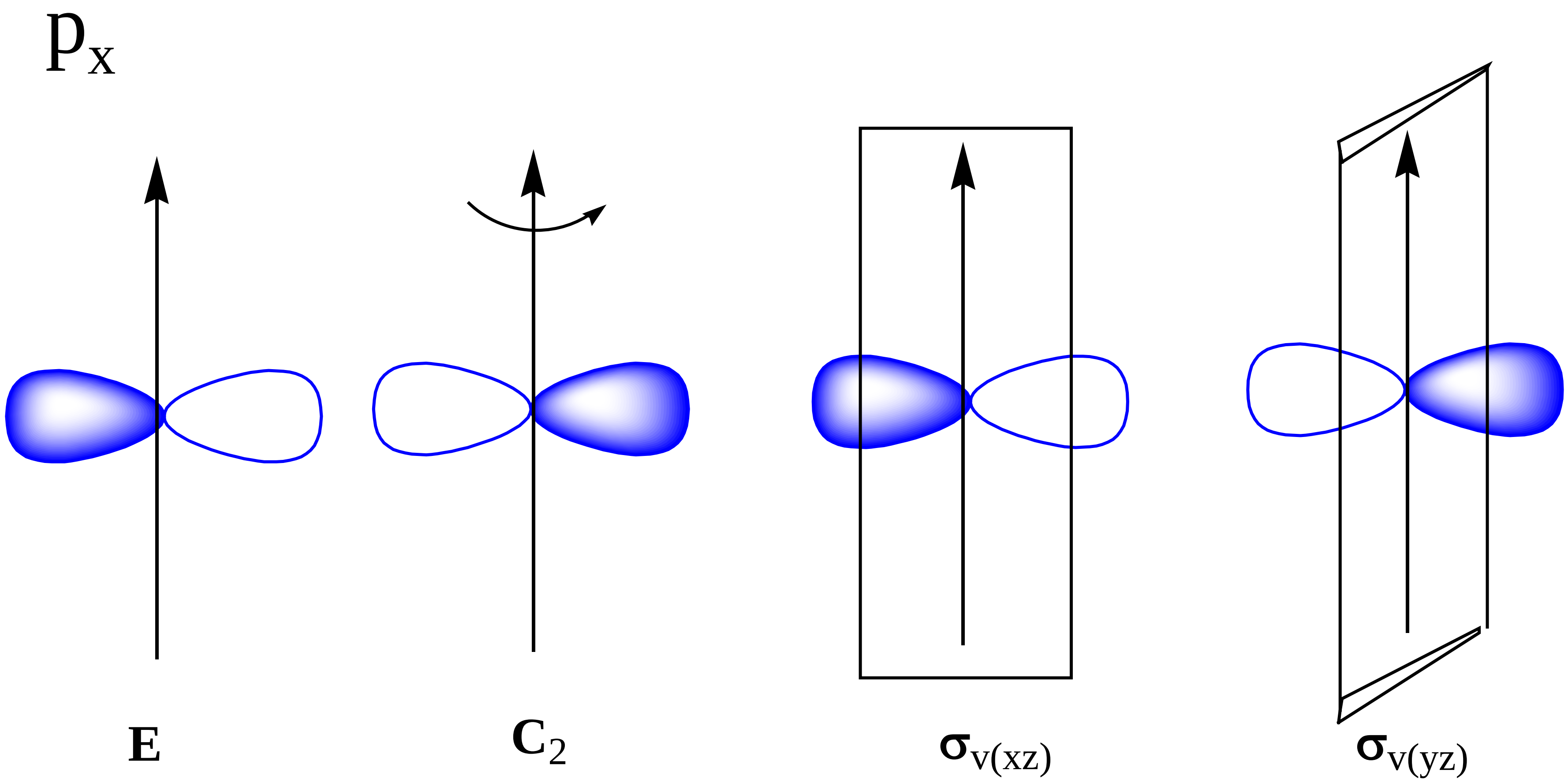
s-orbitals on central elements will always transform as the totally symmetric representation but are not included in character tables



p_z
E
C_2
$\sigma_{v(xz)}$
$\sigma_{v(yz)}$

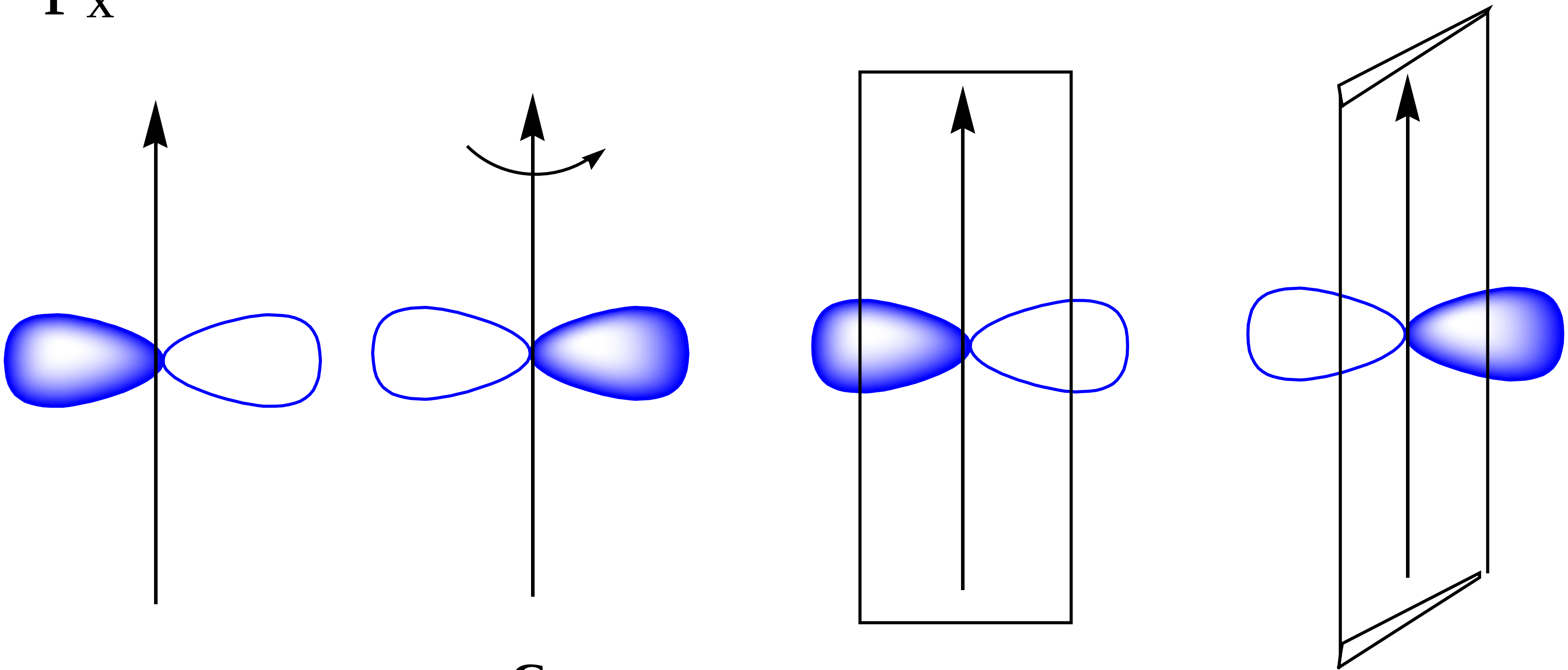


p_z
E
C_2
$\sigma_{v(xz)}$
$\sigma_{v(yz)}$
1
1
1
1



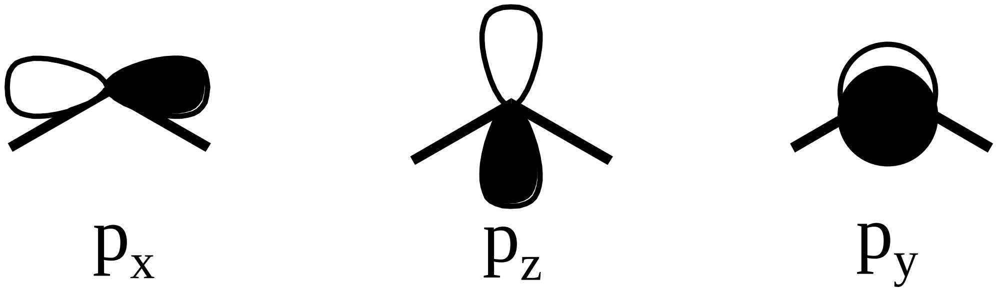
p_x
E
C_2
$\sigma_{v(xz)}$
$\sigma_{v(yz)}$

p_x



E	C_2	$\sigma_{v(xz)}$	$\sigma_{v(yz)}$
1	-1	1	-1

Oxygen p-orbitals in water,

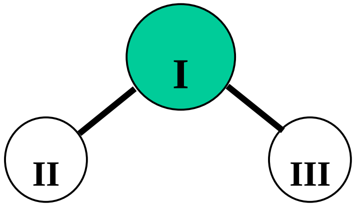


C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	
p_z	+1	+1	+1	+1	a_1
p_x	+1	-1	+1	-1	b_1
p_y	+1	-1	-1	+1	b_2
Γ_p	3	-1	1	1	

Thus, $\Gamma_p = a_1 + b_1 + b_2$. The px orbital is said to

- form the basis for the b_1 representation,
- have b_1 symmetry, or
- transform as b_1

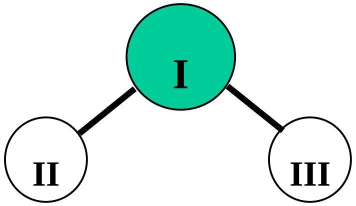
S-orbitals as a basis



E each atom has 1 and not 3 labels so each operation is a 3x3 matrix as opposed to the 9x9 matrices of the Cartesian basis. In addition, there can be no sign change for an s-orbital. The resulting representation is,

$$\boldsymbol{E} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}; \quad \boldsymbol{C_2} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}; \quad \sigma_v = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}; \quad \sigma_v' = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$$

s-orbitals as a basis



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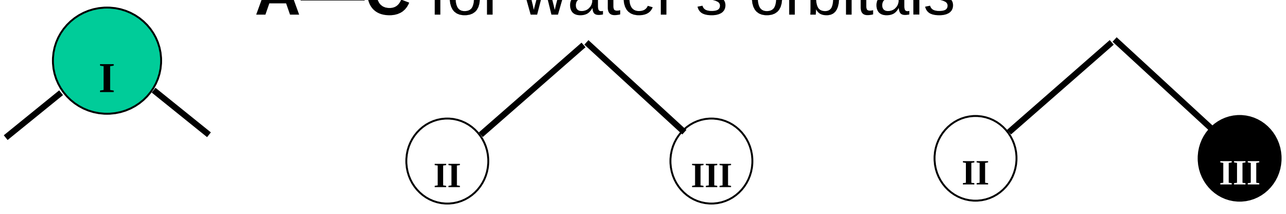
Γ	**3**	**1**	**3**	**1**

Intuitive approach to finding the basis vectors in the s-orbital space

Consider the *symmetry adapted linear combinations* (***SALC's***)

A—C for water s-orbitals



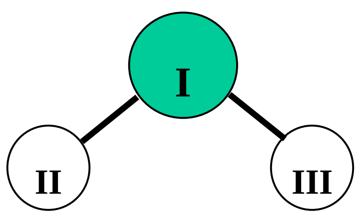
A = I   **B** = II + III   **C** = II - III

$$\begin{pmatrix} A \\ B \\ C \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 1 \\ 0 & 1 & -1 \end{pmatrix} \begin{pmatrix} I \\ II \\ III \end{pmatrix} = \begin{pmatrix} I \\ II + III \\ II - III \end{pmatrix}$$

In this basis, no basis vector is changed into another by a symmetry operation, *i.e.*, this basis is *symmetry adapted*.

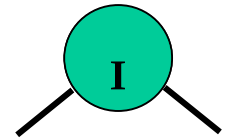
Old 3x3 is now three 1x1 matrices and reducible representation Γ_S is now three ***irreducible representations***, Γ_A, Γ_B and Γ_C.

***i.e.*, $\Gamma_S = \Gamma_A + \Gamma_B + \Gamma_C$**



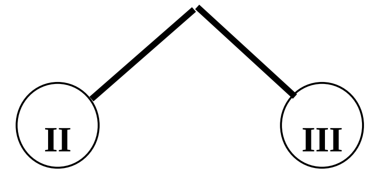
Γ_S = **3 1 3 1**

	E	C_2	σ	σ'
Γ_A	1	1	1	1
Γ_B	1	1	1	1
Γ_C	1	-1	1	-1
Γ_s	**3**	**1**	**3**	**1**



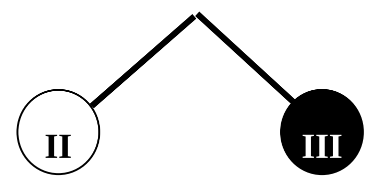
A

Γ_A = **1 1 1 1**



B

Γ_B = **1 1 1 1**

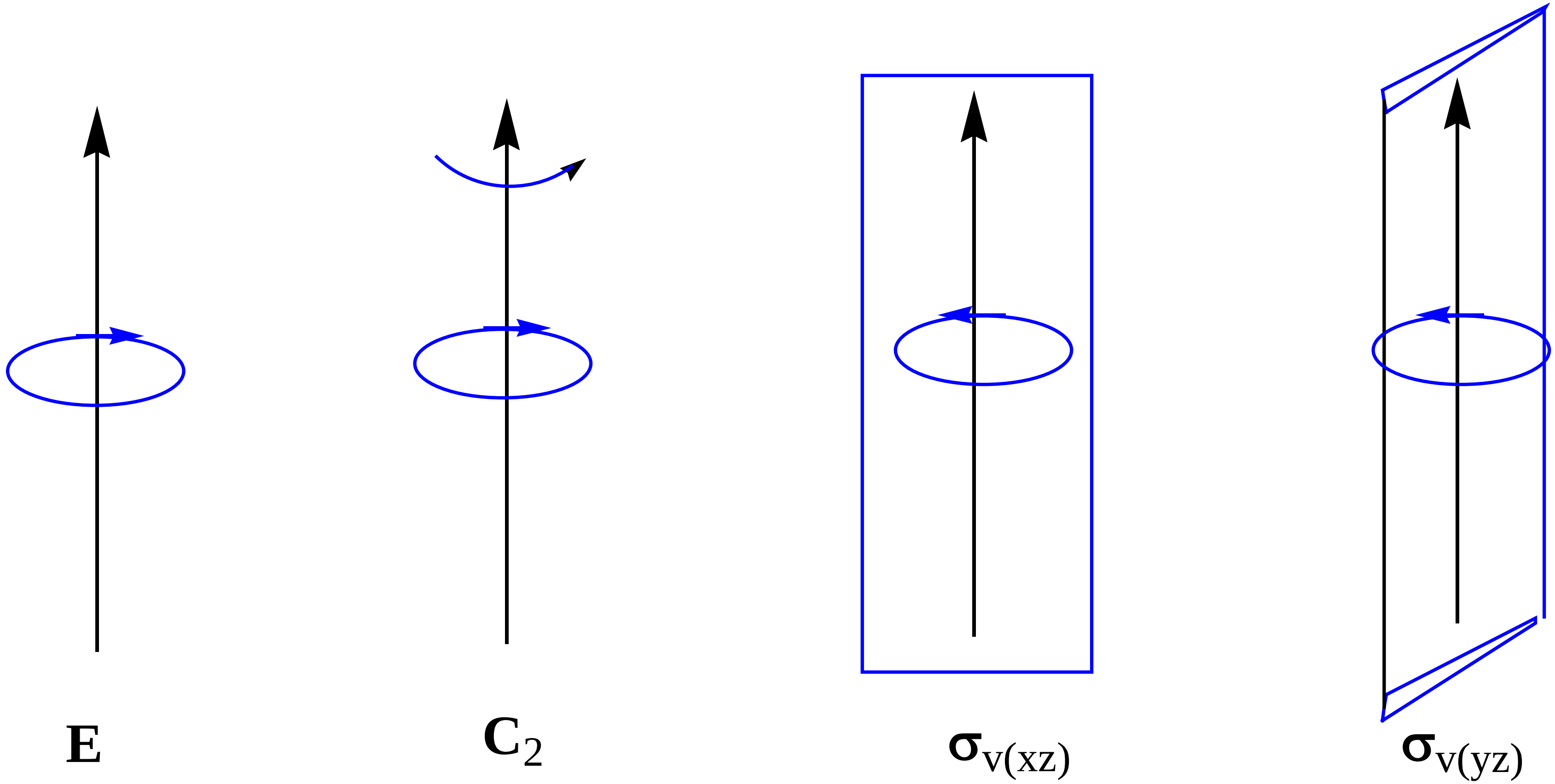


C

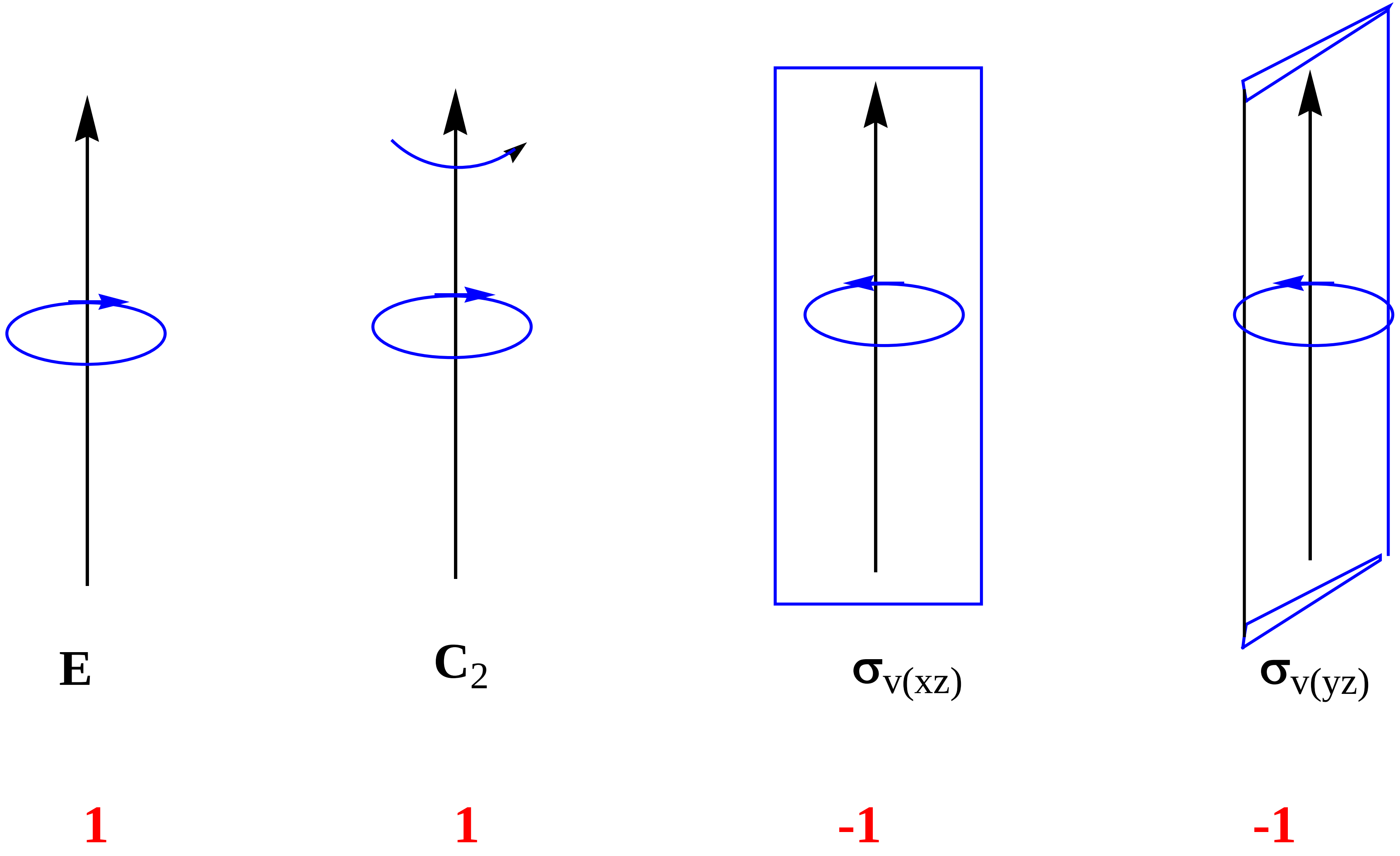
Γ_C = **1 -1 1 -1**

Rotation basis

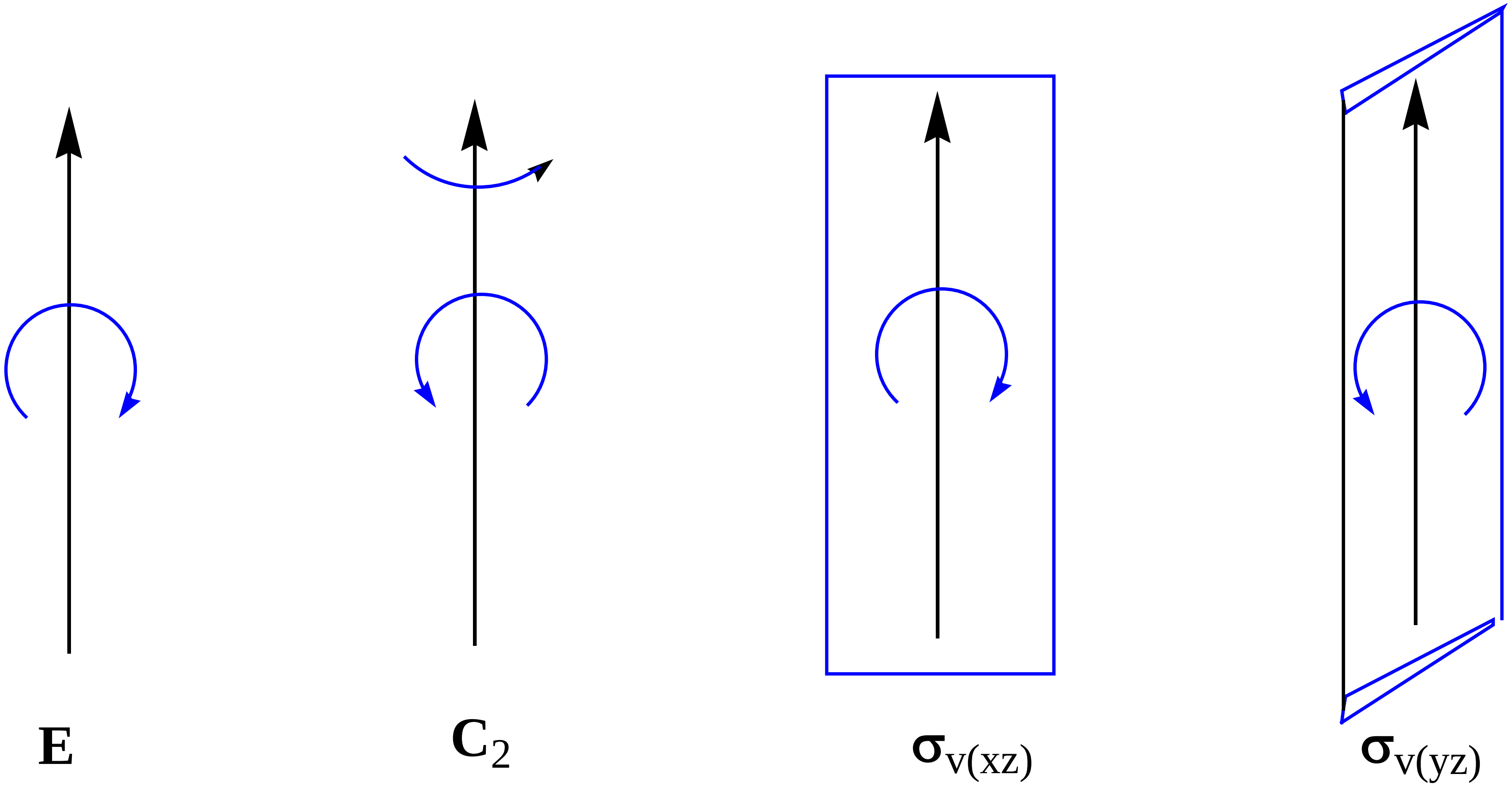
R_z



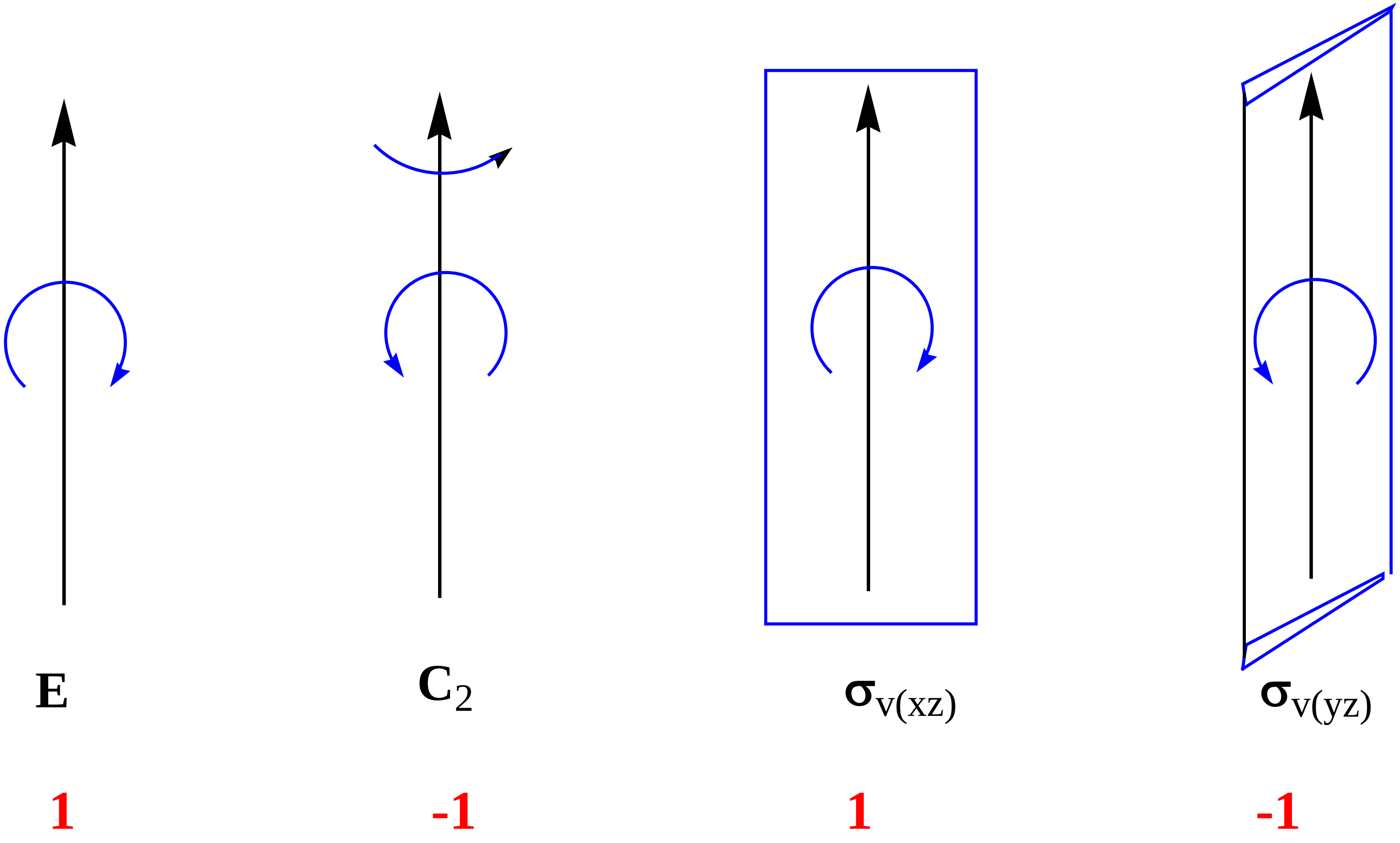
R_z



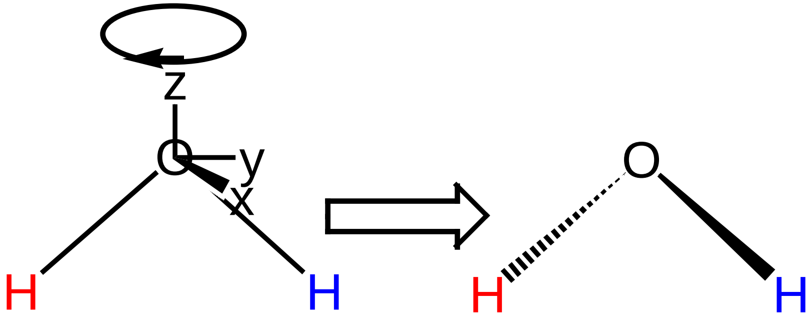
R_y



R_y



Rotation of the water molecule,



$\Gamma R(z) = 1 \;\; 1 \;\; -1 \;\; -1$

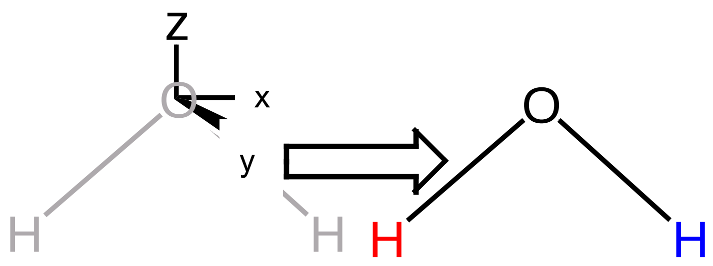
C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	
R_z	+1	+1	-1	-1	a_2
R_x	+1	-1	-1	+1	b_2
R_y	+1	-1	+1	-1	b_1
Γ_{rot}	3	-1	1	1	

Thus, $\Gamma_{rot} = a_2 + b_1 + b_2$

Translation basis

Cartesian basis

Translations along the x, y and z directions (x, y, z) transform in the same way as px, py and pz.



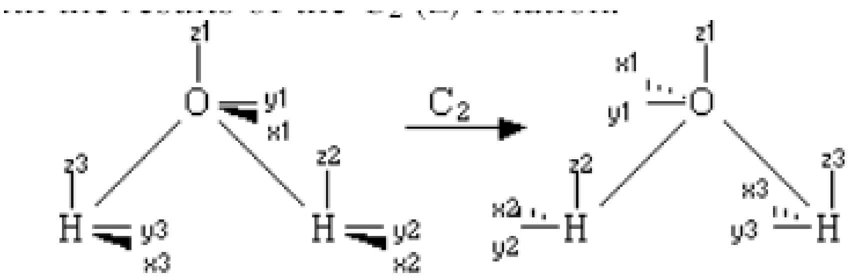
$\Gamma T(x) = 1 \;\; -1 \;\; 1 \;\; -1$

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	
T_z	+1	+1	+1	+1	a_1
T_y	+1	-1	-1	+1	b_2
T_x	+1	-1	+1	-1	b_1
Γ_{trans}	3	-1	1	1	

Thus, $\Gamma_{trans} = a_1 + b_1 + b_2$

Motions of H_2O

The basis vectors are shown for the three atoms of water. Also shown is the result of the C_2 rotation:



Using analysis of the 3N Cartesian vectors we can determine a reducible representation. We have already seen that the method involves counting the characters of the unmoved atoms. The important realization is that all atoms that are unmoved by a particular symmetry operation must have the same character.

We showed previously that C_2 has a character of -1 and $\sigma_v(yz)$ has a character of 3. For a reflection through the plane bisecting the H-O-H bond angle, $\chi(\sigma v') = +1$ since only the O is unshifted and a plane contributes +1 for each unshifted atom.

The **character for the identity element will always be the dimension of the basis** since all labels are unchanged. For water then, $\chi(E) = 9$.

The representation (Γ) for water **in this Cartesian basis** is:

	E	C_2	$\sigma_v(yz)$	$\sigma_v'(xz)$
Γ	9	-1	3	1

Reducible and irreducible representations

We call the representation Γ a reducible representation. Here we write the reducible representation as:

	E	C_2	$\sigma_v(yz)$	$\sigma_v'(xz)$
Γ	9	-1	3	1

The irreducible representations form the basis of the point group in the same way that the vectors along x, y and z form the basis for three dimensional space.

H_2O belongs the point group C_{2v}. In this point group There are 4 irreducible representations, A_1, B_1, A_2, B_2. The decomposition of the reducible representation is a Unique determination of the irreducible reps (or irreps)z spanned by Γ.

Internal coordinates as a basis

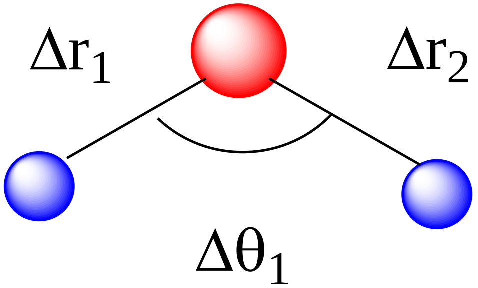
The internal coordinates are
- Stretch Δr
- Bend $\Delta\theta$
- Torsion $\Delta\tau$
- Wag $\Delta\omega$

The advantages of this coordinate system are:
- Translation and rotation are eliminated.
- Force constant are defined in terms of bond stretches, valence angle bends, torsions, and wags. These quantities can be related to bond strengths and barriers for internal rotation.

Example of H_2O

For example, for H_2O we have the following internal coordinates.

$$s = \begin{pmatrix} \Delta r_1 \\ \Delta r_2 \\ \Delta \theta_1 \end{pmatrix}$$



The bond coordinates Δr_1 and Δr_2 transform as:

$\mathbf{C_{2v}}$	E	C_2	$\sigma_{v(xz)}$	$\sigma_{v(yz)}$
Γ	2	0	2	0

This is a reducible representation.