Decomposing Reducible Representations

In the determination of molecular orbital or vibrational symmetries, a reducible representation is generated from an appropriate basis set and then decomposed into its constituent irreducible representations.

$$a_i = \frac{1}{h}\sum_{R} g(R)\chi_i(R)\chi(R)$$

a_i: the # of times that ith irrep appears in the reducible representation

h: the order of the group

R: an operation of the group

g(R): the number of operations in the class

χ_i(R): the character of the Rth operation in the ith irrep

χ(R): the character of the Rth operation in the reducible representation

A general example of decomposition of a reducible representation

A reducible representation can also be called a vector in the space of the point group. In order to understand the application of point groups for problems in chemistry we need to have a general way to determine how the vector projects onto the space of the group. The space is defined in terms of the orthogonal basis vectors.

We consider an example in the C_{3v} point group.

C_{3v}	**1**E	**2**C_3	**3**σ_v
Γ_{red}	7	1	1

We can think of this a vector in the space of C_{3v} that has the given lengths in each of the dimensions. We are treating the point group symmetries as dimensions (which they are).

The vector can be composed by taking the dot product.

$$a_i = \frac{1}{h}\sum_R g(R)\chi_i(R)\chi(R)$$

In this standard expression the dot product is $\chi_i(R)\chi(R)$ and $g(R)$ is the degeneracy (i.e. the order of the class).

Γ_{red} = 7 1 1 of the C_{3v} point group, which has an order of 6.

C_{3v}	**1**E	**2**C_3	**3**σ_v
A_1	1	1	1
Γ_{red}	7	1	1

C_{3v}	**1**E	**2**C_3	**3**σ_v
A_2	1	1	-1
Γ_{red}	7	1	1

$a(a_1)$ = 1/6{(**1**)(1)(7)+(**2**)(1)(1)+(**3**)(1)(1)} = 1/6{12} = 2

$a(a_2)$ = 1/6{(**1**)(1)(7)+(**2**)(1)(1)+(**3**)(-1)(1)} = 1/6{6} = 1

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A_2	1	1	-1
Γ_{red}	7	1	1

$a(a_1) = 1/6\{(\mathbf{1})(1)(7)+(\mathbf{2})(1)(1)+(\mathbf{3})(1)(1)\} = 1/6\{12\} = 2$

$a(a_2) = 1/6\{(\mathbf{1})(1)(7)+(\mathbf{2})(1)(1)+(\mathbf{3})(-1)(1)\} = 1/6\{6\} = 1$

C_{3v}	**1**E	**2**C_3	**3**σ_v
E	2	-1	0
Γ_{red}	7	1	1

$a(e) = 1/6\{(\mathbf{1})(2)(7) + (\mathbf{2})(-1)(1) + (\mathbf{3})(0)(+1)\} = 1/6\{12\} = 2$

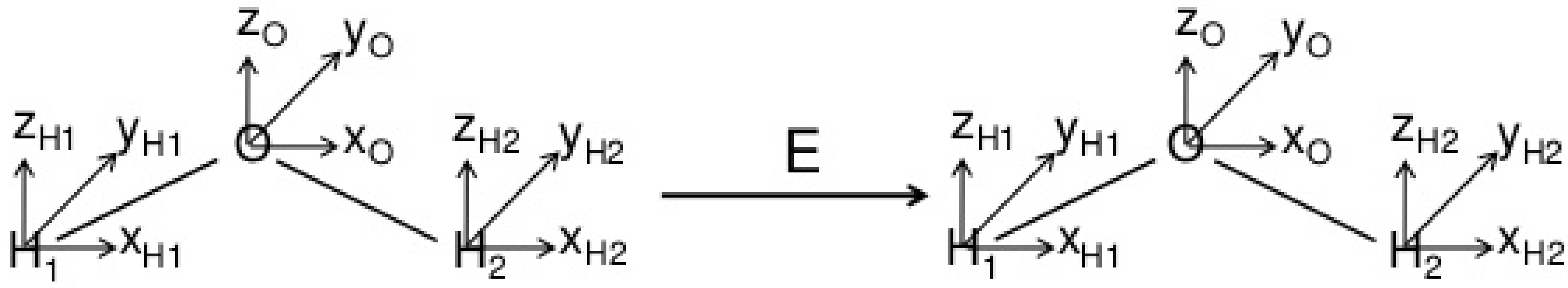
The reducible representation is decomposed as:

$$\Gamma_{red} = 2a_1 + a_2 + 2e$$

The results can be verified by adding the characters of the irreps,

C_{3v}	**1**E	**2**C_3	**3**σ_v
$2a_1$	2	2	2
a_2	1	1	-1
2e	4	-2	0
Γ_{red}	**7**	**1**	**1**

Consider the effect of the operations of C_{2v} on the vector of displacements. The identity has no effect on any displacement, i.e.



$Ex_{H1} = x_{H1}$
$Ey_{H1} = y_{H1}$
$Ez_{H1} = z_{H1}$

$Ex_O = x_O$
$Ey_O = y_O$
$Ez_O = z_O$

$Ex_{H2} = x_{H2}$
$Ey_{H2} = y_{H2}$
$Ez_{H2} = z_{H2}$

- These results may be summarized in matrix form

$$E\begin{pmatrix} x_{H1} \\ y_{H1} \\ z_{H1} \\ x_o \\ y_o \\ z_o \\ x_{H2} \\ y_{H2} \\ z_{H2} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x_{H1} \\ y_{H1} \\ z_{H1} \\ x_o \\ y_o \\ z_o \\ x_{H2} \\ y_{H2} \\ z_{H2} \end{pmatrix}$$

- The character of this representation = 9

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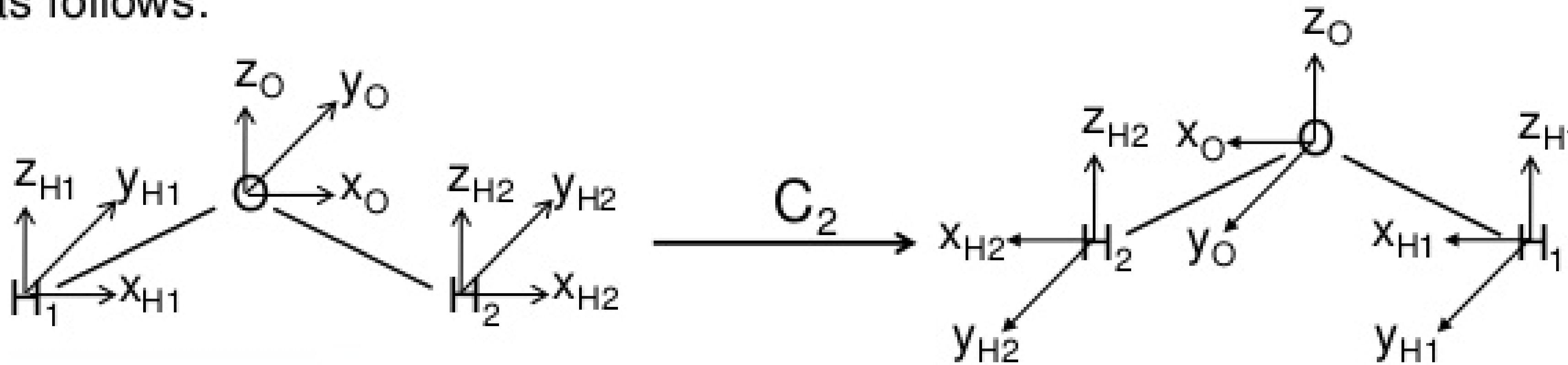
The rotation C_2 leaves unchanged only the component z_O. Its full effect is as follows:



$C_2 x_{H1} = - x_{H2}$
$C_2 y_{H1} = -y_{H2}$
$C_2 z_{H1} = z_{H2}$

$C_2 x_O = -x_O$
$C_2 y_O = -y_O$
$C_2 z_O = z_O$

$C_2 x_{H2} = -x_{H1}$
$C_2 y_{H2} = -y_{H1}$
$C_2 z_{H2} = z_{H1}$

- These results may be summarized in matrix form

$$
c_2 \begin{pmatrix} x_{H1} \\ y_{H1} \\ z_{H1} \\ x_o \\ y_o \\ z_o \\ x_{H2} \\ y_{H2} \\ z_{H2} \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} x_{H1} \\ y_{H1} \\ z_{H1} \\ x_o \\ y_o \\ z_o \\ x_{H2} \\ y_{H2} \\ z_{H2} \end{pmatrix}
$$

- The character of this representation = -1

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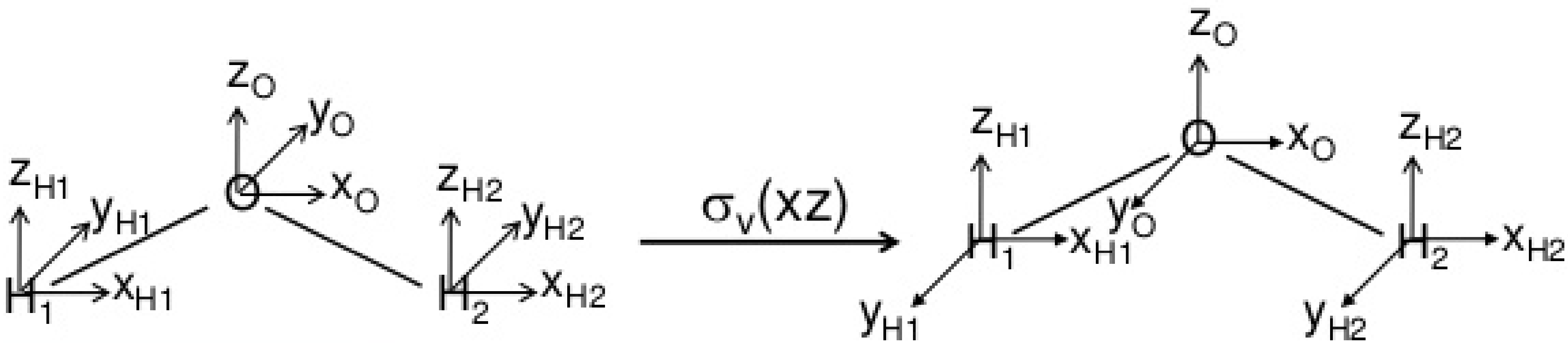
The effect of $\sigma_v(xz)$ is as follows:



$\sigma_v(xz)x_{H1} = x_{H1}$
$\sigma_v(xz)y_{H1} = -y_{H1}$
$\sigma_v(xz)z_{H1} = z_{H1}$

$\sigma_v(xz)x_O = x_O$
$\sigma_v(xz)y_O = -y_O$
$\sigma_v(xz)z_O = z_O$

$\sigma_v(xz)x_{H2} = x_{H2}$
$\sigma_v(xz)y_{H2} = -y_{H2}$
$\sigma_v(xz)z_{H2} = z_{H2}$

- These results may be summarized in matrix form

$$\sigma_v(xz)\begin{pmatrix} x_{H1} \\ y_{H1} \\ z_{H1} \\ x_o \\ y_o \\ z_o \\ x_{H2} \\ y_{H2} \\ z_{H2} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x_{H1} \\ y_{H1} \\ z_{H1} \\ x_o \\ y_o \\ z_o \\ x_{H2} \\ y_{H2} \\ z_{H2} \end{pmatrix}$$

- The character of this representation = 3

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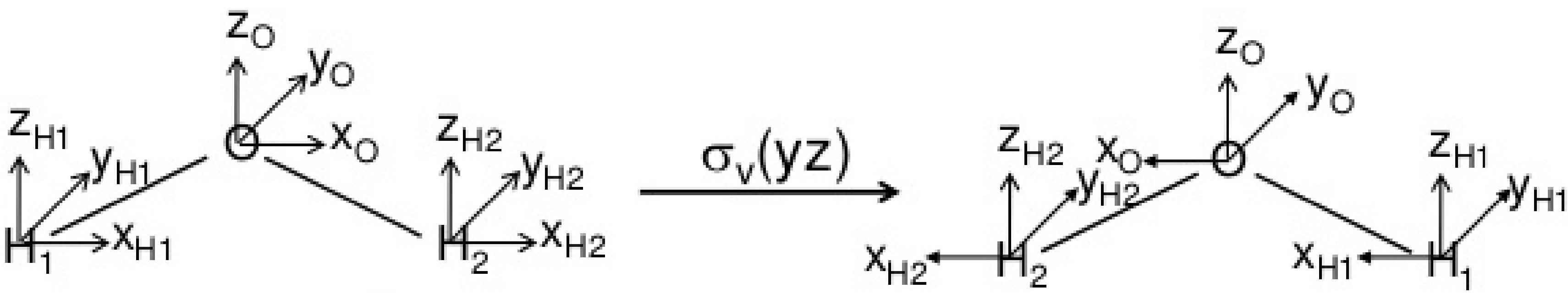
The effect of $\sigma_v(yz)$ is as follows:



$$\sigma_v(yz)x_{H1} = -x_{H2}$$
$$\sigma_v(yz)y_{H1} = y_{H2}$$
$$\sigma_v(yz)z_{H1} = z_{H2}$$

$$\sigma_v(yz)x_{O} = -x_{O}$$
$$\sigma_v(yz)y_{O} = y_{O}$$
$$\sigma_v(yz)z_{O} = z_{O}$$

$$\sigma_v(yz)x_{H2} = -x_{H1}$$
$$\sigma_v(yz)y_{H2} = -y_{H1}$$
$$\sigma_v(yz)z_{H2} = z_{H1}$$

- These results may be summarized in matrix form

$$\sigma_v(yz)\begin{pmatrix} x_{H1} \\ y_{H1} \\ z_{H1} \\ x_o \\ y_o \\ z_o \\ x_{H2} \\ y_{H2} \\ z_{H2} \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} x_{H1} \\ y_{H1} \\ z_{H1} \\ x_o \\ y_o \\ z_o \\ x_{H2} \\ y_{H2} \\ z_{H2} \end{pmatrix}$$

- The character of this representation = 1

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Our conclusion from the analysis of the Cartesian vectors of H_2O was that the reducible representation has the form.

C_{2v}	E	C_2	σ_v	σ'_v	
Γ_{cart}	9	-1	3	1	

The decomposition of this reducible representation can
Be carried out in the same way using the dot product of
This vector with each of the basis vectors in the space.

We call the basis vectors irreducible representations. In C_{2v} the order of each class is 1 so g(R) = 1 always.

$$a_i = \frac{1}{h}\sum_R \chi_i(R)\chi(R)$$

The reducible representation of the Cartesian displacement vectors for water was determined earlier and is given in the following table as Γ_{cart}

$$\Gamma_{cart}(E) = 3N$$

Here is a shortcut for generating Γ_{cart} for any system:

$$\Gamma_{cart} = \Gamma_{unshift}\Gamma_{xyz} = \Gamma_{unshift}\,[\Gamma_x + \Gamma_y + \Gamma_z]$$

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

Here is a shortcut for generating Γ_{cart} for any system:

$$\Gamma_{cart} = \Gamma_{unshift}\Gamma_{xyz} = \Gamma_{unshift} [\Gamma_x + \Gamma_y + \Gamma_z]$$

C_{2v}	E	C_2	σ_v	σ'_v	
$\Gamma_{unshift}$	3	1	3	1	
B_1	1	-1	1	-1	x
B_2	1	-1	-1	1	y
A_1	1	1	1	1	z
Γ_{x+y+z}	3	-1	1	1	

Here is a shortcut for generating Γ_{cart} for any system:

$$\Gamma_{cart} = \Gamma_{unshift}\Gamma_{xyz} = \Gamma_{unshift}\,[\Gamma_x + \Gamma_y + \Gamma_z]$$

C_{2v}	E	C_2	σ_v	σ'_v	
$\Gamma_{unshift}$	3	1	3	1	
Γ_{x+y+z}	3	-1	1	1	
Γ_{cart}	9	-1	3	1	

C_{2v}	E	C_2	σ_v	σ'_v	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	R_z
B_1	1	-1	1	-1	x, R_y
B_2	1	-1	-1	1	y,R_x
Γ_{cart}	9	-1	3	1	

Decomposition of Γ_{cart} yields,

$a(a_1)$ = 1/4 {(1)(1)(9) + (1)(1)(-1) + (1)(1)(3) + (1)(1)(1)} = 1/4 {12} = 3

$a(a_2)$ = 1/4 {(1)(1)(9) + (1)(1)(-1) + (1)(-1)(3) + (1)(-1)(1)} = 1/4 { 4} = 1

$a(b_1)$ = 1/4 {(1)(1)(9) + (1)(-1)(-1) + (1)(1)(3) + (1)(-1)(1)} = 1/4 {12} = 3

$a(a_2)$ = 1/4 {(1)(1)(9) + (1)(-1)(-1) + (1)(-1)(3) + (1)(1)(1)} = 1/4 { 8} = 2

$$\mathbf{\Gamma_{cart} = 3a_1 + a_2 + 3b_1 + 2b_2}$$

Of these 3N degrees of freedom, three are translational, three are rotational and the remaining 3N-6 are the vibrational degrees of freedom.

Thus, to get the symmetries of the vibrations, the irreducible representations of translation and rotation need only be subtracted from Γ_{cart}, but the irreps of rotation and translation are available from the character table.

For the water molecule,

$$\Gamma_{\mathbf{vib}} = \Gamma_{cart} - \Gamma_{trans} - \Gamma_{rot}$$

$$= \{3a_1 + a_2 + 3b_1 + 2b_2\} - \{a_1 + b_1 + b_2\} - \{a_2 + b_1 + b_2\}$$

$$= \mathbf{2a_1 + b_1}$$

Problem Determine the symmetries of the vibrations of NH_3, $PtCl_4^{2-}$ and SbF_5.