

(11) Today

4.3 Character Tables

4.4 Uses of Character Tables

Second Class from Today

Test 1 on Chap 1 through Chap 4 section 4.2
(symmetry operations and finding Point
Groups)

Next Class (12)

4.4 Uses of Character Tables

Third Class from Today (13)

4.4 Uses of Character Tables

operations

Functions

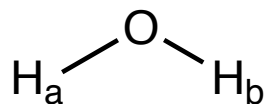
C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

labels

characters

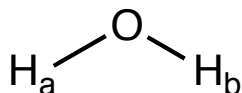
classes

a summary of all of the symmetry in a given point group

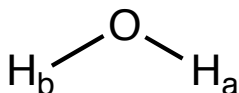


C_{2v} operations: E, C_2 , $\sigma_v(xz)$, $\sigma_v(yz)$

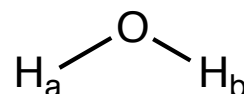
E



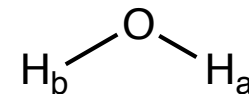
C_2



$\sigma_v(xz)$



$\sigma_v(yz)$



Matrix representations

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

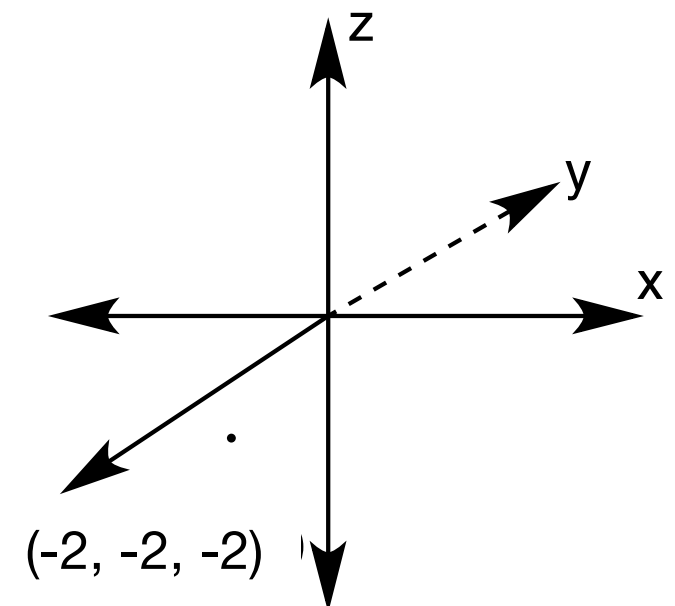
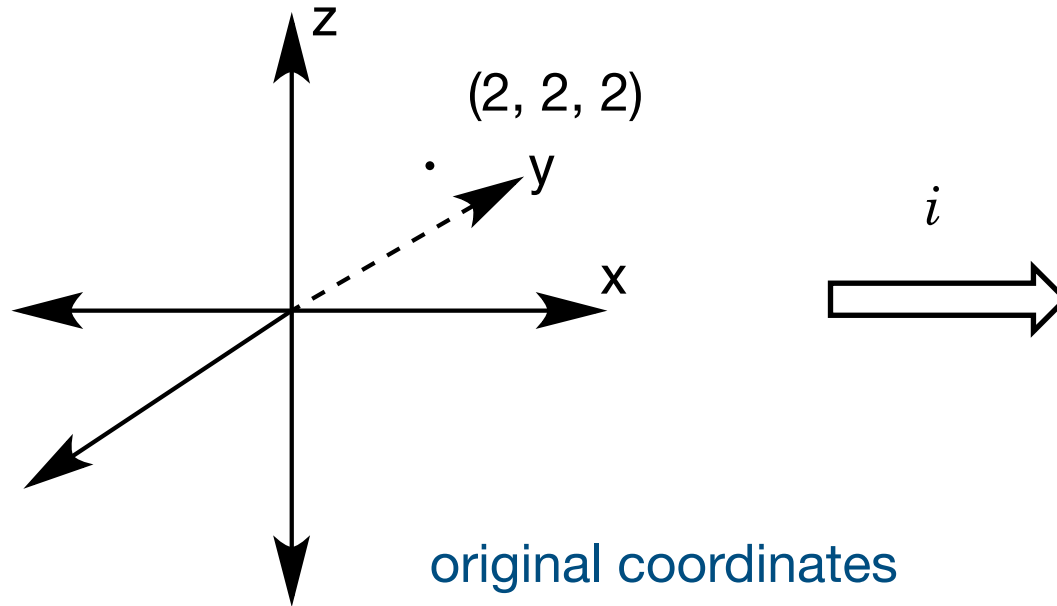
$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

1x1 transformation matrices for each individual axis

1	-1	1	-1	x
1	-1	-1	1	y
1	1	1	1	z

The traces of the 3x3 transformation matrices

3	-1	1	1
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original coordinates

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix}$$

transformation matrix

new coordinates

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} -2 \\ -2 \\ -2 \end{bmatrix}$$

Matrix Multiplication...

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Number of columns in the first matrix must equal number of rows in the second

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

new x value = sum of Row 1 x Column 1

new y value = sum of Row 2 x Column 1

new z value = sum of Row 3 x Column 1

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} -1(x) + 0(y) + 0(z) \\ 0(x) + -1(y) + 0(z) \\ 0(x) + 0(y) + -1(z) \end{bmatrix}$$

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} -x \\ -y \\ -z \end{bmatrix}$$

	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

1x1 transformation matrices for each individual axis in the C_{2v} point group

✂	1	-1	1	-1	x
✂	1	-1	-1	1	y
✂	1	1	1	1	z

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

|
 Mulliken symbols summary symmetry for each
 irreducible representation

symmetric

antisymmetric - thing doesn't move but its
 sign changes (phase of p orbital
 dir

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

Letters (There are other letters we will see later)

- A symmetric w.r.t. principle axis
- B antisymmetric w.r.t. principle axis

Subscript numbers are based on symmetry w.r.t. rotation about a C_2 perpendicular to the principal axis. In the absence of a C_2 a vertical mirror plane perpendicular to the plane of the molecule is used instead

- subscript 1 symmetric w.r.t. a C_2 that is perpendicular to the principle axis
- subscript 2 antisymmetric w.r.t. a C_2 that is perpendicular to the principle axis

Subscripted u and g

- subscript g symmetric w.r.t. inversion
- subscript u antisymmetric w.r.t. inversion

Tick Marks

- ' symmetric w.r.t. σ_h
- " antisymmetric w.r.t. σ_h

How do we use Character Tables.

To examine the symmetry of the thing we are interested in (molecular motions, orbitals, symmetry adapted linear combinations of atomic orbitals...) we create a reducible representation of the symmetry operations acting on the thing we are interested in.		For each operation and each item add 1, 0 or -1 to the value for χ based on whether there is no change (1), the items changes position (0), or doesn't change position but changes sign (-1).
We use linear algebra to determine the irreducible representations that must be combined to form the reducible one that we just found.		
We use the functions in the character tables to interpret our results.		

Number of IR Active Vibrational Modes for Water

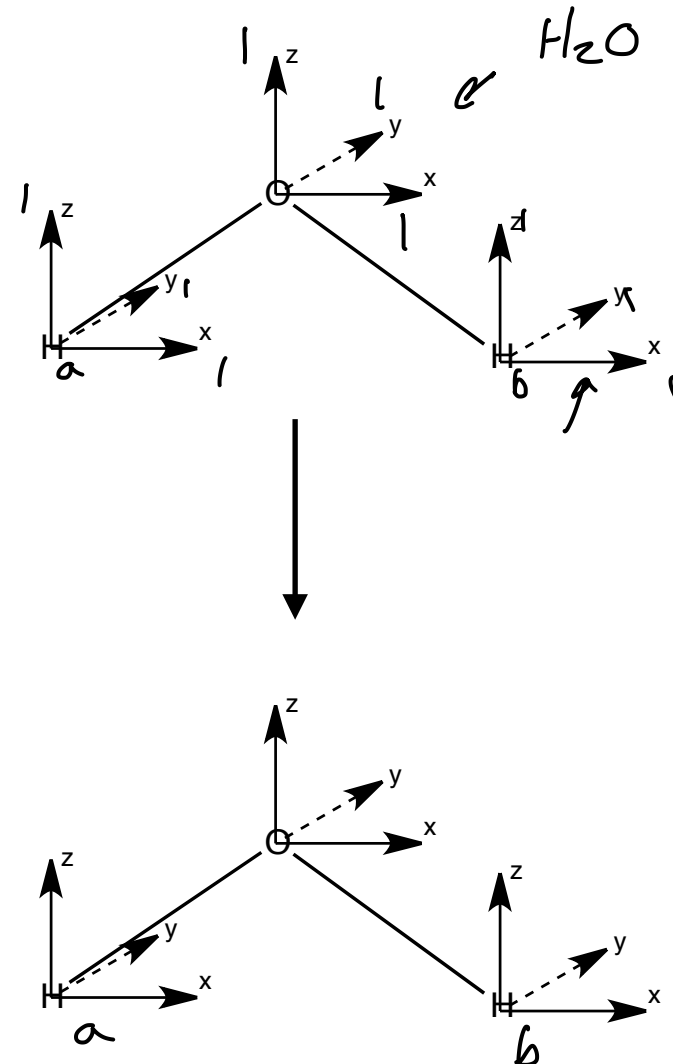
Find this by analyzing all possible motions of the atoms in

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C_{2v}	E	C_2	$\sigma(xz)$	$\sigma(yz)$
	9			

O	x'_O		1	0	0	0	0	0	0	0	X_O
	y'_O		0	1	0	0	0	0	0	0	Y_O
	z'_O		0	0	1	0	0	0	0	0	Z_O
H _a	x'_{Ha}		0	0	0	1	0	0	0	0	X_{Ha}
	y'_{Ha}		0	0	0	0	1	0	0	0	Y_{Ha}
	z'_{Ha}		0	0	0	0	0	1	0	0	Z_{Ha}
H _b	x'_{Hb}		0	0	0	0	0	0	1	0	X_{Hb}
	y'_{Hb}		0	0	0	0	0	0	0	1	Y_{Hb}
	z'_{Hb}		0	0	0	0	0	0	0	0	Z_{Hb}

Summarize this matrix using its trace 9 which is the sum of the diagonal



Number of IR Active Vibrational Modes for Water

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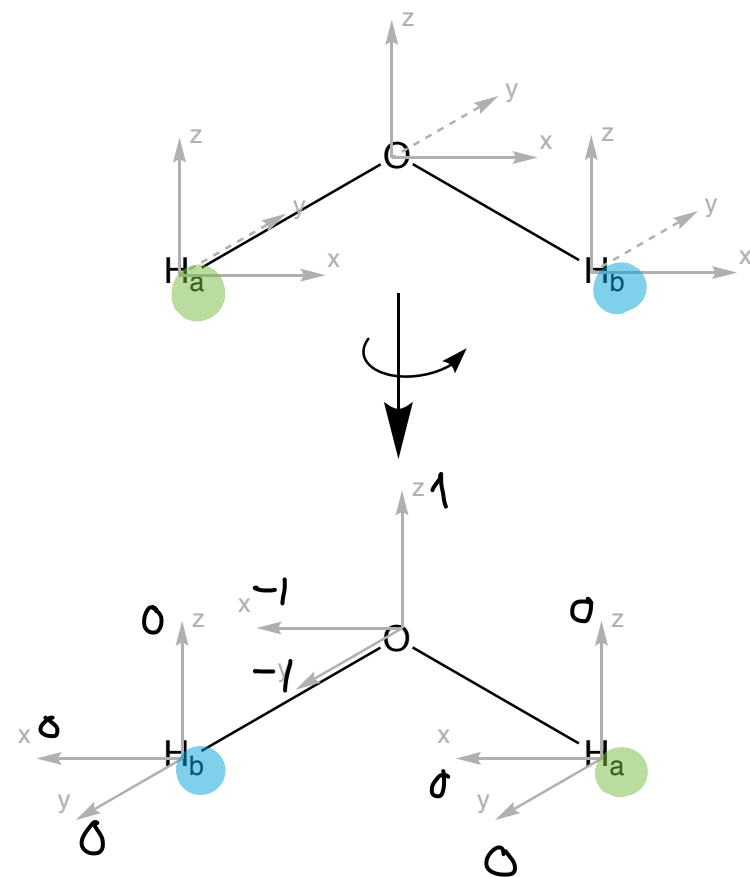
C_{2v}	E	C_2	σ_{xz}	σ_{yz}
	9	-1		

O	x'_O	-1	0	0	0	0	0	0	0	x_O
	y'_O	0	-1	0	0	0	0	0	0	y_O
	z'_O	0	0	1	0	0	0	0	0	z_O
H _a	x'_{Ha}	0	0	0	0	0	-1	0	0	x_{Ha}
	y'_{Ha}	0	0	0	0	0	0	-1	0	y_{Ha}
	z'_{Ha}	0	0	0	0	0	0	0	1	z_{Ha}
H _b	x'_{Hb}	0	0	0	-1	0	0	0	0	x_{Hb}
	y'_{Hb}	0	0	0	0	-1	0	0	0	y_{Hb}
	z'_{Hb}	0	0	0	0	0	1	0	0	z_{Hb}

$$\text{trace} = -1$$

create the characters for the
reducible representation for all the
possible motions

did it change position no
did it change sign or direction
add 1 for each
vector that did nothing

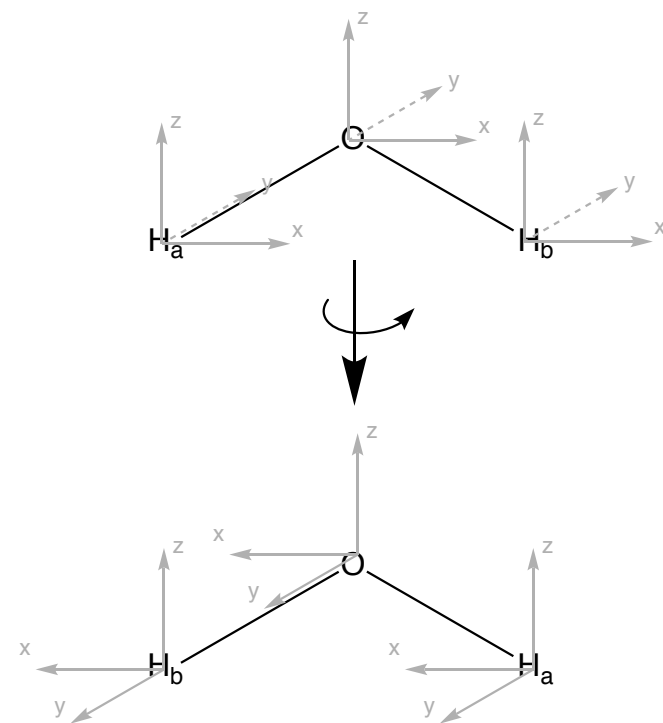


Easier way to determine the trace?

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C_{2v}	E	C_2	$\sigma_{(xz)}$	$\sigma_{(yz)}$
	9			

$$\begin{array}{c}
 \text{O} \\
 \text{H}_a \\
 \text{H}_b
 \end{array}
 \begin{array}{c}
 \begin{array}{c}
 x'_O \\
 y'_O \\
 z'_O \\
 x'_{Ha} \\
 y'_{Ha} \\
 z'_{Ha} \\
 x'_{Hb} \\
 y'_{Hb} \\
 z'_{Hb}
 \end{array}
 \end{array}
 =
 \begin{array}{c}
 \begin{array}{cccccccc}
 -1 & & & & & & & \\
 & -1 & & & & & & \\
 & & 1 & & & & & \\
 & & & 0 & & -1 & & \\
 & & & & 0 & & -1 & \\
 & & & & & 0 & & 1 \\
 & & & -1 & & 0 & & \\
 & & & & -1 & & 0 & \\
 & & & & & 1 & & 0
 \end{array}
 \end{array}
 \begin{array}{c}
 \begin{array}{c}
 x_O \\
 y_O \\
 z_O \\
 x_{Ha} \\
 y_{Ha} \\
 z_{Ha} \\
 x_{Hb} \\
 y_{Hb} \\
 z_{Hb}
 \end{array}
 \end{array}$$



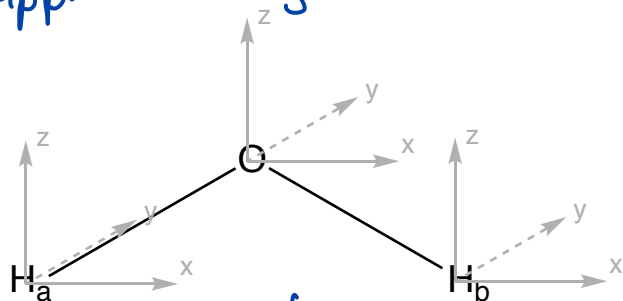
For each operation add 1, 0 or -1 to the value for χ based on whether there is no change (1), the items changes position (0), or doesn't change position but changes sign (-1).

Number of IR Active Vibrational Modes for Water

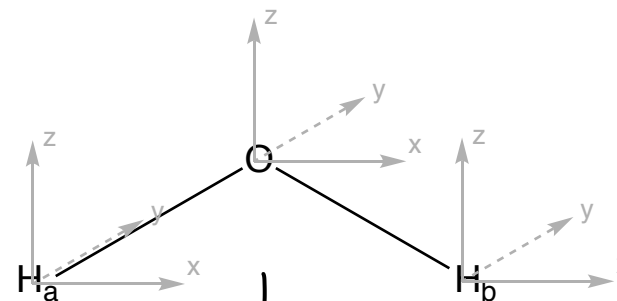
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C_{2v}	E	C_2	$\sigma_{(xz)}$	$\sigma_{(yz)}$
Γ	9	-1	3	1

upper case gamma



$\sigma_{(xz)}$



$\sigma_{(yz)}$

For each operation add 1, 0 or -1 to the value for χ based on whether there is no change (1), the items changes position (0), or doesn't change position but changes sign (-1).

